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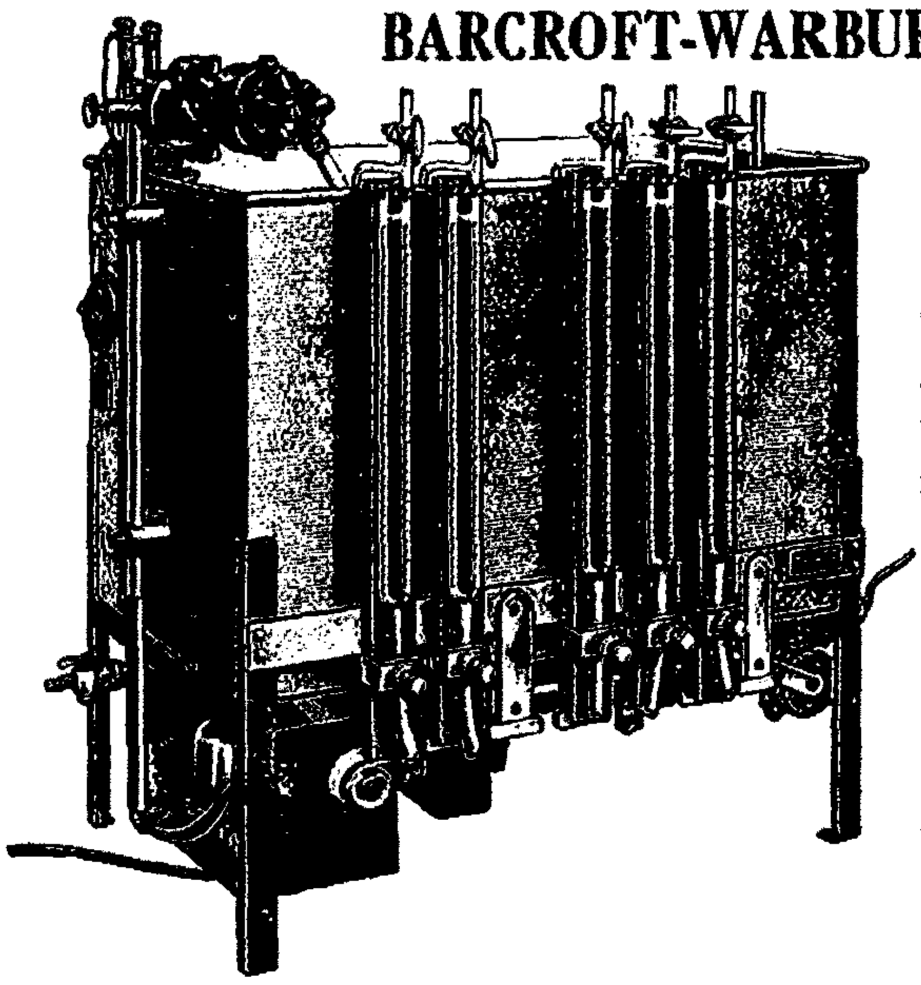

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THE PRECISION AND ACCURACY OF A PHOTOELECTRIC METHOD FOR COMPARISON OF THE LOW LIGHT INTENSITIES INVOLVED IN MEASUREMENT OF ABSORPTION AND FLUORESCENCE SPECTRA

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Received May 27, 1933

The usual photographic methods for measurement of continuous absorption spectra of solutions are not satisfactory for accurate measurement of extinction coefficients; the greatest care is necessary to obtain an accuracy of even 5 per cent (1). Visual methods are affected by inaccuracies of the eye and are practically limited to the visible region of the spectrum.

A more precise method, which involves the use of a monochromator and a photoelectric cell, avoids the errors of both the photographic plate and the eye. The photoelectric current measurement is not affected by uncertain amplification factors when an electrometer and a high resistance leak are employed. Because of the high sensitivity and precision of the photocell and electrometer, very narrow regions of a continuous spectrum may be used. Although the use of a line source permits precise definition of wave lengths, the usual intensity fluctuations make it less desirable for this photoelectric method. Because its intensity may be conveniently controlled, a continuous source is preferable when the resolution of the monochromator and the precision of current measurements can be made sufficiently great. Furthermore, the continuous spectrum does not display the abrupt changes in intensity with wave length which characterize line spectra, and it permits the convenient use of arbitrarily selected wave lengths.

Although the essentials of this method are not new, we have not found a detailed description of the complete assembly, its operation, errors, and precision. The method is especially suitable for the detection of compounds and for quantitative analysis of complex mixtures, particularly the biological pigments, such as the chlorophylls. It will undoubtedly become more generally used.

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[1] National Research Fellow, 1931-1933.

DESCRIPTION OF EXPERIMENTAL EQUIPMENT

Figure 1 is a diagram of the entire experimental system. Light from source S, after being condensed by a lens (focal length 12 cm.; diameter 4.5 cm.) is focused on slit 1 of the monochromator. By adjustment of the wave length scale, the prism is so rotated that light of the desired wave length will travel from slit 1 to slit 2, providing lenses l_1 and l_2 are in proper focus. Between slit 2 and the photoelectric cell P, is a camera shutter with a 2-cm. diaphragm opening. The shutter, set for "time," is opened and closed by a cable release which reaches to the telescope.

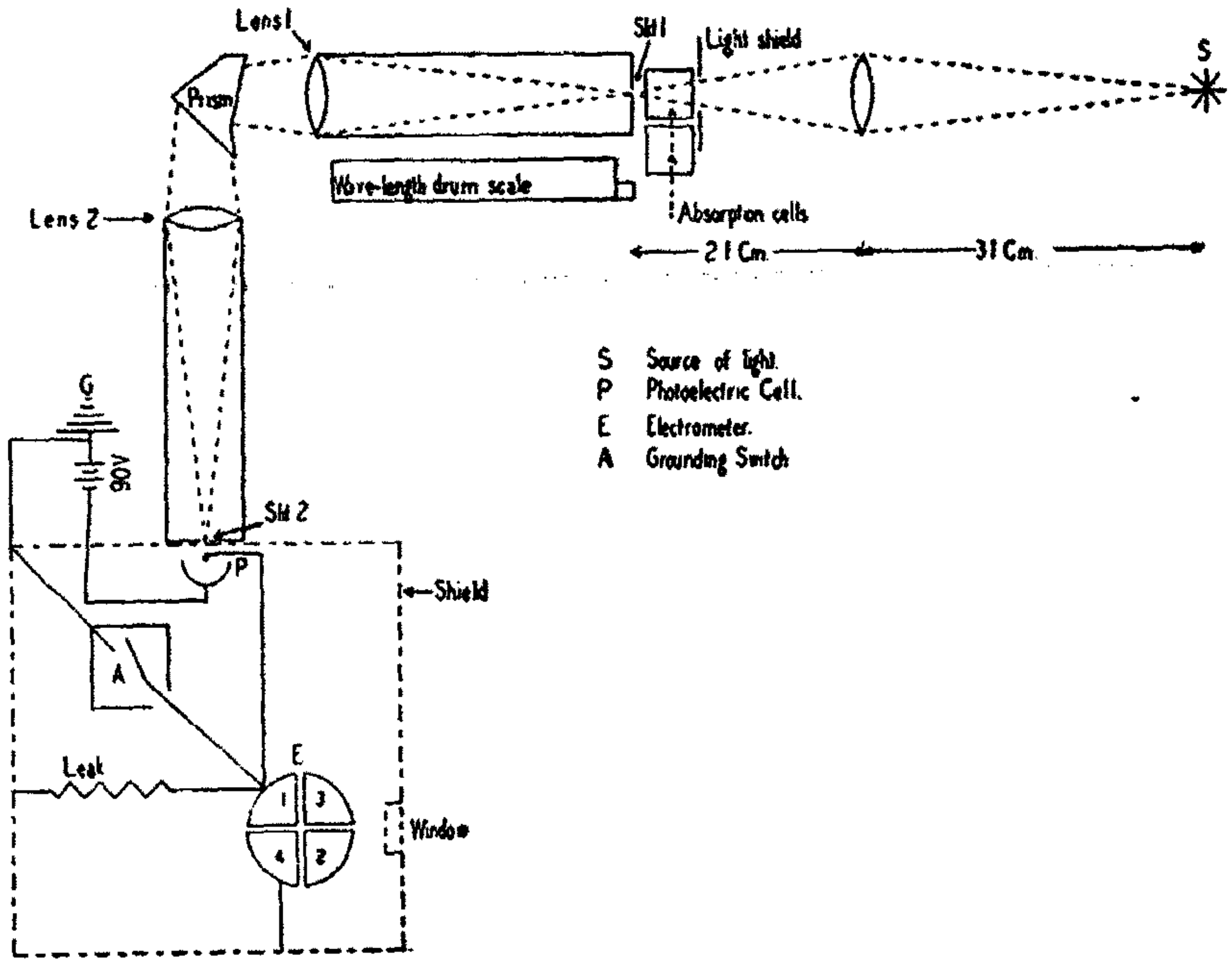

FIG. 1. INTENSITY COMPARISON SYSTEM

Across P is impressed a potential of 90 volts from radio "B" batteries. The photoelectric current, caused by light from slit 2, is measured by means of a quadrant electrometer. The vane deflections are determined by means of a telescope and scale, which in our case is 2.5 meters from the electrometer mirror. After calibration of the electrometer, deflections are accurate measures of the photoelectric currents, and hence of the relative intensities of the light of any wave length entering slit 1.

In figure 2 is a diagram of the electrical circuit used to measure the small currents involved. The electrometer, photocell, ground leak, and grounding switch are enclosed completely in a tinned iron case, which is grounded and acts as a shield against stray electric fields. The case is lined on the inside with loose cotton felt 5 mm. thick, which diminishes temperature fluctuations to which electrometers, especially the Compton, are sensitive. Around the case, on the outside, is a hood of black felt which helps to keep out stray light. All wires enter the case through Bakelite insulators. The case and all of its contents are placed on a concrete pillar, which in turn rests on a 1 cm. rubber pad on a larger concrete pillar extending into the ground.

When 90 volts are impressed on P by the closing of switch B, the photoelectric current flows to the ground if A is closed. The grounding switch A is insulated with paraffin and has platinum contacts. When A is opened, the current must flow through the high resistance leak to the ground and the quadrant pair 1–2 is charged, in accordance with Ohm's law, proportionally to the photoelectric current. The non-polarizable leak is a nearly saturated solution of iodine in benzene and has a resistance of 1.65 × 10^{11} ohms. Rollefson (2) gives specific resistances of such solutions. The solution was made of benzene, distilled from phosphorus pentoxide, and of triply sublimed iodine. It is sealed in a 5-mm. Pyrex tube with platinum wire contacts about 4 cm. apart. The whole is enclosed in a block of paraffin.

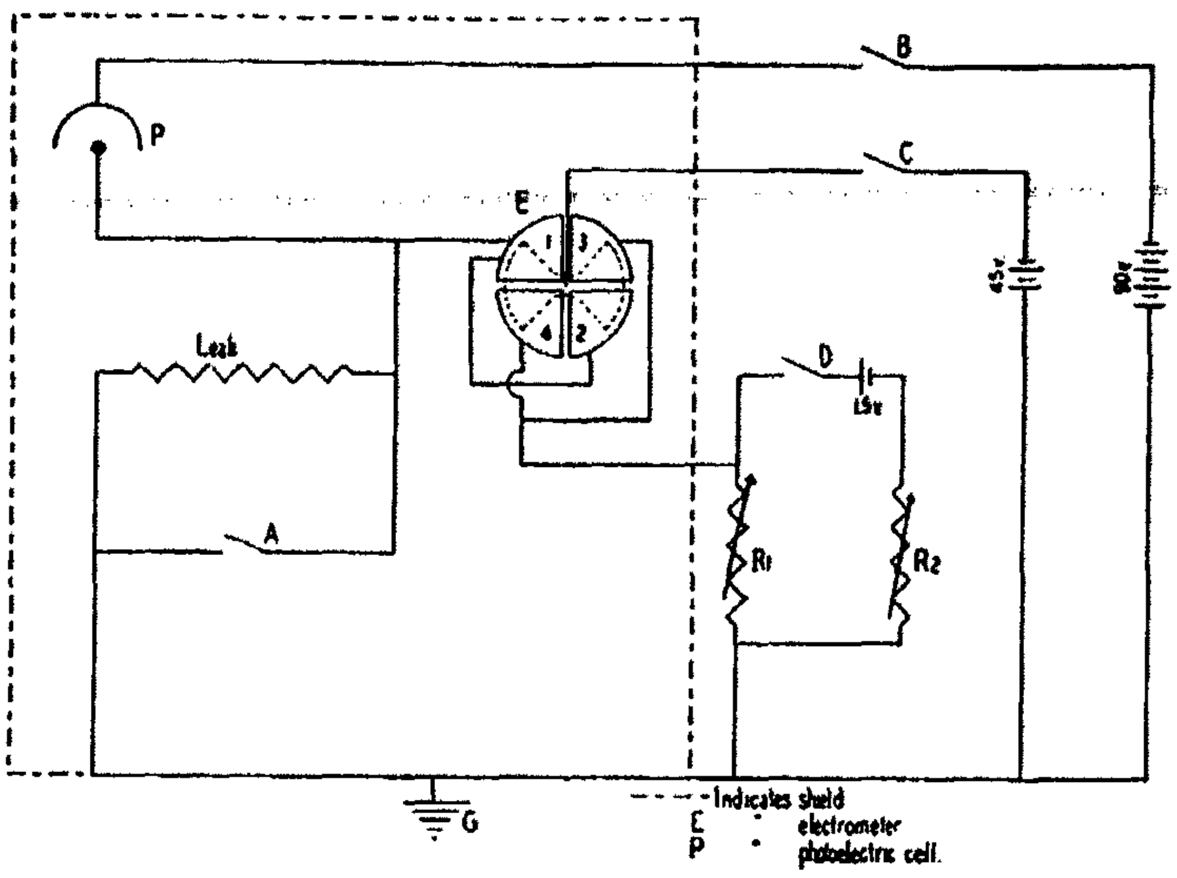

FIG. 2. ELECTRICAL CONNECTIONS

During light measurements, quadrants 3 and 4 are grounded through R_1. To calibrate the electrometer, switch D is closed, R_2 (10,000 ohms) is kept constant, and R_1 is varied. A plot is then made of quadrant potentials against deflections, and is used to convert deflections to potentials existing across the leak.

The photoelectric cell used in the work here presented is the same cell whose wave length–sensitivity curve was described by Young and Pierce (3). It is quartz enclosed, has a cesium oxide surface, and is sensitive to both visible and ultraviolet light.

Within 4 mm. of slit 1, which is 1 cm. long, are two quartz absorption cells, 4 cm. in length and 2.4 cm. in diameter, with plane quartz windows. The cells, which are filled through tubes equipped with ground quartz stoppers, are mounted on a heavy metal carriage, adjustable in height and angle, by means of which either cell may be placed in the light beam. The moving part of the carriage and the ground switch A are controlled from the experimenter's position at the telescope through a pulley system. One cell contains pure solvent and the other the solution being studied. The solution cell is emptied through a stopcock connected to the quartz outlet with rubber tubing. The rubber is placed 5 cm. below the cell bottom, to prevent contamination of the solution in the illuminated portion. The solution cell may be emptied and refilled without being moved, at intervals determined by the solution's stability toward light. The light shield, with opening 16 mm. in diameter, between the condensing lens and the absorption cells confines the beam to the solution, preventing light reflection from the sides and edges of the cells. The light paths of different parts of the beam while passing through the solution are equal within 0.5 per cent.

From a measurement of I_0, the intensity of light passed through the solvent-filled cell of length x, and of I_x, the intensity of light passed through a similar solution-filled cell, the specific light absorption coefficient β may be calculated according to Lambert's law.

$$I_x = I_0e^{-\beta x}$$

$$\beta = \frac{2.3 \log \frac{I_0}{I_x}}{x}$$

SENSITIVITY DATA

When it is desired to make many readings over a period of several days, as when the absorption spectrum is being investigated systematically at short intervals of wave length, the Dolezalek is a suitable electrometer. Its sensitivity is sufficient, remains constant for five or six days at a time (often for a period of a month or more), and is not subject to small temperature changes. The vane is charged at 45 volts because the corresponding sensitivity curve is a straight line for deflections up to 35 cm. Deflections of 0.74 to 1.25 mm. per millivolt are obtained. This sensitivity may be varied somewhat by a change in the height of the vane. The vane is of aluminum, suspended by a quartz fiber, sputtered with gold.

For the much lower intensities encountered in the measurement of fluorescent light, the Compton electrometer yields good results. An aluminum vane, suspended by a Wollaston wire suspension 0.0003 cm. in diameter, is used. With the vane at a potential of 67.5 volts, the sensitivity in the useful range varies from 5.8 to 7.4 mm. per millivolt. The sensitivity may be regulated by the position of the vane or of the adjustable quadrant. The sensitivity curve deviates more from a straight line than does that of the Dolezalek, and the sensitivity varies appreciably from day to day and even from hour to hour, so that readings must be taken quickly or the sensitivity measured very often if results are to be accurate.

The "dark current," i.e., the current through the photocell when the shutter is closed, is reduced by a grounded pool of mercury placed in the depression of the photocell around the glass tubes that contain the tungsten conductors. The dark current is thus confined to the glass between the conductors and to the inner surface of the glass. It is somewhat variable, causing 1 to 10 mm. deflections of the Dolezalek electrometer and 8.5 cm. deflection of the Compton when the leak of 1.65×10^{11} ohms is used.

From the sensitivity of the Dolezalek electrometer and a measurement of the time required for a known small photoelectric current to cause a deflection of 24 cm., the *effective* capacity of the system was calculated. The value obtained was 1.33×10^{-3} microfarads (i.e., 120 cm.). This is larger than the true capacity, since some current passed through the leak to the ground during the measurement. The capacities of the Dolezalek and Compton electrometers are 80 cm. and 12 cm., respectively. When the Dolezalek is replaced by the Compton electrometer, the *effective* capacity of the system, including photocell anode, leak, and connections, is therefore about 50 cm. Capacity is a factor in the time of charging when such small currents are used.

Large changes in the sensitivity of either system may be produced by substitution of leaks of different resistances. This may be accomplished most easily by a variation of the iodine concentration. A second leak (L_2) was prepared from a solution of about 1 g. of iodine per 100 g. of solution. With L_2 and a Compton electrometer at a sensitivity of 7.4 mm. per millivolt, the dark current produces a deflection of about 100 cm. These deflections may be eliminated by a negative charge imparted to the quadrant pair 3–4 by a potentiometer circuit. From the potential required, the resistance of L_2 is estimated to be about 6×10^{12} ohms, i.e., about thirty-five times that of L_1.

CURRENT SENSITIVITIES

The maximum current sensitivities of the Compton, as used in this work (vane at 67.5 volts), are of the order of 8×10^{-16} amperes per millimeter with L_1, and 2.2×10^{-17} amperes per millimeter with L_2. With the Dolezalek, these sensitivities are about one-sixth as great; one of 5×10^{-15} amperes per millimeter has often been used. With L_1, the time required for the vane to be deflected and come to rest is about one minute. With L_2, because of the smaller currents involved, this period is 10 minutes or longer, far too long when many readings are desired.

From the magnitudes of the current sensitivities, the resistances of L_1 and L_2, and the dark currents given above, the resistance of the photocell in the dark is estimated to be approximately 10^{16} ohms, about 10,000 times that of L_1 or 300 times that of L_2. This is about the order of magnitude expected for the resistance of Pyrex glass (4).

MONOCHROMATIC QUALITY OF LIGHT

A Zeiss fixed-arm spectroscope with deviation of 90° was converted into a monochromator by replacement of the eye-piece with a slit provided for the purpose. The lens (l_2) was clamped in a fixed position. The position of l_1 was then found for which the more brilliant mercury lines were in sharp focus at slit 2. When the lenses were so adjusted, the distances from the slits to the corresponding lenses were equal and the light was parallel when it passed through the prism. By use of the mercury arc, the prism was then fixed in such a position that the settings of the wave length scale were accurate to within one or two Ångström units.

The effectiveness of certain slit apertures was studied; the half-intensity widths, *H*, figure 3, of several mercury lines, were estimated from the intensity curves determined with the Dolezalek electrometer. By this method the widths of spectral regions, isolated by the monochromator with narrow slits, were found to vary from approximately 3 A.U. at $\lambda 4000$ A.U. to 13 A.U. at $\lambda 7000$ A.U. To investigate the ability of our system to isolate and measure narrow regions of the spectrum, the *D* doublet emitted by an Akatos sodium lamp was studied. The electrometer deflection curves are given in figure 4 for two experiments. The Compton electrometer was not available when this experiment was performed. If it were employed, narrower slits could probably be used and a precise comparison of the intensities of the two lines might be practical even with a small monochromator such as ours. With sufficient light intensity such as may be obtained from line spectra, and with greater resolving power, better separation can, of course, be obtained.

USES OF APPARATUS

Absorption spectra

The equipment has been used chiefly for obtaining specific light absorption coefficients of solutions, with a Dolezalek electrometer and the leak of 1.65 × 10^{11} ohms resistance. The light source is a 900-watt T-20 Mazda C clear projection lamp, operating on a maximum of 30 volts. The voltage

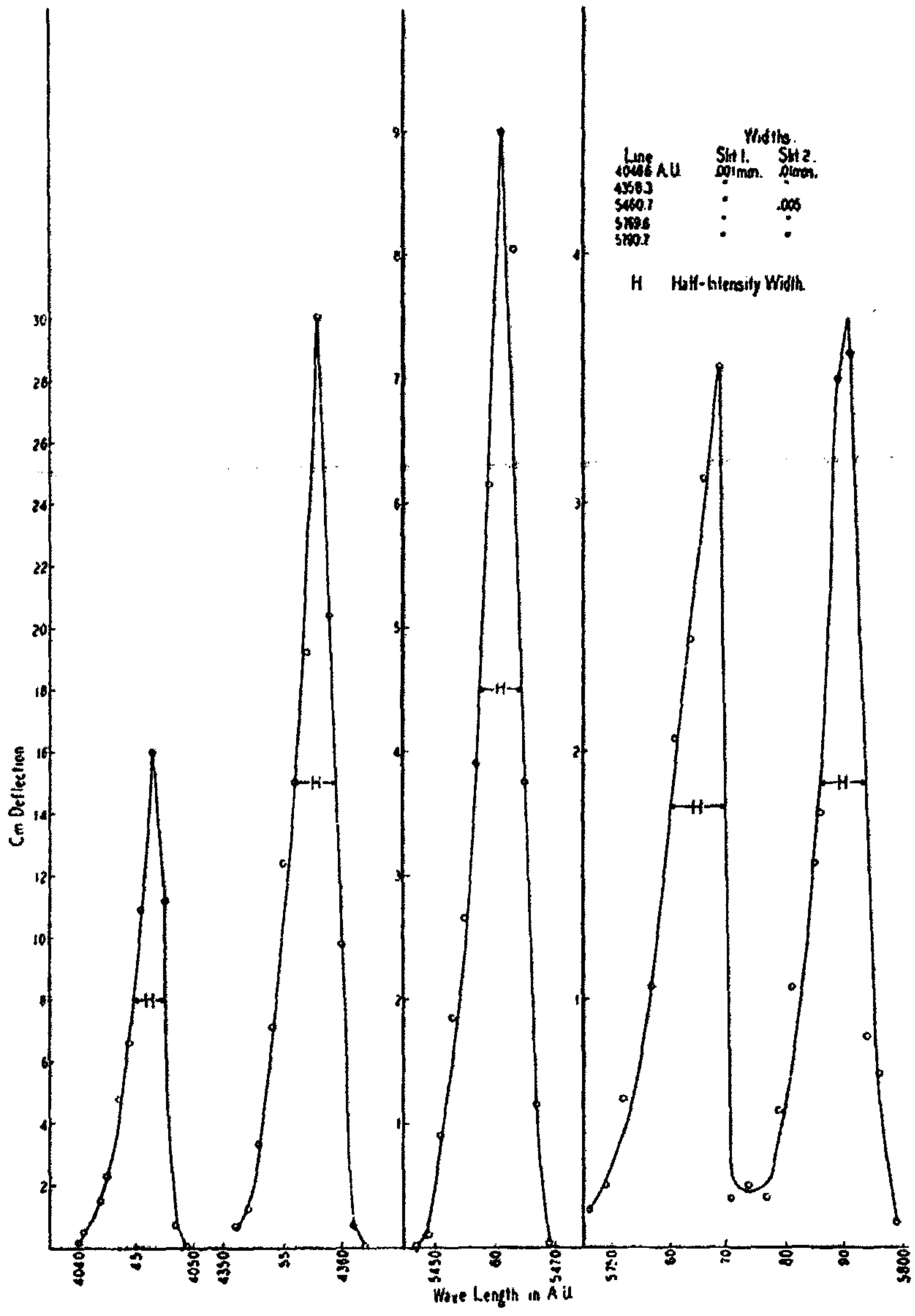

Fig. 3. Lines of Mercury Arc

is supplied by a direct current generator in parallel with a series of 6-volt radio "A" batteries, so arranged with resistance coils that the battery voltage is slightly above the generator voltage delivered to the lamp. Only 0.1 to 1.0 ampere is drawn from the batteries and a current nearly free from fluctuations is delivered to the lamp. The lamp gives sufficient light in the visible when operating on 20 to 26 amperes. It is surrounded on four sides with shields, which decrease fluctuations in temperature caused by air currents.

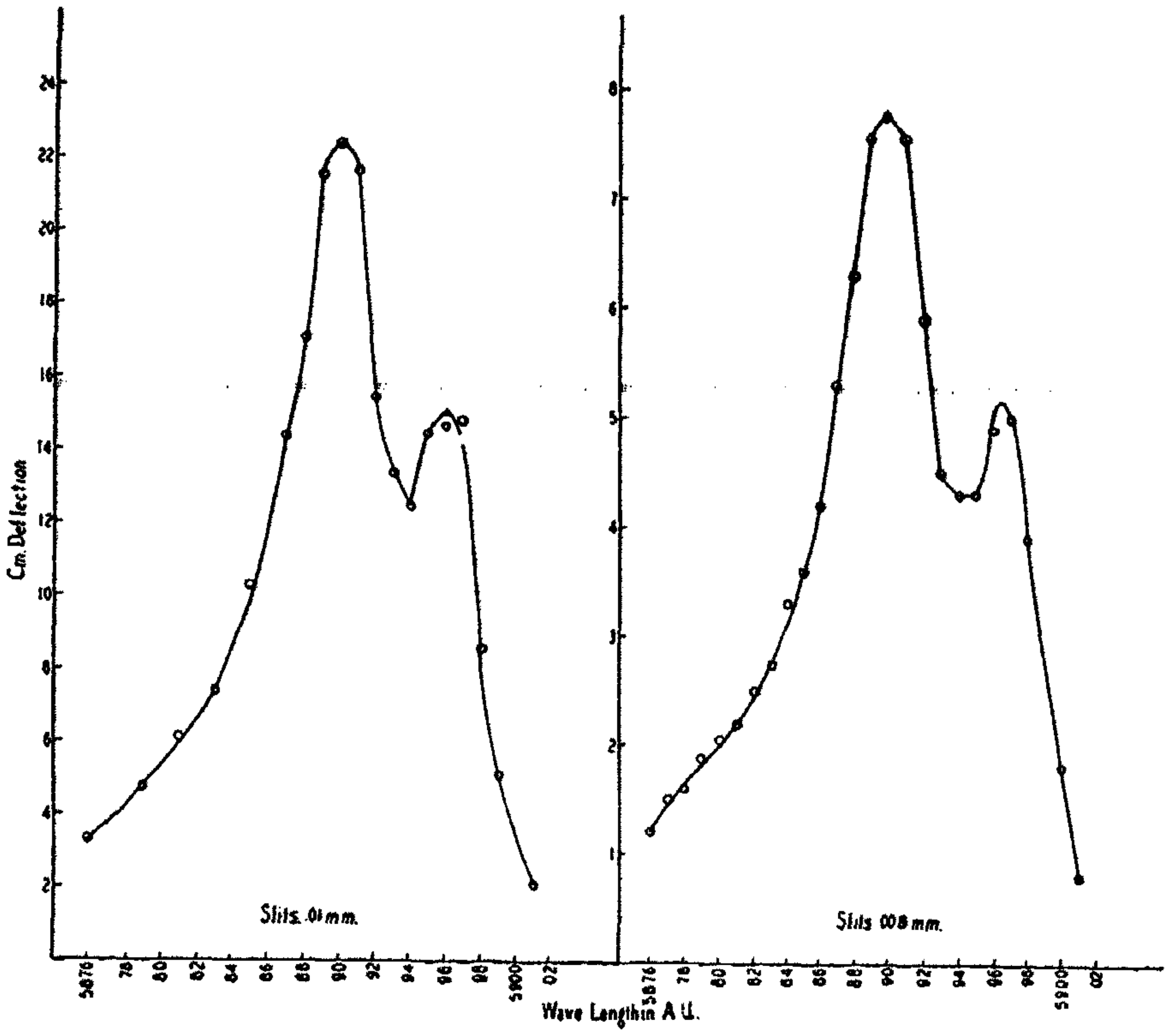

Fig. 4. Sodium *D* Lines

To illustrate resolution with small monochromator

The slit widths are so chosen that I_0 produces a deflection of 20 to 35 cm. For the Mazda lamp, operating at 600 watts or less, they are approximately 0.001 mm. at λ7800 A.U., 0.002 mm. at λ6000–7000 A.U., 0.004 mm. at λ5000 A.U., 0.02 mm. at λ4000 A.U. and 0.03 mm. at λ3950 A.U. Such slit apertures make it possible to isolate regions varying in width from about 6 A.U. at λ4000 A.U. to 13 A.U. at λ7000 A.U. To isolate a spectral region 3 A.U. wide at λ4000 A.U. by the use of narrower slits, the current consumption of the lamp should be increased.

About three minutes are required for the three determinations necessary for the calculation of one absorption coefficient. I_x is compared with the mean of two values of I_0, one taken before and one after I_x. Differences in I_0 reveal any accidental variations in light intensity.

The absorption cells, filled with solvent, should transmit as nearly as possible the same amount of light. There is no difficulty in placing them so that 30-cm. deflections agree within 3 mm., i.e., 1 per cent. With care they may be made to agree within 0.5 mm. After a series of many readings, during which the solution cell is emptied and refilled as many as ten times, the relative transmission of the cells containing solvent does not differ from the original value by more than 1 per cent. This small difference between the cells is thus relatively constant and affects but slightly the relative values of absorption coefficients.

TABLE 1*

Absorption data for solution of chlorophyll

Source of light a Mazda lamp

WAVE LENGTH	SOLVENT FIRST DEFLECTION	SOLVENT SECOND DEFLECTION	MEAN SOLVENT DEFLECTION	SOLUTION DEFLECTION	I_0	I_x	$\frac{I_0}{I_x}$	LOG $\frac{I_0}{I_x}$
A.U.	*cm.*	*cm.*	*cm.*	*cm.*	*millivolts*	*millivolts*		
4300	25.10	25.05	25.07	13.50	337	184	1.831	0.2627
4300	25.05	25.00	25.02	13.50	337	184	1.831	0.2627
4300	24.50	24.45	24.47	13.20	329	180	1.828	0.2620
6600	24.65	24.60	24.62	15.00	331	204	1.622	0.2101
6600	24.60	24.35	24.47	14.90	329	203	1.621	0.2098
6600	24.35	24.60	24.47	14.95	329	203	1.621	0.2098

* Examples of absorption data from certain ether solutions of chlorophyll used in this laboratory. For each wave length, the data and calculations of three successive determinations of log I_0/I_x are given. The solvent deflections, taken before and after the solution deflections, are in columns 2 and 3, respectively. In column 4 is the mean of the solvent deflections. Column 5 contains the solution deflections. In columns 6 and 7 are the quadrant potentials (taken from the Dolezalek electrometer sensitivity curve) necessary to produce the deflections listed in columns 4 and 5, respectively. These potentials are directly proportional to the photoelectric current.

Since the refractive indices of the solvent and dilute solutions are nearly equal, no appreciable change of the light focus on the slit is caused by an exchange of the absorption cells. For comparisons of some media having widely different refractive indices it may be necessary to take precautions to eliminate serious errors due to change of focus.

Magnitude of error

When conditions are steady and the lamp filament has reached a constant temperature (usually within fifteen minutes), the deflection caused by light of any wave length may be reproduced after three minutes within the precision of reading, 0.5 mm. In routine spectral analysis most readings of I_0 check within 0.5 per cent; determinations are repeated when I_0 is not reproduced within 1 per cent. I_x is equally precise if the deflection is large enough.

With the electrometer working under good conditions, the zero point may be reproduced within 0.5 mm. after as many as twenty successive determinations of β, without a return of the vane to the zero position in the meantime.

If 0.5 per cent errors in I_0 and I_x both contribute to a 1 per cent error in I_0/I_x, the ratio may appear to be 2.02 when the true value is 2.00. The log of 2.02 is 0.3054, about 1.5 per cent larger than the log of 2.00 (0.3010). Since log I_0/I_x is proportional to the specific absorption coefficient β (and the molecular absorption coefficient α, if Beer's law holds), the precision in this example is 1.5 per cent. Most of the values obtained are more precise than this. As deflections for I_x or I_0 decrease to small values, however, the error in log I_0/I_x increases.

Table 1 illustrates the reproducibility of results for a Mazda source.

Fluorescence spectra

This system is well adapted to the spectral measurement of fluorescent light from strongly fluorescent solutions, such as that of chlorophyll in ether. A tapering fluorescence tube is placed next to the slit, from which the guard window has been removed so that the point of origin of the fluorescent light may be as near the slit as possible. The exciting light from the 900-watt Mazda lamp enters the tube at right angles to the collimator through a plane window. About 1 mm. from this window and just in front of slit 1, it is brought to a focus.

With a Compton electrometer having a sensitivity of 6 mm. per millivolt, leak 1, and slits 0.03 mm. wide, maximum deflections of 25 cm. are produced by fluorescent light of λ6690 A.U. from ether solutions containing 0.015 g. of chlorophyll *a* per liter. Twenty-five seconds are required for each reading. Smooth curves were obtained for the fluorescence bands, whose maxima may be reproduced within 10 A.U. Successive deflections for the same wave length may be repeated within 0.5 per cent. To obtain the true fluorescence intensity-wave length curve, the sensitivity-wave length curve of the photocell must be determined and combined with these fluorescence data.

Data for chlorophylls *a* and *b*, obtained by use of this instrument, are to be reported soon by one of us (F. P. Z.).

SUMMARY

The photographic method is not satisfactory for measurement of opacity with a precision better than 5 per cent. In the usual photoelectric methods, comparatively wide spectral regions are employed. A photoelectric method of higher precision is available, which may be used for the measurement of relative intensities of light emitted from a continuous source, though limited to very narrow spectral ranges. A monochromator, photocell, electrometer, and high resistance leak are used. Photoelectric current sensitivities as great as 2×10^{-17} amperes per millimeter permit the use of slits so narrow that spectral regions varying in width from 3 A.U. at λ4000 A.U. to 13 A.U. at λ7000 A.U. may be investigated with a small standard monochromator, without amplification of the photoelectric current. A 900-watt Mazda lamp may be used for absorption spectra measurements.

Specific absorption coefficients and opacities may be determined with a precision better than 1.5 per cent and 1.0 per cent, respectively. Examples of data are presented. The method is well adapted to the spectral measurement of fluorescent light from strongly fluorescent solutions.

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THE ADSORPTION OF COPPER SULFATE BY SPHALERITE AND ITS RELATION TO FLOTATION

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Received August 11, 1933

In the recovery of sphalerite (ZnS) by the flotation process, the mineral must almost invariably be activated, i.e., a soluble heavy-metal salt (in practice, copper sulfate) must first be added before the mineral can be successfully floated. The problem of the activation of sphalerite by copper sulfate has been the object of a great deal of attention, and the general consensus of opinion is that the copper sulfate reacts with the zinc sulfide to form the more insoluble cupric sulfide at the surface of the sphalerite (1). Although Taggart (2) seems to consider the film to be cuprous sulfide, and Cox and Wark (3) are skeptical as to the completely chemical nature of the activation, the formation of a film of cupric sulfide appears to be the most probable explanation from the experimental evidence which exists.

If the formation of a film of cupric sulfide according to the reaction

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

be accepted as a working hypothesis, the thickness of the film is a matter of considerable interest. In order to obtain information concerning this, a series of tests was made to determine the amounts of copper adsorbed by various sizes of sphalerite. The mineral was carefully sized and deslimed as described by Kidd and Wall (4).

Since cupric ion reacts with metallic iron, it was very essential to remove all traces of the latter (which might have been introduced into the mineral in the crushing and grinding processes) from the sphalerite. Most of the iron was removed by means of a strong electromagnet, the mineral being cleaned with the magnet both before and after grinding and before and after sizing. To remove the final traces, the sized and deslimed mineral was leached for eighteen hours with 6 normal hydrochloric acid, and then thoroughly washed with copper-free distilled water and allowed to dry. A 50-g. sample was weighed out and treated with 1 normal hydrochloric acid to remove any oxide film which might have formed during drying. The acid was washed out as before, and 250 cc. of 0.02 *M* copper sulfate was added. The solution was very carefully analyzed iodimetrically with

0.01 *N* thiosulfate before it had been added to the mineral and also after it had been in contact with the mineral for varying lengths of time. It was found, however, that practically all the adsorption took place during the first minute, there being no appreciable change in the concentration of the solution after that length of time. In column 4 of table 1 are given the amounts of copper adsorbed per gram of sphalerite for the various sizes studied.

Some of the results obtained by Kidd and Wall (4) are also of interest in this problem. Using 0.15 lb. of potassium ethyl xanthate and 0.15 lb. of cresylic acid per ton of sphalerite, they found that best flotation recoveries were obtained with 0.1 lb. of $CuSO_4 \cdot 5H_2O$ per ton of mineral for particles larger than 104 microns, with 0.2 lb. per ton for particles between 104 and 74 microns, and with 0.3 lb. per ton for particles finer than 74 microns. With greater or smaller amounts than these, the recoveries decreased. These results, expressed as milligrams of copper per gram of sphalerite, are listed in column 3 of table 1.

TABLE 1

PARTICLE SIZE	MILLIGRAMS OF COPPER PER GRAM OF ZINC SULFIDE FOR MONOMOLECULAR FILM	MILLIGRAMS OF COPPER PER GRAM OF ZINC SULFIDE FOR MAXIMUM RECOVERY	MILLIGRAMS OF COPPER PER GRAM OF ZINC SULFIDE ADSORBED IN ADSORPTION TESTS	"THICKNESS" OF FILM
microns				
−295+208	0.01012	0.0127	0.53	51.3
−208+147	0.01433	0.0127	0.60	41.8
−147+104	0.02033	0.0127	0.68	33.5
−104+74	0.02867	0.0254	0.76	26.5
−74+52	0.04050	0.0381	0.88	21.7
−52+37	0.05733	0.0381	1.00	17.5
−37+26	0.08099	0.0381	1.20	14.8
−26+18.5	0.1147	0.0381	1.40	12.2
−18.5+13	0.1620	0.0381	1.60	9.9
−13+9.2	0.2298	0.0381	1.80	7.8
−9.2+6.5	0.3250	0.0381	2.20	6.8

In order to interpret the results of these two sets of experiments, it is first necessary to determine, for the various sizes, the amounts of copper required to form a monomolecular film on the surfaces of all the particles in one gram of sphalerite. This was done in the following manner, the −295+208 micron size being used as an example.

For this size range, the average particle size is 0.0252 cm. If it be assumed that the particles are in the form of regular tetrahedra (the ideal crystal form of sphalerite) having edges of this length, the volume of each particle is 1.886×10^{-6} cc. and the area is 1.10×10^{-3} sq. cm. (For regular tetrahedra, $V = 0.11785\ L^3$ and $A = 1.732\ L^2$, where L is the length of the edge.) Since the density of sphalerite is 4.1, the volume occupied by 1 g. is 0.244 cc. Dividing this by the volume of one particle gives 1.293×10^5 as the number of particles per gram, which, multiplied by the surface area of one particle, gives 142.2 sq. cm. as the total surface area of 1 g. of the mineral.

The lattice constant for sphalerite is 5.43 A.U. (5) and the unit cell contains two zinc atoms in one surface. Consequently there is one zinc atom in a surface area of $\frac{1}{2}$ $(5.43 \times 10^{-8}$ cm.$)^2$, or 1.474×10^{-15} sq. cm. Dividing this into the total surface area of 1 g. of the sphalerite gives 9.647×10^{16} as the number of atoms of zinc present in the surface of 1 g. of the $-295+208$ micron sphalerite. If, in accordance with the reaction given above, it be assumed that each of these zinc atoms reacts with a copper ion, this will also be the number of copper ions required to form a monomolecular film, and is equivalent to 0.01012 mg. of copper per gram of sphalerite. The corresponding amounts of copper for all the sizes studied are given in column 2 of table 1.

DISCUSSION

A comparison of the second and third columns of table 1 shows that for particles larger than about 37 microns the amount of copper which gives the best flotation recovery is equal, within experimental error, to the amount required to form a monomolecular film. For smaller particles, however, maximum recoveries are obtained with considerably less copper than is required for a monomolecular film, and the difference increases rather rapidly with decrease in particle size. A probable explanation of these facts is that with the larger particles a practically complete monomolecular film is required in order to provide sufficiently strong attachment to the air bubbles to enable the particles to remain attached throughout the flotation process; the reason that a greater amount of copper decreases the recovery may be due to reaction between the excess copper and xanthate, decreasing the concentration of the latter below its optimum value. (Kidd and Wall (4) found that 0.15 lb. of potassium ethyl xanthate per ton of sphalerite gave the optimum recoveries with particles larger than about 37 microns; with either more or less xanthate the yields were decreased.) With the smaller particles it seems quite likely that strong enough attachment could result with less than a complete monomolecular film, and since the weight of a particle decreases more rapidly than its area, the fraction of the area which would have to be filmed with copper would decrease with decrease in size.

In column 5 of table 1 are given the "thicknesses" of the films of copper sulfide obtained in the adsorption experiments. These values were obtained by dividing the figures in the fourth column by the corresponding figures in the second, and are given purely for the purpose of comparison, since nothing is known of the arrangement of the molecules in the adsorption layer. Two facts, however, are immediately evident: first, the films formed on sphalerite in a solution of the strength used (many times that used in flotation practice) are apparently many molecules thick, and second, this "thickness" decreases as the particle size decreases. When the logarithm of the "thickness" is plotted against the logarithm of the average particle size, a straight line (figure 1) is obtained, which, when extrapolated, indicates that a monomolecular film would result with particles 0.37 micron in size. The equation

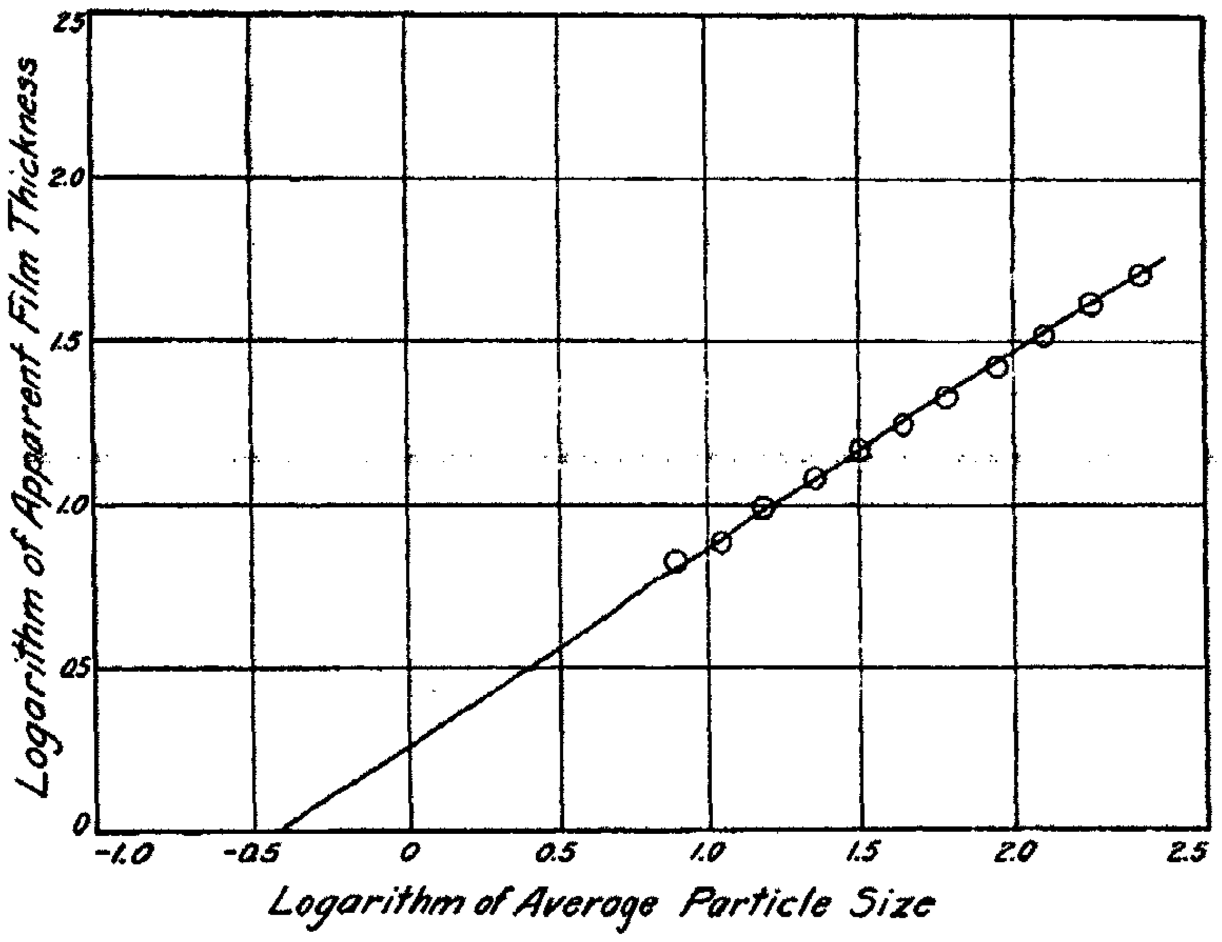

FIG. 1. VARIATION OF APPARENT THICKNESS OF ADSORBED FILM WITH SIZE (IN MICRONS) OF SPHALERITE PARTICLES

$$T = \left(\frac{d}{0.37}\right)^{0.608}$$

where T is the apparent film thickness and d the particle size in microns, fits the curve very well.

These facts are difficult to explain on the basis of familiar concepts. A possible explanation may lie in the change of surface forces with size; as the size decreases the initially formed layers of copper sulfide may become more compact, thus rendering diffusion more difficult, which would tend to decrease the thickness of the films. It is rather difficult, however, to conceive of any change in surface forces becoming appreciable in the larger sizes studied.

The recent theory of the mosaic or block structure of crystals leads to a more probable explanation. This theory, developed theoretically by Zwicky (6) and supported by the excellent experimental work of Goetz (7) on single bismuth crystals, states that all crystals have, besides their regular crystal structure, a much larger secondary structure manifested by periodic changes in density. Goetz found the resulting "blocks" to be approximately 1.4 microns in length. The work of Dean, Gross, Brighton, and St. Clair (8) indicates that in the case of galena the blocks have a length of less than 20 microns, and they consider it possible for certain molecules (e.g., H_2S) to penetrate between these blocks.

The results of the adsorption experiments can be explained by assuming that the copper ions penetrate to a certain extent between the elementary blocks of the sphalerite crystals, as well as forming a monomolecular film on the surfaces. When the individual blocks are liberated, only the amount of copper required to form a monomolecular film will be adsorbed, and from figure 1 it appears that for sphalerite the size of these blocks is 0.37 micron. It is obvious that the larger the particles, the more crevasses between blocks there will be for copper ions to diffuse into, and accordingly, the greater will be the apparent film thickness. This explanation does not necessarily conflict with that offered for the results of the flotation experiments. In the latter, the solutions were very dilute in copper and the total amount present was never appreciably greater than the amount required for a monomolecular film. It seems quite reasonable to suppose that the copper ions would react with zinc atoms in the surfaces exposed in preference to penetrating between the blocks.

SUMMARY

1. With sphalerite particles larger than about 37 microns, the amount of copper sulfate which gives the best flotation recoveries is equal to the amount required to form a monomolecular film of cupric sulfide.
2. With smaller particles, maximum recovery is obtained with less than the amount of copper sulfate required for a monomolecular film, the difference between the amount required for maximum recovery and that required for a monomolecular film increasing with decrease in particle size.
3. A simple explanation is offered to account for these flotation results.
4. The amounts of copper adsorbed by sphalerite of various sizes from a 0.02 *M* copper sulfate solution are equivalent to surface films of copper sulfide many molecules thick. These "thicknesses," however, decrease as the particles become smaller.
5. An explanation of the results of the adsorption tests by change of surface forces with size appears improbable. The theory of the mosaic structure of crystals, however, provides an explanation which agrees very satisfactorily with the results obtained.

6. The adsorption tests indicate that the unit blocks of sphalerite are approximately 0.37 micron in length.

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A NEW THEORY OF FERRIC OXIDE HYDROSOLS

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INTRODUCTION

Among the contributions to the chemistry of so-called iron oxy hydrosols, three originated in this laboratory. Thomas and Frieden (1), studying iron oxychloride sols, reported a constant ratio of iron to chloride when sols were dialyzed to incipient precipitation, and they offered the solution link theory to explain the nature of sol stability, according to which the micellar agglomerate was kept in solution by the solution forces inherent to the ferric chloride associated with the other constituents forming the micelle. Hamburger (2) prepared iron oxybromide sols and reported no constant ratio of iron to anion (purity) although, on the whole, the bromide sols appeared to be more stable than the chloride sols studied simultaneously. Mabee (3) prepared and studied the properties of ferric oxyacetate hydrosols. He found a constant purity and, in general, lower stability than was reported for the two types of sols previously studied. Both Hamburger and Mabee believed their results to be in harmony with an hydrolytic definition of hydrosols, and with the above mentioned solution link theory.

It was thought that a study of ferric oxypropionate sols might be an interesting comparison with these sols investigated earlier.

PRELIMINARY EXPERIMENTS

Ferric hydroxide was made by electrolysis of water, to which was added a few drops of sodium hydroxide solution to provide conductivity, using an iron anode and a carbon cathode. The ferrous hydroxide thus formed was oxidized by air, and the resulting ferric hydroxide was washed by decantation.

Attempts to peptize this product with propionic acid seemed unsuccessful, and this method of sol preparation was discarded. It was thought that the precipitate was too granular and too little hydrated to be readily peptized. Next, some pure iron filings were dissolved in dilute propionic acid; after standing several days, during which time there was a very slow evolution of hydrogen, a sample of the ferrous propionate solution was oxidized

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by treatment with hydrogen peroxide to absence of ferrous iron test with ferricyanide. (If the solution were not completely oxidized, it was found that addition of ammonium hydroxide yielded a black precipitate, which, upon drying, proved to be magnetic.)

The ferric propionate solution was then put into collodion membranes for dialysis to incipience of precipitation. In a very short time, small amounts of reddish-brown flocculate had appeared, so four different sols were immediately analyzed, without centrifuging out the excess precipitated iron. The respective purities $\frac{(\text{equiv. Fe})}{(\text{equiv. Anion})}$ were found to be 1.2, 4.3, 3.8, and 1.1, while still another sample, intentionally somewhat beyond incipience of precipitation, was found to have a purity of only 5.1.

In these analyses, the iron was determined (4) by heating to white fumes with sulfuric acid, passing through a Jones' reductor, and titrating with standardized permanganate solution. The propionate was determined (5) by heating, hydrolyzing, salting out, and titrating with standard sodium hydroxide solution, using phenolphthalein as an indicator.

The fact that these iron propionate solutions should contain such a relatively small amount of iron in proportion to anion, as compared to sols previously studied, was entirely unexpected, and led to consideration of the possibilities suggested in the following section.

THEORETICAL

Besides the investigators already mentioned, several other colloid chemists have expressed beliefs that colloidal iron solutions underwent hydrolytic changes. Among these are Malfitano (6), Buzágh (7), Pauli and Matula (8), Tian (9), and others, but none of them has suggested any theoretical treatment or procedure to enlarge such beliefs. Therefore, the following development has been made, while fully realizing that in such complex systems as are dealt with, the considerations of equilibria must of necessity be rather loosely construed; this method of treatment is thus offered and utilized as a means to arrive at some interesting relations.

Keeping this in mind, we may say at once that if colloidal solutions are formed by progressive hydrolysis, they should follow laws analogous to those derived for the hydrolytic relations from the law of mass action. According to these derivations, a salt of the type MA_3 may have two possibilities in hydrolyzing, the distinction being based upon whether the acid formed is weakly or highly dissociated. First considering the strong acid type, from the equation

$$MA_3 + 3H_2O \rightleftharpoons M(OH)_3 + 3HA$$

letting x represent the amount hydrolyzed, and v the volume in liters containing one mole of salt, and assuming both salt and acid to be completely ionized, we have

$$k = \frac{[M(OH)_3]\,[HA]^3}{[MA_3]\,[H_2O]^3}$$

Since the $[H_2O]$ is constant in aqueous solution

$$K_{\text{hyd.}} = \frac{[M(OH)_3]\,[HA]^3}{[MA_3]} = \frac{\left[\frac{x}{v}\right]\left[\frac{3x}{v}\right]^3}{\frac{1-x}{v}} = \frac{27\,x^4}{(1-x)\,v^3} \tag{1}$$

Since

$$[H^+]\cdot[OH^-] = s_{H_2O}$$

then

$$[H^+] = 3x = \frac{s_{H_2O}}{[OH^-]}$$

so

$$[OH^-] = \sqrt[3]{K_{M(OH)_3}\frac{[M(OH)_3]}{[M^{+++}]}}$$

and since

$$[M^{+++}] = \frac{1-x}{v}$$

then

$$[OH^-]^3 = K_{M(OH)_3}\frac{[M(OH)_3]}{\frac{1-x}{v}}$$

Moreover

$$[\text{Total acid}]^3 = \frac{s^3_{H_2O}}{K_{M(OH)_3}\frac{[M(OH)_3]}{\frac{1-x}{v}}}$$

Therefore

$$K_{\text{hyd.}} = \frac{27\,x^4}{(1-x)\,v^3} = \frac{[M(OH)_3]\left[\frac{s^3_{H_2O}}{[K_{M(OH)_3}]\frac{[M(OH)_3]}{\frac{1-x}{v}}}\right]}{\frac{1-x}{v}} = \frac{s^3_{H_2O}}{K_{M(OH)_3}}$$

But when the acid formed by the hydrolysis is little ionized:

$$[\mathrm{M(OH)_3}] = \frac{x}{v},\ [\mathrm{OH^-}] = \sqrt[3]{K_{\mathrm{M(OH)_3}} \frac{[\mathrm{M(OH)_3}]}{[\mathrm{M^{+++}}]}},\ [\mathrm{M^{+++}}] = \frac{1-x}{v},\ \text{and}$$

$$[\mathrm{A^-}] = \frac{3(1-x)}{v}$$

$$[\mathrm{OH^-}] = \frac{s_{\mathrm{H_2O}}}{[\mathrm{H^+}]} = \frac{s_{\mathrm{H_2O}}}{K_{\mathrm{HA}} \frac{[\mathrm{HA}]}{[\mathrm{A^-}]}}$$

$$K_{\mathrm{M(OH)_3}} \frac{[\mathrm{M(OH)_3}]}{[\mathrm{M^{+++}}]} = \frac{s^3_{\mathrm{H_2O}}\,[\mathrm{A^-}]^3}{K^3_{\mathrm{HA}}\,[\mathrm{HA}]^3}$$

$$K_{\mathrm{hyd.}} = \frac{s^3_{\mathrm{H_2O}}}{K^3_{\mathrm{HA}} \cdot K_{\mathrm{M(OH)_3}}} = \frac{[\mathrm{M(OH)_3}]\,[\mathrm{HA}]^3}{[\mathrm{M^{+++}}]\,[\mathrm{A^-}]^3} = \frac{\left(\frac{x}{v}\right)\left(\frac{3x}{v}\right)^3}{\left(\frac{1-x}{v}\right)\left(3\left(\frac{1-x}{v}\right)\right)^3} = \frac{x^4}{(1-x)^4}$$

$$K_{\mathrm{hyd.}} = \frac{x^4}{(1-x)^4} = \frac{s^3_{\mathrm{H_2O}}}{K^3_{\mathrm{HA}} \cdot K_{\mathrm{M(OH)_3}}} \qquad (3)$$

Therefore in the latter type of hydrolysis the reaction is independent of dilution, whereas in the first type the extent of the hydrolysis varies as $\sqrt[4]{v^3}$.

Now in the case of colloidal solutions, if we consider the complex as a somewhat soluble but little ionized *base*, ionized into $\mathrm{Fe^{+++}}$ and $\mathrm{OH^-}$ ions, we have exactly the same conditions if the so-called chemical (hydrolytic) point of view of hydrosols is correct,—up to the point of incipience of precipitation when the relations expressed above break down, and undergo a complete change due to the formation of insoluble bases. But from the point of true (ionic) solution through colloidal (micelle) formation to the beginning of precipitation, there is no apparent reason why colloidal iron solutions should not follow some such laws as those derived above, provided the solutions themselves are undergoing purely chemical reactions. This state of affairs might be expressed by some such system as

$$\begin{array}{l} \mathrm{(Fe(OH)_3)}_M \cdot (x)\mathrm{Fe^{+++}} + 3(x)\ \mathrm{A^-} \\ \quad\ \ \downarrow\!\uparrow \\ (\mathrm{Fe^{+++}}) + 3(\mathrm{OH^-}) \end{array}$$

This might be progressively hydrolyzed to

$$\begin{array}{l} \mathrm{(Fe(OH)_3)}_N \cdot (y)\mathrm{Fe^{+++}} + 3(y)\mathrm{A^-} + (x-y)\mathrm{HA} \\ \quad\ \ \downarrow\!\uparrow \\ (\mathrm{Fe^{+++}}) + 3(\mathrm{OH^-}) \quad \text{where} \quad x > y \quad \text{and} \quad N > M \end{array}$$

For a sol of purity = 20, the hydrolytic "equation" might be written

$$20\mathrm{FeA_3} + 57\mathrm{H_2O} \rightleftharpoons (\mathrm{Fe(OH)_3})_{19} \cdot \mathrm{FeA_3} + 57\mathrm{HA}$$

As the acid formed is dialyzed away, the sol would analyze to 60 equivalents of iron and 3 equivalents of anion, thereby giving a purity of 20. If dialysis were continued, successive stages of hydrolysis would be reached, more $Fe(OH)_3$, less (Fe^{+++}) and (A^-) present, and hence higher purities. Then for the progressive hydrolysis of iron salts to colloidal solutions we have the two types of reactions, and the respective "colloidal hydrolysis constants:"

$$K_{\text{coll. hyd.}} = \frac{s^3_{H_2O}}{k_b} = \frac{27x^4}{(1-x)\,v^3} \tag{4}$$

and

$$K_{\text{coll. hyd.}} = \frac{s^3_{H_2O}}{K^3_a \cdot K_b} = \frac{x^4}{(1-x)^4} \tag{5}$$

where K_a is the dissociation constant of the acid formed, and K_b represents the dissociation constant of the complex colloidal radical *as a base.*

Then the colloidal solutions of ferric chloride, bromide, nitrate, etc. should follow equation 4, while those of the acetate, propionate, and butyrate should follow equation 5.

Now although we do not know the respective K_b values of various iron colloids, at least we may safely assume that they are very small, and of the same order of magnitude.

Then if we consider the two salts $Fe(A_1)_3$ and $Fe(A_2)_3$, both of which form weak acids upon hydrolysis, we may write as the relation between their respective "colloidal hydrolysis constants:"

$$\frac{K_1}{K_2} = \frac{\dfrac{s^3_{H_2O}}{K^3_{HA_1} \cdot K_{b_1}}}{\dfrac{s^3_{H_2O}}{K^3_{HA_2} \cdot K_{b_2}}} = \frac{K^3_{HA_2}}{K^3_{HA_1}} \tag{6}$$

Then we see that the ratio of the "constants" is inversely proportional to the cubes of the dissociation constants of the respective acids produced by the hydrolysis, after having assumed that K_{b_1} and K_{b_2} are nearly equal.

If we call R this ratio,

$$\frac{K_1}{K_2} = \frac{K^3_{HA_2}}{K^3_{HA_1}} = R$$

then it is also true that

$$R = \frac{\dfrac{x_2^4}{(1-x_2)^4}}{\dfrac{x_1^4}{(1-x_1)^4}} \tag{7}$$

from which

$$\frac{x_2}{1 - x_2} = \sqrt[4]{R} \cdot \frac{x_1}{1 - x_1} \tag{7a}$$

or, in other words, the fraction of one salt hydrolyzed will always be a constant times the fraction hydrolyzed of the other salt (under the same conditions of time and temperature).

Dividing both sides of equation 7 by x_1^4, and multiplying both sides by x_2^4, we arrive at

$$\frac{\left(\frac{1}{1 - x_1}\right)^4}{\left(\frac{1}{1 - x_2}\right)^4} = \frac{x_2^4}{x_1^4} \cdot R$$

therefore

$$\frac{\frac{1}{1 - x_1}}{\frac{1}{1 - x_2}} = \frac{x_2}{x_1} \sqrt[4]{R}$$

Now as soon as appreciable purities are reached —high ratios of iron over anion—x_1 and x_2 become very nearly equal, and $\frac{1}{1 - x}$ is equal to the purity at incipience of precipitation as previously defined, therefore, approximately,

$$\frac{P_1}{P_2} = \sqrt[4]{R} \tag{8}$$

But for weak acids, R is quite small—for acetic and propionic it is only 2.4—so we may conclude that very nearly equal purities at incipience of precipitation should be found for two iron salts both of which yield weak acids upon hydrolyzing.

Another interesting application when a weak acid is formed is seen in the equalities set down below:

$$[H^+] = K_{HA} \frac{[HA]}{[A^-]} = K_a \frac{x}{1 - x} = K_a \times \sqrt[4]{\frac{s^3_{H_2O}}{K_a^3 \cdot K_b}} \tag{9}$$

or,

$$[H^+] = \text{a constant} \tag{10}$$

Also, it is interesting to point out that from equation 9 one may find the magnitude of K_b, if the pH is first determined.

Such calculations cannot be applied to sols where a strong acid is formed; first, because the changing dilution during dialysis must change the purity relationships, and secondly because the acid is dialyzed away, and there is no constancy possible here as was the case with the acetate.

Now again turning to the strong acids, it is evident, since the extent of the hydrolysis varies as $\sqrt[4]{v^3}$, that constant optimum purity values can be obtained only if no dilution takes place during dialysis. In other words, the purities of this type of sol at incipient precipitation should *not* be constant.

Neidle (10) reports this qualitatively for the oxychloride; Hamburger (2) for the ferric oxybromide sol. Thomas and Frieden report a constant purity for ferric oxychloride sol, but this may be due to the fact that the determinations were made on a sol of low concentration, which was divided into samples of various dilutions, after first undergoing the same preliminary dialysis, both of which procedures would help in masking differences in the sols at the end of the experiments.

It has been known for a long time that sulfate ion was a good precipitation or flocculation agent for iron oxysols. The theoretical derivations demand this, as may be seen from the following relationships:

$$\mathrm{Fe_2(SO_4)_3} + 6\mathrm{H_2O} \rightleftharpoons 2\,\mathrm{Fe(OH)_3} + 3\mathrm{H_2SO_4}$$

Using the same notations,

$$K = \frac{[\mathrm{Fe(OH)_3}]^2\,[\mathrm{H_2SO_4}]^3}{[\mathrm{Fe_2(SO_4)_3}]} = \frac{\left(\frac{2x}{v}\right)^2\left(\frac{3x}{v}\right)^3}{\frac{1-x}{v}} = \frac{108\,x^5}{(1-x)\,v^4}$$

also

$$[\mathrm{H^+}] = \frac{s_{\mathrm{H_2O}}}{[\mathrm{OH^-}]}$$

$$[\text{Total acid}] = \tfrac{1}{2}\,[\mathrm{H^+}],$$

and

$$[\mathrm{OH^-}] = \sqrt[3]{K_{\mathrm{Fe(OH)_3}}\frac{[\mathrm{Fe(OH)_3}]}{[\mathrm{Fe^{+++}}]}}$$

then

$$[\text{Total acid}]^3 = \tfrac{1}{8}\left(\frac{s^3_{\mathrm{H_2O}}}{[\mathrm{OH^-}]^3}\right) = \tfrac{1}{8}\,\frac{s^3_{\mathrm{H_2O}}}{K_{\mathrm{Fe(OH)_3}}\frac{[\mathrm{Fe(OH)_3}]}{[\mathrm{Fe^{+++}}]}}$$

$$K = [\mathrm{Fe(OH)_3}]^2\cdot\tfrac{1}{8}\,\frac{s^3_{\mathrm{H_2O}}}{K_{\mathrm{Fe(OH)_3}}\frac{[\mathrm{Fe(OH)_3}]}{[\mathrm{Fe^{+++}}]}} \div [\mathrm{Fe_2(SO_4)_3}] = \frac{\left(\frac{2x}{v}\right)^2\frac{s^3_{\mathrm{H_2O}}\cdot 2\left(\frac{1-x}{v}\right)}{8K_{\mathrm{Fe(OH)_3}}\cdot 2\left(\frac{x}{v}\right)}}{\frac{1-x}{v}}$$

$$= \frac{s^3_{\mathrm{H_2O}}\cdot x}{2K_{\mathrm{Fe(OH)_3}}\cdot v} = \frac{108\,x^5}{(1-x)\,v^4} \qquad (11)$$

from which it is evident, comparing equation 11 with equation 4, that K for ferric sulfate must be smaller than in the case of the chlorides, etc., for x is always less than 1 (in the case of the sulfate, indeed, it is probably very small) and V is always greater than 1, as fairly dilute solutions must be used if colloidal solutions are to be formed. In addition we have the factor 2 appearing in the denominator, which would make the sulfate even less "colloidal" compared with the other strong acid types.

The micelle as pictured according to the above relationships agrees very closely with the "solution link" theory of colloidal stability, the ferric hydroxide formed by the hydrolysis being dragged into solution by a soluble ferric salt which has previously been called the peptizing agent. As hydrolysis proceeds, the $Fe(OH)_3$ chain gets larger and larger until finally there is not enough of the peptizing agent present, and precipitation occurs. It should be noted that the law of mass action as used above has always been applied to the ("solution link") salt—not to the dispersed phase.

If the views here presented are the correct explanation of iron hydrosol stability, it would be natural to expect that flocculation should occur in a manner similar to ordinary precipitation, owing to the formation of insoluble compounds. Opponents of the chemical theory of hydrosol behavior have long used the known facts of different amounts of anions (sulfates, for instance), for sol precipitation in apparently no chemical or equivalent relationships, in their arguments. Nevertheless, it is possible that flocculation may be due to the formation of insoluble compounds which precipitate when a certain relationship similar to a solubility product constant is exceeded, and a theory is presented below in an endeavor to reconcile the conflicting views and evidence in this interesting matter.

As was pointed out above, the iron salt upon hydrolyzing acquires a longer and longer $Fe(OH)_3$ tail, or chain, the sol becoming more unstable as the purity rises. Then, coinciding with this progressive hydrolysis, it is not too far-fetched to expect successively lower "solubility product constants" (called below ion product constant) with successive hydrolytic stages (i.e., as N in $(Fe(OH)_3)_N \cdot FeA_3$ increases). According to this hypothesis the amount of sulfate necessary for precipitation should *decrease* with rising purity, which corresponds to lower Fe^{+++} ion concentration, as opposed to the analogous inorganic (ionic) solutions where a higher anion concentration is required if the cation concentration is lowered to satisfy a $K_{s.p.}$ As pointed out above, the reason for this anomaly is that as the purity increases the ferric ion concentration decreases, but as the constant governing the precipitation is also becoming successively smaller to govern the new conditions of the next stage of hydrolysis, then the sulfate ion concentration necessary for precipitation also decreases.

However, if there be any such governing factor analogous to a $K_{s.p.}$, it is evident that the ratio of ferric ions to sulfate ions in moles per liter should remain constant throughout the range of purity changes. In table 1 are calculations from the data of Hamburger's dissertation (p. 20).

In table 1, Fe/Cl, or purity, and SO_4^{--} (in millimoles) are reported. $[Fe^{+++}]$ in millimoles per liter has been calculated from

$$\frac{\text{Total Fe (in milliequivalents)}}{P} = \text{Anion}$$

and

$$\frac{\text{Anion}}{3} = Fe^{+++} \text{ (in millimoles)}$$

Thus, the ratio SO_4^{--}/Fe^{+++} was computed. Similar calculations are given in the tables that follow. (The error in measuring the precipitation or "liminal" values, defined as the average between the amount just flocculating, and that failing to precipitate, is about ± 5 per cent.) Table 1 showed the precipitation values for a chloride sol; in table 2 are the values for a bromide sol.

TABLE 1*

Precipitation values for a chloride sol

Iron per liter = 415 milliequivalents

Fe/Cl on *P*	$[Fe^{+++}]$	$[SO_4^{--}]$	RATIO $[SO_4^{--}]/[Fe^{+++}]$
	millimoles per liter	*millimoles per liter*	
20	7	5.05	0.72
23	6	3.94	0.65
24	5.7	3.94	0.69
25.7	5.4	3.49	0.65
30.3	4.6	2.69	0.58
			Average = 0.66

* Calculations from the data of Hamburger's dissertation (see reference 2).

Thus we see that these ratios are in harmony with the known facts concerning the relative stabilities of the two halides as "solution links." In other words, ferric oxy(bromide) sulfate is more soluble than ferric oxy(chloride) sulfate, at the same purity.

From Mabee's dissertation (pp. 31, 34, and 35) we can use data for the ferric acetate sols he studied, and make similar calculations (see table 3). Thus, ferric oxy(acetic) sulfate is less soluble than the other two considered above, which is in complete harmony with the known facts about these sols.

Using the above values for the respective ratios $[SO_4^{--}]/[Fe^{+++}]$, we can readily calculate from Hamburger's sulfate ion values, initially and at precipitation (for this the values were taken from the dotted line indicating incipience of precipitation in the tables), the purity of the sols at these two stages of aging. (The data used in table 4 are taken from his tables VII to XII, pp. 24–6); from the average ratio value as found above, and the reported $[SO_4^{--}]$ value, Fe^{+++} can be calculated. The total iron in milliequivalents divided by this $[Fe^{+++}]$ gives the purity.

TABLE 2

Precipitation values for a bromide sol

Iron per liter = 415 milliequivalents

Fe/Br	$[Fe^{+++}]$	$[SO_4^{--}]$	RATIO $[SO_4^{--}]/[Fe^{+++}]$
	millimoles per liter	*millimoles per liter*	
20.4	6.7	7.47	1.11
22.2	6.2	7.15	1.15
25.6	5.4	6.12	1.13
25.7	5.37	5.96	1.10
29.8	4.6	5.00	1.09
33.5	4.1	4.24	1.03
38.5	3.6	3.65	1.01
41.8	3.3	3.62	1.10
			Average = 1.09

TABLE 3

Precipitation values for an acetate sol

Fe PER LITER	Fe/Ac	$[Fe^{+++}]$	$[SO_4^{--}]$	RATIO $[SO_4^{--}]/[Fe^{+++}]$
		millimoles per liter	*millimoles per liter*	
567	12	15.7	1.7	0.108
358	12.8	9.3	0.95	0.102
555	13	14.2	2.0	0.140
567	20*	9.4	1.0†	0.106
358	20*	5.9	0.5†	0.084
555	20*	9.3	1.0†	0.107
				Average = 0.108

* The value given by Mabee for purity at incipient precipitation.

† Values read off aging data at description of "brown, turbid," indicating incipient precipitation.

In some instances above, the precipitation purity is less than the starting purity. This discrepancy may be due to the fact that the difference between the initial and precipitation SO_4^{--} values is less than the 5 per cent error in determining these values. Similarly the allowable differences between calculated *P* and analytically determined *P* at the start is also at least ±5 per cent.

Since the calculated initial P agrees fairly well with P by analysis, it seems that this calculation should apply equally well to P at incipient precipitation, and thus it will be noted in the above table that the purity upon aging to incipient precipitation is *not* constant for either bromide or chloride sols, which is in accordance with the predictions based upon hydrolytic considerations given in the derivations above. The reason for these P's being so low compared with previously reported values is that these solutions are much more concentrated than those dialyzed to precipitation.

Returning now to the idea of a "$K_{s.p.}$," if we consider the micelle as $(\mathrm{Fe(OH)_3})_N \cdot \mathrm{FeA_3}$ to present an exceedingly simplified picture, then for a "solubility product" at any particular hydrolytic stage, we could write (for the sulfate)

TABLE 4

SOL	TABLE	TOTAL IRON	INITIAL SULFATE	INITIAL			PRECIPITATION SO_4^{--}	CALCULATED Fe^{+++}	PRECIPITATION (CALCULATED) P
				Calculated Fe^{+++}	Calculated P	Analytical P			
		milliequiv. per liter	*millimoles per liter*						
Br	VII	415	7.74	21	19.8	20.4	6.68	18.3	22.6
Cl	VIII	415	5.05	23	18.0	20.0	4.66	21.0	19.8
Br	IX	415	5.96	16.2	25.6	25.5	(6.20)*	16.8	24.5
Cl	X	412	3.50	15.9	25.9	25.7	(3.40)*	15.3	26.9
Br	XI	415	4.24	11.6	35.7	33.5	4.67	12.7	32.7
Br	XII	402	3.26	9.0	44.7	40.3	(3.67)*	10.0	40.3

* Interpolated at dotted line.

$$\text{“}K_{s.p.}\text{”} = [(\mathrm{Fe(OH)_3})_N\mathrm{Fe}^{+++}]^2\,[\mathrm{SO_4^{--}}]^3$$

or merely,

$$= [\mathrm{Fe}^{+++}]^2\,[\mathrm{SO_4^{--}}]^3$$

$[\mathrm{Fe}^{+++}]$ being calculated from $\dfrac{(\text{total Fe})}{P}$; but it was thought best in developing the analogy to refrain from calling this constant a "$K_{s.p.}$," since it cannot definitely be stated what solid phase is in equilibrium with the constant. It was therefore decided to name this constant an "ion product constant:"

$[\mathrm{Fe}^{+++}]^2\,[\mathrm{SO_4^{--}}]^3 = K_{i.p.}$ (a factor governing the conditions existing in a sol at the determination of its sulfate liminal value.)

For the different stages in the acetate sols tabled above, this would give:—

(1) $K_{\text{i.p.}} = (15.7 \times 10^{-3})^2\ (1.7 \times 10^{-3})^3 = 1.2 \times 10^{-12}$

(2) $K_{\text{i.p.}} = (9.3 \times 10^{-3})^2\ (0.95 \times 10^{-3})^3 = 7.4 \times 10^{-14}$

(3) $K_{\text{i.p.}} = (14.2 \times 10^{-3})^2\ (2 \times 10^{-3})^3 = 1.6 \times 10^{-12}$

(4) $K_{\text{i.p.}} =$ Same as (6)

(5) $K_{\text{i.p}} = (6 \times 10^{-3})^2\ (0.5 \times 10^{-3})^3 = 4.5 \times 10^{-15}$

(6) $K_{\text{i.p.}} = (9.3 \times 10^{-3})^2\ (1 \times 10^{-3}) = 8.6 \times 10^{-14}$

It appears by inspection that the respective successive $K_{\text{i.p.}}$'s progress exponentially, with increase in P. If there is such an exponential progression, then if P is the purity, the P^{th} root of the $K_{\text{i.p.}}$ at that purity should give the $K_{\text{i.p.}}$ of ferric oxy(halide) sulfate when x is exceedingly small. From which it is immediately apparent that if we take the root (of different $K_{\text{i.p.}}$'s) corresponding to the purities, we should obtain the same value.

TABLE 5

FOR THE ACETATE SOLS		FOR THE CHLORIDE SOLS (FROM TABLE 1)			FOR THE BROMIDE SOLS (FROM TABLE 2)		
		$K_{\text{i.p.}}$	$\sqrt[P]{K_{\text{i.p.}}}$		$K_{\text{i.p.}}$	$\sqrt[P]{K_{\text{i.p.}}}$	
(1) 0.1015	1 to 2 × 10^{-1}	(1) 6×10^{-12}	0.27	3 to 4 × 10^{-1}	(1) 1.8×10^{-11}	0.29	3 to 5 × 10^{-1}
(2) 0.095		(2) 2×10^{-12}	0.31		(2) 4.4×10^{-12}	0.33	
(3) 0.0102		(3) 1.8×10^{-12}	0.32		(3) 6.6×10^{-12}	0.37	
(4) 0.222		(4) 1.2×10^{-12}	0.35		(4) 2.6×10^{-12}	0.41	
(5) 0.191		(5) 4×10^{-13}	0.39		(5) 1.2×10^{-12}	0.47	
(6) 0.222					(6) 6.6×10^{-13}	0.48	
					(7) 5×10^{-13}	0.5	

In table 5 are shown these values, found by taking the P^{th} root of the $K_{\text{i.p.}}$'s as calculated above.

Thus we see that all give a value of the same order of magnitude, 10^{-1}. It should be pointed out that if a different method of measuring "liminal values" were used, the above figures might be changed somewhat, but would be expected to hold similarly comparative values.

The above calculations may be reversed, affording a means of calculating and predicting the amount of sulfate ion necessary to precipitate a given iron sol:

$$[\text{SO}_4^{--}] = \sqrt[3]{\frac{(k)^P}{\left(\frac{\text{Fe}}{P}\right)^2}}$$

where k is about 10^{-1}, P is the purity, and (Fe) the total iron.

The evidence presented above is strictly in accordance with the chemical hydrolytic definition of iron hydrosols, based upon the law of mass action. The theory of preferential ionic adsorption seems unnecessary to explain iron sol behavior, and if there is such a phenomenon as preferential ionic adsorption in these systems, the effects of such adsorption seem to be governed by the law of mass action, as applied to the solution link part of the micelle.

EXPERIMENTAL

In accordance with the hypothesis presented above, the following generalities should be considered:

(1) The purity of a sol, at incipient precipitation, of the chloride type, should increase with dilution.

(2) At incipient precipitation, sols of the weak acid type should have constant purities, independent of dilution.

(3) For two sols of the weak acid type, the difference in their respective purities at incipient precipitation should depend upon the relative values of the dissociation constants of the acids formed; therefore their purities should be nearly equal.

(4) From the liminal value–ion product constant relation, it is evident, if the ideas presented above are correct, that peptization should occur even if sulfate be present, and the greater the concentration of sulfate, the smaller the final obtainable purity, provided the chloride (or other anion) remain constant.

For the purpose of testing these ideas, the peptization experiments shown in table 6 were started.

The ferric hydroxide used in the series given in table 6 was prepared by slow precipitation from the chloride with ammonium hydroxide and then washing daily by decantation with large volumes of water (about 25 liters) for six weeks, until samples of the wash water gave no test whatsoever with equal volumes of 0.1 *N* silver nitrate solution on six successive days. The acids used were the purest obtainable from the Eastman Kodak Co., and were standardized against known sodium hydroxide solution. In all cases there was excess of ferric hydroxide. After standing nine months these solutions were analyzed, after being centrifuged for 60 minutes at about 1000 r.p.m. The iron and organic anions were determined as in the preliminary part described above, the chloride in a similar manner, and the sulfate as the barium salt. The results are given in tables 7 and 8.

In table 8 are shown the results obtained with the same three weak acids but with ferric hydroxide that had been washed only a few times, and so still contained occluded chloride. Anion calculated from normality of acid and final volume.

The results of this last experiment indicated that Mabee's value of 20 (as against the low purity shown in table 7) might be due to the presence of chloride in his sols. Fortunately, there was available in the laboratory some of the iron acetate he used, as well as one of his sols. Both revealed the presence of chloride upon addition of silver nitrate, after heating with nitric acid.

TABLE 6

Peptization experiments

SOL NO.	$Fe(OH)_3$ SUSPENSION	ACID	ACID	ACID	WATER	M/2 SODIUM SULPATE
	cc.		*N*	*cc.*	*cc.*	*cc.*
1	40	Acetic	0.0853	200	10	
2	40	Acetic	0.0853	150	60	
3	40	Acetic	0.0853	100	110	
4	40	Butyric	0.0871	200	10	
5	40	Butyric	0.0871	150	60	
7	40	Propionic	0.0884	200	10	
8	40	Propionic	0.0884	150	60	
9	40	Propionic	0.0884	100	110	
11	100	Hydrochloric	0.50	15	135	
12	100	Hydrochloric	0.50	25	125	
13	40	Propionic	0.0884	200	0	
15	40	Propionic	0.0884	200	0	
16	40	Butyric	0.0871	200	0	
17	40	Butyric	0.0871	200	0	
18	40	Butyric	0.0871	200	0	
19	40	Acetic	0.0853	200	0	
21	40	Acetic	0.0853	200	0	
22	20	Propionic	0.0884	200	0	
23	20	Propionic	0.0884	200	0	
24	20	Butyric	0.0871	200	0	
25	20	Butyric	0.0871	200	0	
26	20	Acetic	0.0853	200	0	
27	20	Acetic	0.0853	200	0	
28	100	Hydrochloric	0.520	19.2	280.8	
33	100	Hydrochloric	0.520	11.5	288.5	0
34	100	Hydrochloric	0.520	11.5	287.5	1
35	100	Hydrochloric	0.520	11.5	286.5	2
36	100	Hydrochloric	0.520	11.5	285.5	3
37	100	Hydrochloric	0.520	11.5	283.5	5

An iron propionate solution from iron filings and pure acid, oxidized with hydrogen peroxide and centrifuged, gave a purity of 1.1 upon analysis. Similarly, using acetic acid, a purity of slightly less than 1 was obtained.

It is at once apparent that these results are in accordance with the main points outlined above, and hence help to strengthen the hydrolytic point of view of micelle stability, and the chemical reaction ("solubility product" or ion product) idea of sol precipitation. It also seems quite probable that

TABLE 7

SOL	IRON	ANION	PURITY
	Acetate		
	milliequiv. per liter	*milliequiv. per liter*	
1	114	68.2	1.7
2	141	51.2	2.8
3	135	34.1	4.0
19	148.5	71.1	2.1
20	123	66.1	1.9
21	127.5	71.1	1.8
26	130.5	71.1	1.8
	Butyrate		
4	57	70	0.8
5	66	52.3	1.7
16	82.5	72.6	1.1
17	88.5	72.6	1.2
18	76.5	72.6	1.1
24	52.5	22.6	2.3
25	45.0	23.6	1.9
	Propionate		
7	147	70.7	2.0
8	138	53.0	2.6
9	153	35.4	4.3
13	147	73.6	2.0
15	158	73.6	2.1
22	100.5	73.6	1.3
23	142.5	73.6	1.9
	Chloride		
11	324	30	10.8
12	338	50	6.8
28	346.5	25	13.9
33	366	12.5	29.3

Chloride and sulfate ion

SOL	IRON	ANION		PURITY (Fe)/(Cl)
		Chloride	Sulfate	
	milliequiv. per liter	*milliequiv. per liter*	*milliequiv. per liter*	
33	366.0	12.5	0	29.3
34	339	12.5	1.3	27.1
35	336	12.5	2.5	26.9
36	126	12.5	3.8	10.8
37	(no apparent peptization—clear solution)			10.8

Mabee really studied a mixture of ferric oxychloride sol and ferric acetate sol, and thus found properties intermediate between the two. The differences between two sols of the weak acid type apparently are too small to be significant in view of the fact that this type of sol in general appears to peptize such extremely small amounts of $Fe(OH)_3$.

TABLE 8

SOL	IRON	ANION	PURITY
	milliequiv. per liter	*milliequiv. per liter*	
Chloride	241	17	14.2*
Acetate	195	21.7	9.0
Propionate	186	22.1	8.4
Butyrate	180	21.8	8.2

* No Fe_2O_3 residue; all added was peptized.

SUMMARY

1. The purities at incipient precipitation of iron hydrosols are in agreement with the hydrolytic definition of sols.
2. A chemical theory of sol precipitation, based upon the solubility product concept, is supported by the experimental data.
3. Weak acids, such as acetic, propionic, and butyric, bring little more than equivalent amounts of iron into solution, but small amounts of chloride will greatly increase the amount of iron peptized.
4. All the above is in agreement with the chemical-complex theory of hydrosols.

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PHASE CHANGES IN ENZYME SYSTEMS: AZOTASE ACTIVITY IN RELATION TO pH

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The phase rule has seldom been employed in interpreting enzyme behavior. It represents, nevertheless, a relatively simple method of analysis that is often highly determinate. It makes possible distinction between change in number or kind of phase and mere change in phase composition. This paper will present a phase rule analysis of the abrupt activity–pH function of the nitrogen-fixing enzyme system azotase.[1] General applications to enzyme chemistry and kinetics, whether homogeneous (23, 27, 38) or heterogeneous (2, 7, 12, 13, 15, 16, 17, 18, 25, 34, 35, 37), will be indicated. Azotase will represent a fundamental type case.

PHASE RULE ANALYSIS OF USUAL ENZYME ACTIVITY–pH FUNCTION

The influence of pH on enzyme reactions has been variously explained on some one of the bases that either the enzyme or the substrate is a weak acid or base and that activity is correlated with the concentration of undissociated molecules or positive or negative dissociated molecules, as the case may be (1, 11, 22, 26). The experimental activity–pH curves are

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[1] *Azotobacter* possesses a highly specific enzyme system, azotase, capable of catalyzing the fixation of nitrogen gas at ordinary temperatures and pressures. Its properties are constant and characteristic, and have been described in detail elsewhere (6). In brief, no activity occurs below a critical concentration of hydroxyl ion of $10^{-8.03}$ *M* (pH 5.97). Ca or Sr and Mo or V are required for its operation, being replaceable by no other elements. The Michaelis dissociation constant, Km_{N_2}, or nitrogen pressure at half-maximum velocity, is 0.215 atmosphere. Km_{N_2} and the pH limit at 5.97 ± 0.02 are not affected by any known factor, including concentration of calcium or strontium. Specific inhibition by hydrogen ion and oxalate is reversible and non-competitive. Finally, unpublished data indicate that the O/R potential (as imposed upon *Azotobacter* cells by various pressures of oxygen gas) must ordinarily be slightly but definitely lower for maximum azotase activity as compared to nitrate reduction, growth, or any other normal activity of *Azotobacter*. Nitrogen gas is ordinarily fixed by *Azotobacter* in intracellular form only, the amount being directly proportional to the amount of growth. The velocity of fixation becomes solely limited by the velocity of growth (generation time for cell division, or increase in cell mass) only when pH, nitrogen pressure, calcium concentration and O/R potential are all adjusted to values specifically optimal for azotase activity.

very similar to dissociation or dissociation-residue curves. Further emphasis is lent by the fact that enzyme systems usually contain protein-like components, and activity-pH curves likewise resemble the continuous pH functions of the physical properties of aqueous amino acids, polypeptides or proteins, viz., solubility, viscosity, swelling, osmotic pressure, surface tension, alcohol number.

The phases, or physically homogeneous regions, involved in enzyme activity are characterized at equilibrium by variability in chemical composition and constancy in number, without regard to quantity or form. The essential element in the concept of phase is characterization of the properties of each phase by a definite number of degrees of freedom, or parameters (14, 19, 20). At constant temperature and pressure the equilibrium concentrations and ratios of the individual components, dissociated and undissociated, of any one phase, alter continuously over the entire pH range. The number of components and phases remains constant. The simplest type of base–acid equilibrium, occurring in dilute aqueous solution within a single phase at constant temperature and pressure, and first order with respect to all individual components, may be represented, in nomenclature resembling that of Brönsted and Guggenheim (4), by the equation

$$B \rightleftarrows A + OH^- \tag{1}$$

where B and A are conjugate weak base and acid, differing in charge algebraically by one.

Equation 1 defines a two-component, one-phase system that is trivariant, since by the phase rule $F = C - P + 2 = 2 - 1 + 2 = 3$ degrees of freedom. The mass law dissociation constant contains all individual components:

$$K_B = (A)(OH^-)/(B) \tag{2}$$

Curve I, figure 1, and curve I, figure 2, illustrate graphically the very common function represented by equation 1. Percentage dissociation is plotted against pH and (OH^-) respectively, and a value of (OH^-) existing when the ratio $(A)/(B)$ is unity is arbitrarily chosen as $10^{-7.94}\,M$. This value represents attainment of 50 per cent maximum activity in the azotase function. Curves II, III, and IV, figure 1, and curves II, III, and IV, figure 2, present the functions obtained when hydroxyl ion is involved in equation 1 to some number (equation 2, some power) moderately but not greatly different from one, viz., 1/2, 2, and 4. Plots against (OH^-) as well as pH are given because although the latter are more common they are somewhat arbitrary and, in connection with equation 1, less direct (36).

As approximations to these theoretical functions, curves V and VI, figures 1 and 2, show typical, reversible, enzyme activity-pH functions, viz., respiration and growth of *Azotobacter* (6), plotted upon a basis of percentage of maximum activity. The differences are of a secondary nature. (OH^-) appears to be involved to a power not far from unity, indicating a relatively simple system. Clark (9) cites numerous references to similar biological pH-functions, enzymic and otherwise. These usual functions have been described as a basis for comparison with the azotase function.

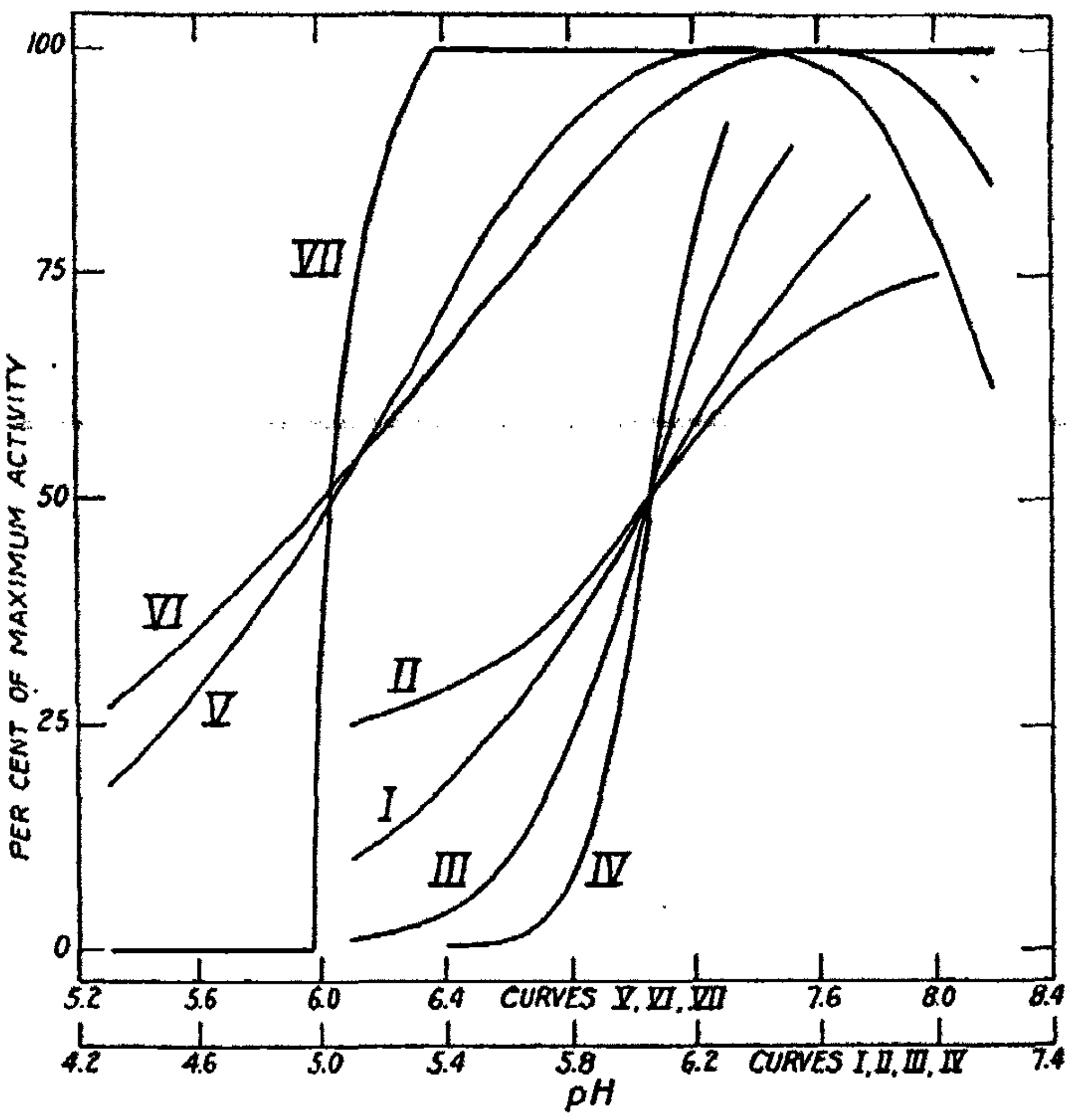

FIG. 1. COMPARISON OF VARIOUS ACTIVITY-pH FUNCTIONS

Curves I, II, III, IV, theoretical curves based on equations 1 and 2, with $K_B = 10^{-7.94}$ and 1/2, 1, 2, and 4 hydroxyl ions, respectively, involved. Curves V, VI, VII, respiration, growth (in nitrate) and nitrogen fixation (by azotase) in *Azotobacter vinelandii*, from data of Burk, Lineweaver, and Horner (reference 6, figure 4).

THE AZOTASE ACTIVITY-pH FUNCTION

The unique activity-pH curve of azotase is reproduced in curve VII, figure 1 (cf. also curve VII, figure 2). The velocity constant of nitrogen fixation is plotted upon the basis of percentage of maximum activity. The distinctive characteristics of the curve upon which the phase rule analysis will be based are as follows.

(1). It approaches a critical threshold pH limit at zero activity in a manner concave downward, substantially perpendicular. The usual curves, plotted against pH as shown in figure 1, are S-shaped or double S-shaped (bell-shaped), and approach the pH axis asymptotically (concave upward). No finite critical pH is involved, except in certain types of minima to be discussed later. In the plot against (OH^-) the curves intersect the (OH^-) axis at the origin.

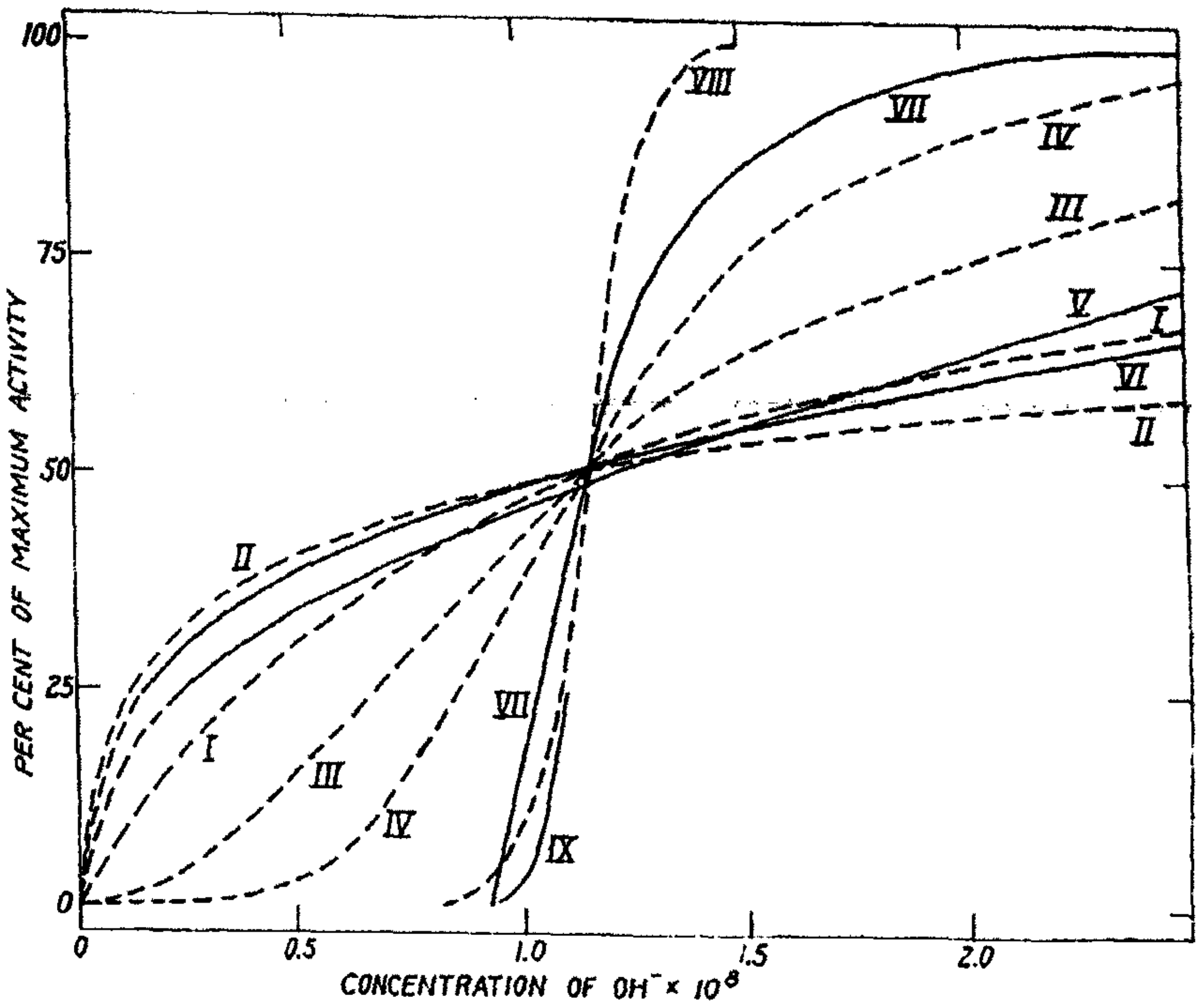

FIG. 2. COMPARISON OF VARIOUS ACTIVITY-(OH^-) FUNCTIONS

Curves I, II, III, IV, VIII, IX, theoretical curves based on equations 1 and 2, with $K_B = 10^{-7.94}$ and 1/2, 1, 2, 4, 16 and 24 hydroxyl ions, respectively, involved. Curves V, VI, VII, respiration, growth (in nitrate) and nitrogen fixation (by azotase) in *Azotobacter*, from data of Burk, Lineweaver, and Horner (reference 6, figure 4).

(2). The azotase function is reversible over an indefinitely extended period of time; this is true even considerably below the pH of zero activity, down to pH 5.0. *A true thermodynamic equilibrium is therefore involved*, approachable from either side of pH 5.97. The usual functions generally show irreversible inactivation in a few minutes or hours at a pH where activity is still 20 per cent of maximum (curve III, figure 3).

(3). The pH limit is a characteristic constant, and has not been observed so far to be changeable beyond ±0.05 pH unit at most, if at all. Usual functions may often be greatly shifted along the pH axis by various factors. An excellent example is the shifting of the oxygen-hemocyanin dissociation constant one and one-half pH units by 0.5 *M* sodium chloride (figure 3, curves I, IA), or similarly that of oxygen-hemoglobin by various salts (reference 3, figure 191, p. 621). Daniel (10) changed the isoelectric point of gelatin over one pH unit by varying alcohol concentration up to 60 per cent.

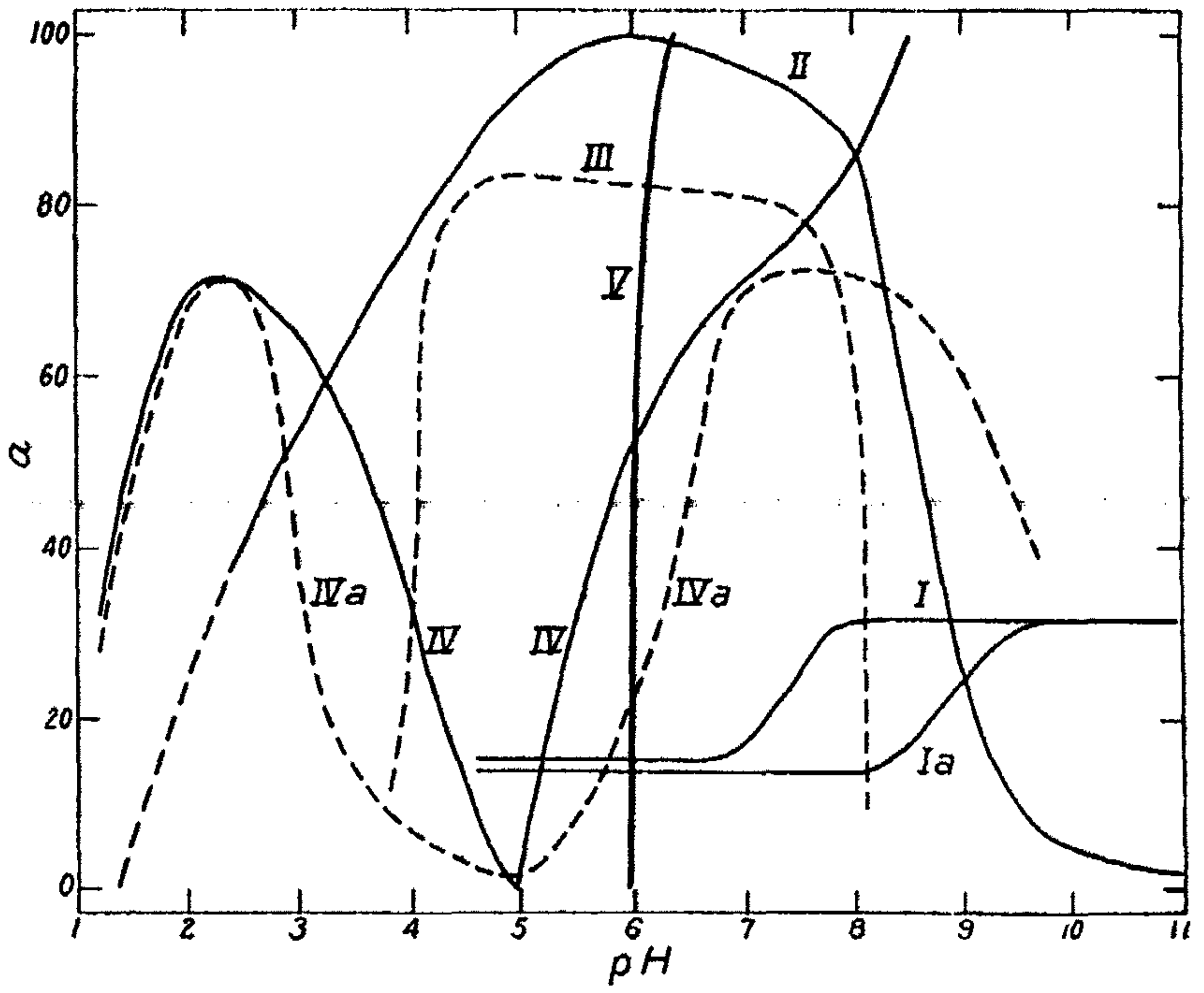

FIG. 3. COMPARISON OF SPECIAL pH FUNCTIONS OBTAINED BY VARIOUS INVESTIGATORS

Curves I and Ia, oxygen affinity constant of hemocyanin of *Busycon canaliculatum*, in presence and absence of 0.5 *M* sodium chloride, respectively, from data of Redfield and Ingalls (reference 31, figures 3 and 4; $a = p_{50} \times 7.5$ mm. mercury). Curve II, relative rate of respiration of *Sarcina lutea*, from data of Rubenstein (reference 32, figure 6). Curve III, sedimentation velocity of hemocyanin of *Helix pomata*, from data of Svedberg and Heyroth (reference 33, figure 5; a = sedimentation velocity $\times 8.22 \times 10^{12}$ cm. per second. Curves IV and IVa, relative concentration of ionized gelatin salt and relative rate of hydrolysis by pepsin (acid to isoelectric point) or trypsin (alkaline to isoelectric point), respectively, from data of Northrup (reference 26, figures 4 and 5). Curve V, relative activity of azotase, from data of Burk, Lineweaver, and Horner (reference 6, figure 4).

(4). The azotase curve shows tremendous molal buffering capacity over the pH range involved, 5.97 ± 0.02 and 6.37 ± 0.02 (curve VII, figure 1). A change in activity from 0 to 100 (±2) per cent takes place in 0.4 pH unit. Usual enzyme curves require at least one and generally several pH units for only 95 per cent change.

Many observations exist in the literature to the effect that a certain biological process has a characteristic pH limit. Thus Clark (8) showed that certain strains of *B. coli* invariably stopped growing when a pH limit of 4.8 was attained. In cases of this sort, however, the data rarely indicate the manner of reversible approach to the pH axis, especially when very close. For example, in curve II, figure 3, it is suggested that the dotted portion represents a certain amount of irreversible pH effect and that the reversible curve really becomes asymptotic as in the alkaline region.

PHASE RULE ANALYSIS OF AZOTASE ACTIVITY-pH FUNCTION

So far as the writers are aware there is only one interpretation, based, namely, on the phase rule, which is consistent with all four of the above-~~cited characteristics of the reversible reaction between hydroxyl ion and the~~ inactive azotase residue:

$$A_{OH^-} \rightleftharpoons A_{H^+} + OH^- \tag{3}$$

where A_{OH^-} and A_{H^+} are the active and inactive forms of the grouping in azotase specifically influenced by pH. The charges on A_{OH^-} and A_{H^+} may be positive, zero, or negative, but differ algebraically by the number of hydroxyl ions involved, presumably one (see later).

Equation 3 and curve VII, figure 1, describe a two-component system which is univariant under ordinary experimental conditions, where temperature, pressure, and total cellular azotase concentration (A_{OH^-} and A_{H^+}) are held constant, and the state of the system is defined by the hydroxyl ion concentration of the external medium, no A_{OH^-} existing below about pH 5.97, no A_{H^+} existing above this value. According to the phase rule the number of phases existing when the system is in equilibrium at pH 5.97 is three, thus: $P = C - F + 2 = 2 - 1 + 2 = 3$. One phase, containing the hydroxyl ion, is aqueous, and the other two, consisting of A_{OH^-} and A_{H^+}, respectively, are therefore non-aqueous, either liquid, solid, or surface phases. It is assumed for the present that curve VII, figure 1, is strictly perpendicular and that the two non-aqueous phases are therefore pure components or compounds of fixed composition. The possibility that A_{OH^-} varies somewhat in composition between pH 5.97 and 6.37 will be considered shortly.

Since in heterogeneous equilibrium the absolute mass or quantity of one phase does not influence the composition of another phase, (A_{OH^-}) and (A_{H^+}) do not appear in the mass law dissociation constant:

$$K = (OH^-) = 10^{-8.03} \tag{4}$$

In view of the equilibrium $(H^+)(OH^-)/(H_2O)$ in the aqueous phase, equations 3 and 4 might be written, so far as available experiments decide,

$$A_{H^+}(\text{non-aq}) \rightleftharpoons A_{OH^-}(\text{non-aq}) + H^+(\text{aq}) \tag{3'}$$

$$K' = (H^+) = 10^{-6.97} \tag{4'}$$

This ambiguity occurs commonly in base-acid equilibria and must be resolved by independent evidence (reference 9, 2nd ed., 1925, pp. 29, 306), e.g., migration experiments. Alteration of K in equation 4 (or K' in 4′) to an extent minute or otherwise, although unobserved so far, is theoretically possible under the phase rule, as a function of temperature, total pressure, or the chemical composition of A_{OH^-}.

Comparable equilibria

The heterogeneous equilibrium of equations 3 and 4 is comparable to well-known univariant gas-solid equilibria involving salt hydration. Thus, with, e.g., anhydrous copper sulfate and water vapor, no hydrate is formed at constant and ordinary temperatures until a certain critical water vapor pressure is reached, about 4.5 mm. This is the dissociation pressure of the monohydrate, at which point the anhydrous salt is all converted into the new compound, the monohydrate, before further rise in the equilibrium vapor pressure may occur, two solid phases (three altogether) existing during the meantime.[2] The equations representing these phenomena of critical phase change, corresponding to equations 3 and 4, are:

$$CuSO_4 \cdot H_2O(s) \rightleftharpoons CuSO_4(s) + H_2O(g) \tag{5}$$

$$K_{\text{diss.}} = (H_2O) = 4.5 \text{ mm. at } 50°\text{C.} \tag{6}$$

Here $F = C - P + 2 = 2 - 3 + 2 = 1$. In the system solid mono- and di-calcium phosphates in aqueous equilibrium at constant temperature and pressure at a given pH, the slightest change of pH in either direction results in the complete conversion of one solid to the other. This system is perhaps more analogous to the azotase system than salt hydration in view of the nature of the independent variable (pH) and the known rôle of calcium

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[2] In Bayliss' phase rule analysis of the system hemoglobin-oxyhemoglobin-oxygen (reference 3, p. 617, last paragraph) three phases and two components were assigned in the equation $F = C - P + 2 = 2 - 3 + 2 = 1$, and it appeared therefore that the system was formally comparable to the univariant system $CaCO_3$ (s)-CaO(s)-CO_2(g) (or, similarly, the case of salt hydration illustrated). This was taken to be anomalous inasmuch as bivariance was observed experimentally. However, from the nature of the dissociation curves (reference 3, pp. 620, 621) oxygen combines with hemoglobin at *all* pressures and hence hemoglobin and oxyhemoglobin occur in one and the same composition-varying phase, so that $F = 2 - 2 + 2 = 2$. This leaves no basis for the alternatives of either the existence of three components, or non-applicability of the phase rule to microheterogeneous systems.

in fixation. Amylase activity apparently involves an essential organic calcium component also (24).

The pH *region 5.97 to 6.37*

The azotase function appears to require some 0.4 pH unit to change reversibly from 0 to 100 per cent activity. Slight non-homogeneity of phase may be involved; it is well-known that even under equilibrium conditions the vapor pressure of liquids depends slightly upon the size of the droplets; the solubility of solids upon the size of the particles; the melting point without decomposition may vary a perceptible fraction of a degree; surfaces may depart somewhat from complete homogeneity, varying perhaps in curvature; and secondary factors ordinarily neglected may affect certain phase rule applications. Mathematically considered, the magnitude of the region of phase change depends upon the phase spaces involved, in the sense employed in statistical mechanics. Zero velocity at pH 5.97 represents in any case complete conversion of A_{OH^-} to A_{H^+}, and the attainment of maximum velocity above pH 6.37 complete conversion of A_{H^+} to A_{OH^-}, within experimental error.

It is scarcely possible that

$$A_{H^+}\text{(non-aq)} + OH^- \rightleftharpoons A'_{OH^-}\text{(non-aq); phase change, pH 5.97} \qquad (7)$$

and

$$A'_{OH^-}\text{(non-aq)} + n_{OH^-} \rightleftharpoons A_{OH^-}\text{(non-aq); non-aqueous solution, pH 5.97 to 6.37} \qquad (8)$$

where A_{H^+} is converted at pH 5.97 into a new but inactive non-aqueous phase, A'_{OH^-}, which becomes active upon further combination with, or solution of, aqueous OH^- ions over the region to pH 6.37, when all A'_{OH^-} is converted into completely active A_{OH^-}. It is evident, comparing the upper portions of curve VII, figure 2, and curves IV or VIII, that the value of n in equation 7 must be much larger than in the usual enzyme dissociation, and, moreover, for the portion below 50 per cent activity that curve VII does not represent merely dissociation with some large power of n. If one plots the logarithm of the ratio of the concentrations of undissociated and dissociated molecules of an electrolyte against pH a line is obtained whose slope represents n, the number of hydroxyl ions involved in the dissociation. Such a plot of the azotase function does not yield a uniformly straight line but one which varies continuously, indicating that n varies. Between 6.3 and 6.15 n appears to possess a fairly constant value of about 6, but at pH 6.0, where activity is only about 25 per cent of maximum, it becomes 12, at 5.98, 31, and at 5.97 substantially infinite.

PHASE CHANGE ALTERNATIVES

A curve at relatively low activities, lying between curves VIII and IX, figure 2 (n = 16 and 24, respectively), would cross curve VII within experimental error of measurement of zero activity (about 1 per cent of maximum, where $A_{H^+}/A_{OH^-} = 100$). The azotase pH *limit* 5.97 might thus be explained homogeneously,

$$A_{OH^-} \rightleftharpoons A_{H^+} + 20\,OH^- \tag{9}$$

$$K'' = (OH^-)^{20}(A_{H^+})/(A_{OH^-}) \tag{10}$$

except for there being no chemical precedent for a molecule with some twenty (basic) groups titratable at the same pH. (The problems of limit (equation 9) and transition range (equation 7), each involving large values of n, are to be clearly distinguished.)

Similarly, A_{OH^-} and A_{H^+} might differ greatly in molecular weight.

$$A_{OH^-} \rightleftharpoons 20A_{H^+} + nOH^- \tag{11}$$

$$K''' = (OH^-)^{n}(A_{H^+})^{20}/(A_{OH^-}) \tag{12}$$

Most properties of a molecule must be considered quantitatively as properties of the whole molecule and not as the sum of the properties of the various composing groups or atoms. It is thus conceivable that the molecule within the azotase system specifically affected by OH^- is active on ly when possessed of a minimum molecular weight. Here again, however, numerous groups all dissociating reversibly at approximately pH 6.0 would have to be involved, for which there is no chemical precedent. Svedberg and Heyroth (33) showed that the sedimentation velocity of hemocyanin from *Helix pomatia* decreases about tenfold between pH 4.8 and 3.8 (curve III, figure 3) and is accompanied by a roughly parallel decrease in molecular weight. Actually, however, the curve is reversible only in the earliest stages at the higher pH values; several hours exposure at 3.4 results in 25 to 75 per cent permanent change.

Certain properties of ampholytes, electric charge and cataphoretic or membrane potential, approach abrupt minima substantially linearly as a function of pH, as illustrated in curve IV, figure 3, for gelatin. In the case of hemoglobin the electric charge involved decreases reversibly to zero between pH 8.4 and the isoelectric point 6.8, where it presumably changes abruptly to positive (26). Compared to curve VII, figure 1, however, such curves extend over a much greater pH range and do not appear capable of offering an alternative explanation for the assigned phase change in azotase, although they may represent accompanying phenomena. Moreover, the corresponding enzyme activity curves, e.g. curve IVa, figure 3, approach their minima concaved upward in the normal continuous manner.

DISCUSSION

The phase rule involves great generality and formality in one sense, but also high specificity, as a means of classifying a great variety of type reactions, homogeneous or heterogeneous. It makes possible distinction between change in number or kind of phase and mere change in phase composition. The use of phase rule analysis will quite possibly be imperative[3] in certain cases of enzyme reaction velocity or enzyme stability where inhibitors, accelerators, carriers, and substrates sometimes appear to act only above certain critical limiting concentrations. Thus Quastel and Whetham (29) find for certain dehydrogenases the equation $v = k \log (S/C)$ where the velocity $v = 0$ when substrate concentration S = critical concentration C; by phase rule analysis there would appear to be a bivariant two-component, two-phase system, with an inactive non-aqueous phase invariant in composition occurring below the critical concentration and an active substrate–solution phase above it (cf. equations 7, 8).

In the case of nitrogen fixation, quite possibly the very nature of the reaction involved accounts for the phase change requirement. The dissociation energy of the nitrogen molecule is some 8½ volts or more (200,000 calories). This is enormously greater than the heats of activation of most enzymic reactions, which are rarely more than 10,000 to 20,000 calories. Generally considered, heterogeneous catalysis is much more effective than homogeneous catalysis in causing unusually unreactive molecules to react. Cannan (7) has reviewed the evidence for the view that the catalytic action of enzymes is restricted to certain surface areas. Quastel's (28, 30) modified electric field theory of dehydrogenase activity and enzyme specificity provides for surface differentiation into specific areas or regions of unequal activity. Langmuir (19) has recently developed a detailed extension of the phase rule to include surfaces of the most varied types, active and inactive, in which a surface may consist of several phases, differing in structure or composition, but not size or shape. The phases may thus be submicroscopic, as well as microscopic or macroscopic as in ordinary phase rule applications. This point is important in view of the fact that the *Azotobacter* cell is only about 2000 A.U. in diameter and the

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[3] However, McBain (21), in common with Loeb, Sörensen, Perrin, Pauli, and Smoluchowski, holds that by phase rule a solution of reversible colloid, no matter how complicated, may be considered to behave toward external equilibria as a single phase. Buchner (5) concludes that while a colloidal solution may be regarded as either a one- or two- (or more) phase system, microheterogeneous systems in general seldom involve the formation of new phases and hence that the concept of phase will rarely be useful in connection therewith. He reviews various opinions on the nature of the concept phase and, while agreeing that heterogeneity may be considered relative and not absolute (depending upon the smallness of particles and roughness of observation), inclines to the single phase view. On the other hand, the three-phase system azotase indicated in this paper throws new light on the problem, and strengthens the view that enzyme systems may consist of more than one phase, and that for some enzymes equation 1 might represent a two-component, two-phase, bivariant system rather than a two-component, one-phase, trivariant system.

enzyme systems within it of course very much smaller. It is not necessary, in fact, that the A_{OH^-} and A_{H^+} phases consist of more than some several hundred molecules, enough to sustain the statistically based, thermodynamic equilibrium observed experimentally.

SUMMARY

1. Azotase (nitrogen-fixing) activity in *Azotobacter* varies with pH abruptly. A characteristic zero limit at 5.97 is approached *reversibly* and perpendicularly. Phase rule analysis implicates a two-component heterogeneous system with three phases in equilibrium at the critical pH: aqueous, active non-aqueous, and inactive non-aqueous. The active (basic) component exists above the critical pH, the inactive (acidic) one below. Slight phase non-homogeneity may occur between pH 5.97 and 6.37. Interpretations of the abrupt pH function, alternative to phase change, such as normal acid-base dissociation, large molecular weight change, multiple basicity, and minimal charge or potential difference have been discarded as inconsistent with one or more characteristics of the reaction.

2. Phase rule applications to microheterogeneous systems, surfaces, and problems of general enzyme reaction velocity and stability have been briefly indicated.

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EFFECTS OF ALPHA PARTICLES ON AQUEOUS SOLUTIONS[1]

I. THE DECOMPOSITION OF WATER

II. THE OXIDATION OF FERROUS SULFATE

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There is much evidence to show that the primary action in gases due to alpha radiation is ionization. Since it is found true in gases at high pressures, it might therefore be expected to be true in many liquids. Water was the first liquid investigated; however, the idea of ionization was not present in the earliest work. In 1907, Cameron and Ramsay (1) studied for the first time the decomposition of water by radon. There soon followed a series (2, 8, 19) of investigations out of which evolved some experiments which practically ended further study of this particular reaction. The experiments were performed by Duane and Scheuer (3) in the laboratory of Madame Curie. They found that 2.9 cc. of gas are formed per curie hour when carefully prepared distilled water is irradiated with alpha rays. Water molecules were decomposed with a yield of nearly one molecule per ion pair. The gas formed, however, was not an electrolytic mixture of hydrogen and oxygen, but always contained an excess of hydrogen. They concluded that hydrogen peroxide was formed by the secondary action of nascent oxygen on water. Kernbaum (8) had observed the same phenomena in an earlier experiment. He measured the amount of hydrogen peroxide in the irradiated water and found a sufficient quantity to account for the excess hydrogen.

In 1911, Lind (10) reported some results on the irradiation of liquid hydrogen bromide and solutions of potassium iodide. Recently Lind and Ogg (16) have cited some further results on the decomposition of liquid and gaseous hydrogen bromide. Liquid hydrogen bromide was decomposed with a yield of 2.6 molecules per ion pair, which is remarkably close to the yield of 2.8 for gaseous hydrogen bromide.

The author wishes to report here some further observations on the decomposition of water and some new studies on the oxidation of aqueous solu-

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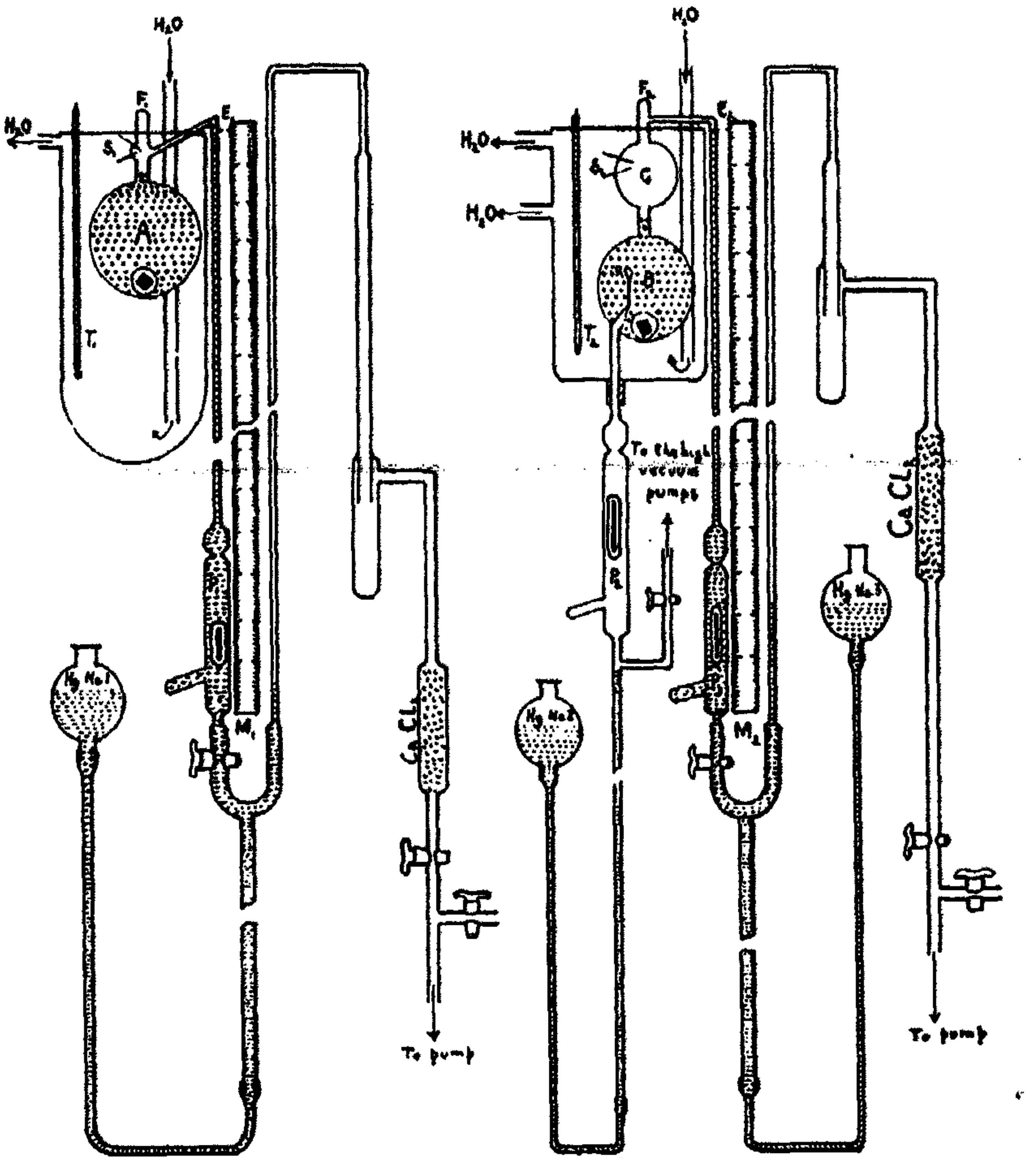
[1] From a thesis submitted by Carl E. Nurnberger to the Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

tions of ferrous sulfate. In particular, it is desirable to follow the reactions by measuring quantitatively the gas produced and the substances changed, and to express them in terms of the ionization produced by alpha particles emitted from the radioactive gas, radon.



Direct method. Indirect method

FIG. 1. APPARATUS FOR THE STUDY OF THE EFFECTS OF ALPHA RAYS ON SOLUTIONS

EXPERIMENTAL

Two different experimental methods have been used and the apparatus for both is shown in figure 1. The methods are designated the direct and the indirect method. In the former, radon is placed in direct contact with the liquid, where a part of it is dissolved and the rest remains in the gas volume above the liquid surface. In the latter method, radon is confined to an alpha-ray bulb (11) immersed in the liquid. Radon in the direct method distributes itself between the liquid and the gas volumes, and the effective amounts in each will depend upon their relative volumes and the area of the liquid surface. The first factor determines the quantity of radon dissolved in the liquid where complete absorption of alpha particles occurs; the second factor determines that portion of the alpha particles which have their source in the gas volume, but which strike the liquid surface. The latter may be partially eliminated by the use of irradiation chambers wherein the liquid surface is small. The dotted portion of chamber A (figure 1, direct method) indicates the liquid volume. The liquid surface rests in the tube F, whose cross-sectional area is about 0.1 sq. cm. The liquid volumes for both methods (A and B) were varied from 15 cc. to 60 cc. for different experiments. The gas volumes (F, direct method, and F_2 plus g, indirect method) were varied from 1 to 5 cc. and from 5 to 10 cc. for the direct and indirect methods, respectively.

Radon, which had previously been collected, purified,[3] and stored in small glass bulbs of about 4-mm. diameter, was brought into the apparatus through a side tube of the traps P_1, P_2, and P_3. The side tube is then sealed and the entire system is evacuated, after which mercury is brought into the manometer (M_1 and M_2, figure 1) to a point above the stopcocks. The radon gas is released directly into the reaction chamber (A and F_1, direct method; B, C, and F_2, indirect method), when the storage bulb is broken. The storage bulb is broken when struck by an iron-glass capsule which had been raised a few centimeters above the bulb by an electromagnet and then allowed to fall. Mercury is then raised to a fixed point near the top of the left-hand side of the manometer. All of the radon is thus confined to the reaction chamber. In the other side of the manometer, which is open to the atmosphere, the mercury surface rests near the bottom at the beginning of the experiments. The gas volume is kept constant by having the stopcocks immediately below the traps closed except when pressure observations are taken. The strengths of the radon storage bulbs were determined beforehand by a careful determination of their gamma-ray activity as compared to the activity of two standard radium preparations.

The alpha-ray bulbs (R, figure 1) were located to one side of the chamber B so that they were protected against breakage when samples of the irradiation liquids were removed. Radon was confined to the alpha-ray bulbs when the gas had been released in the trap P_2, as described previously, and mercury had been raised to the topmost point of the capillary tube sealed to the bulb. The mercury surface maintained this position without fluctuating much in either direction.

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[3] The radon gas was obtained from the Radium Emanation Plant in the Cancer Institute of the University Hospital, Minneapolis.

Clean apparatus, particularly the reaction chamber, is absolutely necessary to obtain consistent results. All substances are probably attacked in one way or another by the rays from radioactive elements. Usually gases are evolved and various forms of impurities are left in the system. In particular, stopcock grease gives off organic gases and, in order to eliminate them, all stopcocks were situated so as not to come in direct contact with radon. Impurities in the liquid chamber may inhibit or accelerate the action of alpha rays and therefore should be eliminated. The entire glass system was thoroughly cleaned and dried preceding each experiment.

The reaction chambers were immersed in a constant temperature water bath. The temperature of the bath was set a few degrees below room temperature in order to eliminate partially condensation of the liquid vapor in the manometer. The liquids were stirred constantly during each experiment by the motion of a round glass bead. The soft iron core of the bead was alternately attracted and released by an electromagnet about twenty times per minute. This arrangement for stirring the liquids proved to be of much help to keep the liquid and gas volumes constant during the evacuation of the system. Without the stirrer large bubbles of gas formed in the liquid. When they were released, drops of liquid were carried with them into the manometer. However, when the stirrer was operating, the gas bubbles were released when small and practically none of the liquid was taken from the reaction chamber.

The gaseous mixture evolved by the rays was exploded by producing a spark between the electrodes S_1 and S_2 (figure 1). In the first experiments platinum wires were used for the electrodes. Irregularity in the pressure during sparking was observed. The gas remaining after several explosions, presumably hydrogen, would on further sparking disappear almost entirely, only to reappear at the next explosion. This troublesome feature was partially eliminated by saturating the system with hydrogen before the experiment began; however some irregularities still remained. They were finally eliminated by using tungsten instead of platinum electrodes.

The irradiated water was collected from a laboratory still and was further purified by repeated distillations in an all-Pyrex glass still. The water was placed immediately in the irradiation chamber and subjected to a partial vacuum for at least two hours before the experiment began. The initial gas pressure was in most experiments not more than 30 mm. of mercury. Even though the surface area of the water was small, about 0.1 sq. cm., most of the absorbed gases were removed, owing to the continuous stirring. After this preparation the water was ready for irradiation and no gases other than those evolved by the rays came in contact with it. Some preliminary measurements on the conductivity of the water gave 3×10^{-6} mhos.

Aqueous solutions of ferrous sulfate, when irradiated with x-rays, were first studied by Fricke and Morse (4). The results of their experiments suggested the possibilities of a similar study using alpha radiation instead of x-rays. Solutions for irradiation with alpha rays were made from a stock solution of 0.5 molar ferrous sulfate in 0.8 normal sulfuric acid, and were standardized by titrating with a standard solution of potassium dichromate. Chemically pure potassium dichromate was recrystallized three times and dried two days at a temperature of 110°C. The titration measurements were made according to the method of Kolthoff and Furman (9). To 5 cc. of the solution was added 50 cc. of 0.8 *N* sulfuric acid. The mixture was stirred and titrated with potassium dichromate from a burette calibrated to read 0.05 cc. accurately and which could be estimated to 0.02 cc. The concentration of each solution was tested immediately before and after each experiment to avoid errors due to spontaneous changes which might occur. At least two independent titrations were made on each sample, and their average value was used to calculate the per cent of ferrous sulfate changed.

RESULTS

I. The decomposition of water

The decomposition of water by alpha rays was studied primarily because it offered a means of standardizing the apparatus by a comparison of the results obtained with it and the results of earlier work, and because it might be used as a method of measuring the transmission of alpha-ray bulbs. This method, to the author's knowledge, has not been used before, and therefore it will be described in detail later in the paper.

The results of one experiment, selected from a large group on the irradiation of water by radon dissolved in the water, are recorded in the top of table 1. The gas volume was kept constant and the gas pressure was observed at regular intervals immediately before and after the explosion of the gaseous mixture. The temperature of the reaction vessel remained constant. All gas pressures and volumes recorded in table 1, and in all tables which follow, are expressed in millimeters of mercury and cubic centimeters at 0°C. and 760 mm. pressure, respectively. The initial quantity of gas in the reaction chamber has been subtracted from all later volumes. The last value of V is, except for certain corrections which shall be discussed later, the total quantity of gas produced by the rays. V_H is practically all hydrogen and represents an excess over the amount which results from the reaction, $2H_2O = 2H_2 + O_2$. V' is equal to V plus an amount of oxygen equivalent to the excess hydrogen.

The course of the reaction is demonstrated in figure 2. The per cent of radon decayed was calculated from the Kolowrat tables. The per cent of completed reaction is equal to $V'/V_\infty \times 100$, where V' is defined in the

TABLE 1

Gas yield in the decomposition of water by radon

Direct method

Water volume = 19.0 cc.; gas volume = 4.33 cc.; initial quantity of radon = 83.0 mc.

DAYS	T_w	p_1	p_2	v_1	v_2	V	V_H	V'	PER CENT V_H	PER CENT RADON USED	$\frac{V'}{V_\infty} \times 100$
0.00	20.4	39.1	35.6	0.207	0.188						
0.15	20.6	92.2	44.5	0.487	0.235	0.299	0.047	0.322	15.6	2.6	2.4
0.71	20.7	260.1	54.6	1.376	0.289	1.440	0.101	1.495	6.7	11.9	10.9
0.96	20.3	160.3	41.8	0.848	0.221	1.999	0.033	2.015	1.6	15.8	14.9
1.17	20.7	120.1	42.0	0.635	0.220	2.413	0.034	2.430	1.4	18.9	17.9
1.69	20.5	218.1	41.8	1.154	0.221	3.345	0.033	3.361	0.9	25.9	24.7
2.15	20.2	187.4	40.0	0.991	0.217	4.315	0.029	4.329	0.6	31.8	31.8
2.58	20.2	170.4	39.0	0.899	0.206	4.997	0.018	5.006		37.2	36.8
3.08	20.1	177.0	40.0	0.936	0.217	5.727	0.029	5.741	0.5	42.6	42.2
3.64	20.6	171.0	39.0	0.905	0.206	6.415	0.018	6.415		47.9	47.2
4.14	20.6	151.0	36.0	0.799	0.191	7.008	0.003	7.009		52.4	52.2
4.67	20.8	148.0	33.0	0.783	0.175	7.600		7.600		56.5	55.9
5.67	20.8	210.0	37.0	1.111	0.196	8.536	0.008	8.540	0.1	64.0	62.7
6.77	20.4	192.0	33.0	1.016	0.175	9.356		9.356		70.5	68.8
7.17	20.4	145.0	30.0	0.767	0.159	9.948		9.948		72.5	73.0
8.27	20.4	143.0	33.0	0.756	0.175	10.54		10.54		77.4	77.4

Indirect method

Water volume = 15.9 cc.; gas volume = 4.33 cc.; initial quantity of radon = 69.1 mc.

DAYS	T_w	p_1	p_2	v_1	v_2	V	V_H	V'	PER CENT V_H	PER CENT RADON USED	$\frac{V'}{V_\infty} \times 100$
0.00	22.0				0.000						
0.72	22.6	12.6	3.2	0.154	0.039	0.154	0.039	0.173	25.5	11.8	6.8
1.83	22.2	38.4	19.9	0.469	0.243	0.584	0.243	0.705	41.6	28.3	27.7
2.99	21.8	41.3	18.4	0.505	0.225	0.846	0.225	0.958	26.6	41.6	37.5
3.89	22.6	37.1	18.6	0.453	0.227	1.073	0.227	1.186	21.1	50.0	46.5
4.81	21.8	33.4	17.5	0.408	0.214	1.254	0.214	1.361	17.0	57.8	53.4
5.97	22.0	33.2	17.3	0.405	0.211	1.445	0.211	1.550	14.6	65.8	60.6
6.99	21.9	31.1	15.6	0.380	0.190	1.614	0.190	1.709	11.7	71.4	66.9
8.21	22.0	25.5	16.0	0.311	0.195	1.735	0.195	1.832	11.2	77.1	71.8
9.94	21.8	27.4	12.5	0.335	0.153	1.875	0.153	1.951	8.1	83.0	76.5
11.01	21.7	21.4	13.4	0.262	0.164	1.984	0.164	2.066	8.2	86.0	81.0
13.98	22.4	28.1	12.5	0.343	0.152	2.163	0.152	2.239	7.0	91.5	87.8

p_1 = gas pressure before each explosion.
p_2 = gas pressure after each explosion.
v_1 = gas volume before each explosion.
v_2 = gas volume after each explosion.
V = sum of the gases produced in the intervals between explosions.
V_H = gas left in the reaction chamber after each explosion.
$V' = V + \frac{1}{2} V_H$.
$\frac{V'}{V_\infty} \times 100$ = per cent of completed reaction.
T_w = temperature of the water bath.

preceding paragraph, and V_∞ is the total quantity of gas which would have been produced if all of the radon initially dissolved in the water decayed. V_∞ is calculated from the total gas yield per millicurie as observed at the end of the experiment.

The results agree in the main with the observations of earlier work. The per cent of radon decayed and the per cent of completed reaction (figure 2) are in approximate agreement throughout the experiment. This is in accordance with the general law deduced by Cameron and Ramsay (1) that the rate of production of gas is proportional to the quantity of radon dissolved in the water. The per cent of excess hydrogen, which is equal to $\frac{V_H}{V} \times 100$ (table 1), decreases as the experiment proceeds, as observed by Duane and Scheuer (3). They explain the decrease as existing when the quantity of hydrogen peroxide formed by the secondary action of nascent oxygen on water reached an amount such that its rate of decomposition, both spontaneous and that caused by the rays, is equal to its rate of formation.

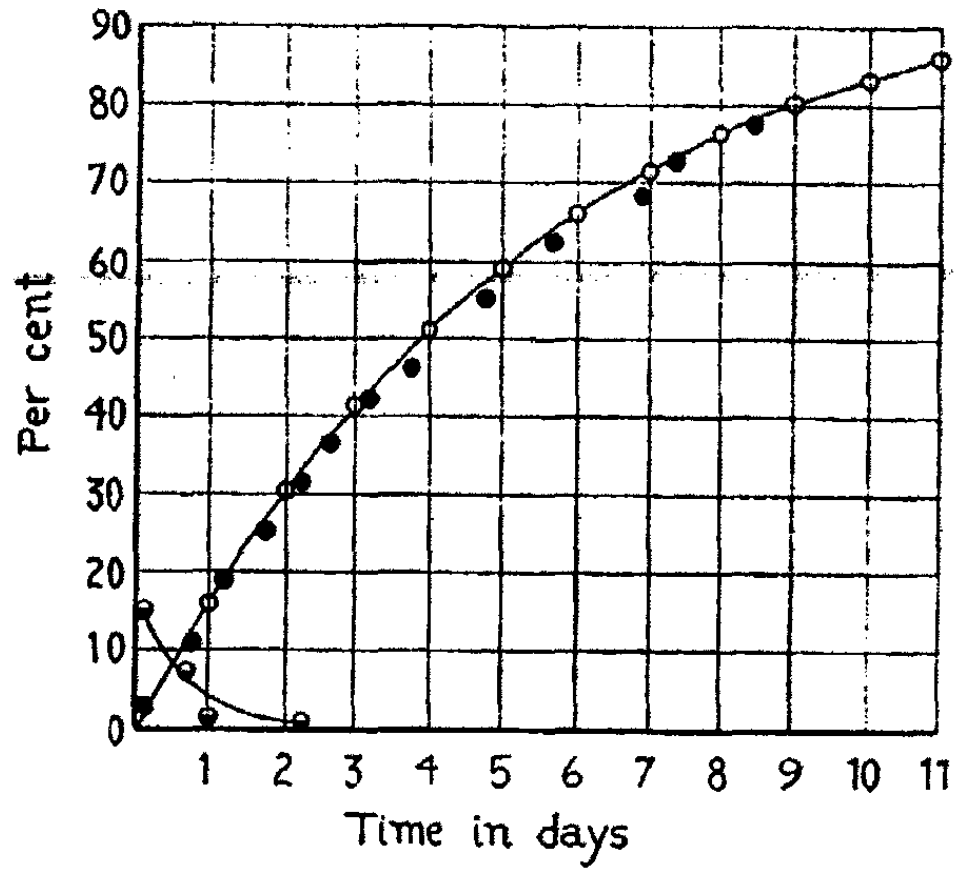

Fig. 2. Decomposition of Water by Radon (direct method)

○ per cent of radon destroyed; ● per cent of completed reaction; ◒ per cent of excess hydrogen.

The most marked departure from the results of Duane and Scheuer occurs in the quantity of gas produced per millicurie of radon destroyed as measured experimentally. Their yield is 0.383 cc. per millicurie, while in table 1 the yield is equal to 0.164 cc. per millicurie. The discrepancy was expected, since their value refers to complete absorption of all alpha-rays in the water, to complete evolution of the hydrogen and oxygen to the gas phase, and without any recombination of the gases. These conditions cannot be had experimentally when the direct method of procedure is used, and therefore, the yield of 0.164 cc. per millicurie is too low.

The distribution coefficient of radon in water at various temperatures (6) has been determined. In particular, at 20.5°C. the coefficient is equal to 0.248. The initial quantity of radon in water and in the gas is given by the formulas,

$$E_0 = E_w + E_g$$

and

$$E_w/E_g = V_w/V_g \ \alpha$$

where E_0 is the total initial amount of radon, E_w is the initial amount dissolved in the water, E_g is the initial amount dissolved in the gas, α is the distribution coefficient, and V_w and V_g are the water and gas volumes, respectively. Application of these formulas to the results recorded in the first part of table 1, gives 43.3 mc. of radon dissolved in the water and 39.7 mc. distributed in the gas. Since 77.4 per cent of the radon was destroyed, 33.5 mc. and 30.7 mc. were destroyed in the water and in the gas, respectively.

The amount of hydrogen and oxygen absorbed by the water is not indicated directly, but can be calculated from the partial pressures of the oxygen in the following manner. When the gaseous mixture is exploded, practically all of the oxygen and an equivalent amount of hydrogen is removed from the water, and hydrogen alone is left in the reaction chamber. This assertion is substantiated by the experimental fact that the gas pressure decreases to a constant value even though the gases were sparked many times thereafter. The amount of oxygen dissolved in the interval between explosions is determined from its average partial pressure in the interval and its solubility in water (0.0286 cc.). There were fifteen explosions in the particular experiment recorded in table 1. A total of 0.464 cc. of oxygen and the equivalent amount, 0.928 cc., of hydrogen, was removed from the water. This oxygen and hydrogen should be added to the total yield, the last value of V', recorded in table 1.

The third correction to be applied to the gas yield results from the recombination of hydrogen and oxygen due to the ionization in the gas by alpha particles and recoil atoms. This particular reaction has been investigated by Scheuer (18), Lind (12), Lind and Bardwell (13), and others. Lind found that for each pair of ions 3.85 molecules of water are formed. Therefore, to determine the quantity of gas used in the formation of water, the intensity of ionization in the gas must be known. The number of ion pairs, which depends upon the average path of the alpha particles, is difficult to obtain, owing to the irregular shape of the reaction chamber, a major portion of which is cylindrical. Lind and Bardwell (14) have tested a formula for the average path of alpha particles in small spheres and found the average path to be 0.61 r, where r is the radius of the sphere. Lunn extended calculations to geometrical forms other than spheres, and concluded that the formula is applicable to cylinders whose lengths are not greater than their diameters by a factor of 10. These cylinders are treated as spheres of equal volumes. Accordingly, the formula, $\bar{p} = 0.61\, r$, is applicable to the major part of the reaction chamber described in figure 1.

The total number of ion pairs produced in the gas is equal to

$$n \times E_0 (1 - e^{-\lambda t}) \times 2.4 \times 10^4 \times \bar{p} \times i \times \frac{P}{760} \times \frac{\alpha + a}{\alpha}$$

where n is the number of alpha particles emitted when 1.0 mc. of radon in equilibrium is destroyed [5.34×10^{13}, (5)]; $E_0(1 - e^{-\lambda t})$ is the amount of radon destroyed in the gas phase; 2.4×10^4 is the number of ion pairs per alpha particle per centimeter of path in air at 0°C. and 760 mm. pressure; $\bar{p}$ is the average path of the alpha particles; i is the specific molecular ionization of the gaseous mixture and is equal to 0.52 when referred to air as unity; P is the gas pressure; and $\frac{\alpha + a}{\alpha}$ (15) is a factor which includes the effects of recoil atoms. For the particular reaction chamber and experiment described in table 1, $\frac{\alpha + a}{\alpha}$ is equal to approximately 1.9. Evaluation of the expression gives 40.5×10^{17} ion pairs. Since 5.76 molecules of $H_2 + O_2$ are recombined per ion pair, then

$$\frac{40.56 \times 10^{17} \times 5.76}{2.705 \times 10^{17}} = 0.5$$

or 0.5 cc. of gas was lost, owing to the ionization produced by alpha particles and recoil atoms.

The total quantity of gas produced takes the value 12.4 cc. (0°C. and 760 mm. pressure) when the gas lost by absorption in the water and recombination in the gas phase is added to the final value of V' in table 1. The new yield per millicurie of radon destroyed in the water is equal to 12.4/33.5, or 0.371 cc. per millicurie.

The gas yield becomes more significant in the theory of ionization and chemical reaction when expressed in terms of molecules reacting per ion pair. It is commonly expressed as M_{H_2O}/N where M_{H_2O} is the number of water molecules decomposed and N is the number of ion pairs produced in the water. M_{H_2O} is equal to $V \cdot 2/3 \cdot 2.705 \times 10^{19}$, where V is cubic centimeters of gas produced per millicurie destroyed, 2.705×10^{19} is Loschmidt's number, and the factor 2/3 is used since two molecules of H_2O decomposed gives three molecules of $H_2 + O_2$. N is equal to 1.78×10^{13} $(1.67 + 1.83 + 2.37) \times 10^5 \times i$, where 1.78×10^{13} is the number of alpha particles emitted when 1 mc. of radon is destroyed, $(1.67 + 1.83 + 2.37) \times 10^5$ is the number of ion pairs produced by one alpha particle from each of the three sources, radon, radium A, and radium C in air under standard conditions, and i is the total specific ionization of water and is equal to 0.82 when referred to air as unity. Evaluation of M_{H_2O}/N gives 0.78. This is below the range of values, 0.86 to 1.02, of Duane and Scheuer (3). Other experiments in addition to table 1, gave M/N values consistently less than Duane and Scheuer's. The discrepancy is probably insignificant, for in systems where large quantities of water are used, the heterogeneous equilibrium of the gases depends upon factors which are difficult to correct.

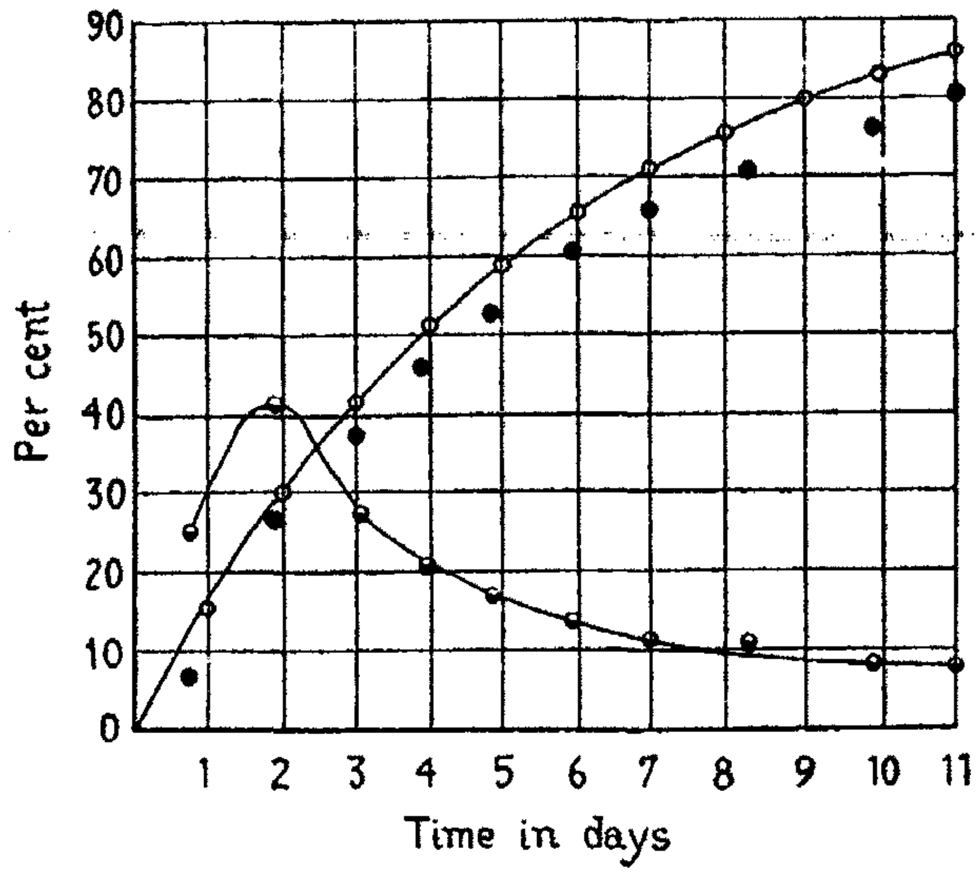

FIG. 3. DECOMPOSITION OF WATER BY RADON (INDIRECT METHOD)

○ per cent of radon destroyed; ● per cent of completed reaction; ⊖ per cent of excess hydrogen.

In the calculation of the gas yield it was assumed that radon is in radioactive equilibrium with its decay products when the experiments began, and furthermore, that radon dissolved quickly in the water. Actually, equilibrium is not reached until about five hours after the experiment begins, so that the alpha particle emission is less for this part of the experiment than it would be if equilibrium really existed. There is, however, no consistent lag in the gas yield during the first few hours, and therefore the errors introduced by the assumptions are negligible.

Quantitative measurements of the irradiation of substances with radon confined to alpha-ray bulbs can be made provided the transmission of the alpha rays through the glass wall of the bulbs is known. The alpha-ray energy available after passage through the bulb is usually expressed in terms of their range in air or their total ionization in air under standard conditions. It is proposed to use here a unit which denotes the number of cubic centimeters of gas produced when the rays are absorbed by water, and in particular, to use the yield, 0.383 cc. of gas per millicurie destroyed, for 100 per cent transmission.

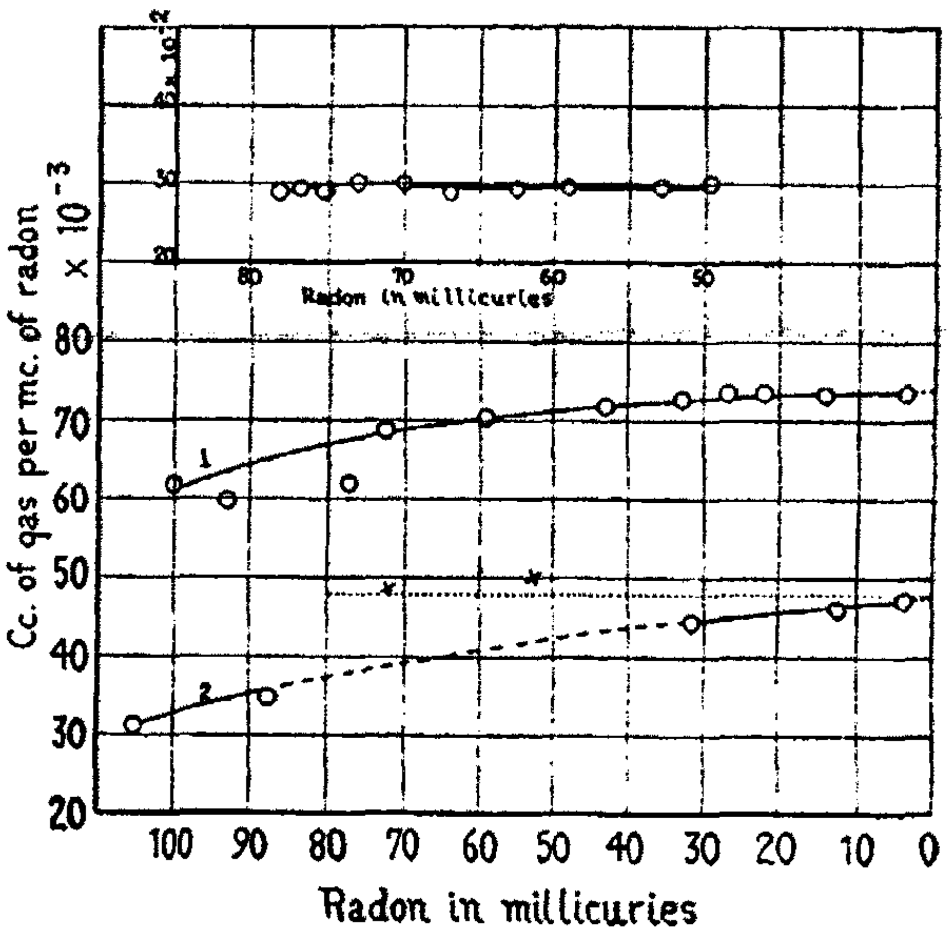

FIG. 4. CALIBRATION OF ALPHA-RAY BULBS NOS. 1 AND 2 BY THE DECOMPOSITION OF WATER

× and × indicate two experiments on ferrous sulfate

The transmissions of several alpha-ray bulbs were tested and the results of a typical experiment are recorded in the bottom half of table 1. The experimental procedure was the same as was used in the other method, except that radon was confined to the alpha-ray bulb (R, figure 1) instead of being dissolved in the water.

The method is complicated somewhat by the failure of the gas yield to follow closely the law of Cameron and Ramsay. The per cent of completed reaction ($\frac{V'}{V_\infty} \times 100$) lags behind the per cent of radon decayed as is indicated in figure 3. Furthermore, the excess hydrogen has a higher initial value and also appears to decrease more slowly than it did in the direct method.

The departure of the gas yield from the general law is demonstrated more clearly in figures 4 and 5. The gas yield per millicurie of radon is not constant, but appears to increase and approach a constant value as the quantity of radon in the bulbs decreases, or as the intensity of the rays decreases. In figure 3, curves 1 and 2 represent results with two different alpha-ray bulbs, and the difference in yields is due to differences in thickness of the bulbs. Plotted in curve 2 of figure 4 are the results of three experiments on water and two on ferrous sulfate solutions. The first experiment on water began immediately after the alpha-ray bulb had been filled with 105 mc. of radon and ended after 1 day and 27 hours. The second began after approximately 60 per cent of the radon had decayed and continued 1 day and 24 hours. The last experiment began after a new supply of radon had been added to the bulb. Between the second and third experiments, indicated by the dashed portion of the curve, concentrated solutions of ferrous sulfate were irradiated with the same alpha-ray bulb, and the gas yields, corrected for excess hydrogen, are indicated by the crosses. The crosses are situated above the curve such that if the gas yield from water had been constant (dotted line) with a value equal to the yield near the end of the last experiment, the crosses and the new points for water would lie approximately on the same straight line. This fact, as will be mentioned later, has an important significance in the explanation of the variation of yield with ray intensity. The top curve in figure 4 represents an experiment on the irradiation of water by the direct method. The radon in millicuries plotted as abscissas is dissolved in the water. The difference in the variation of gas yield with ray intensity for the two methods of experiment is demonstrated clearly.

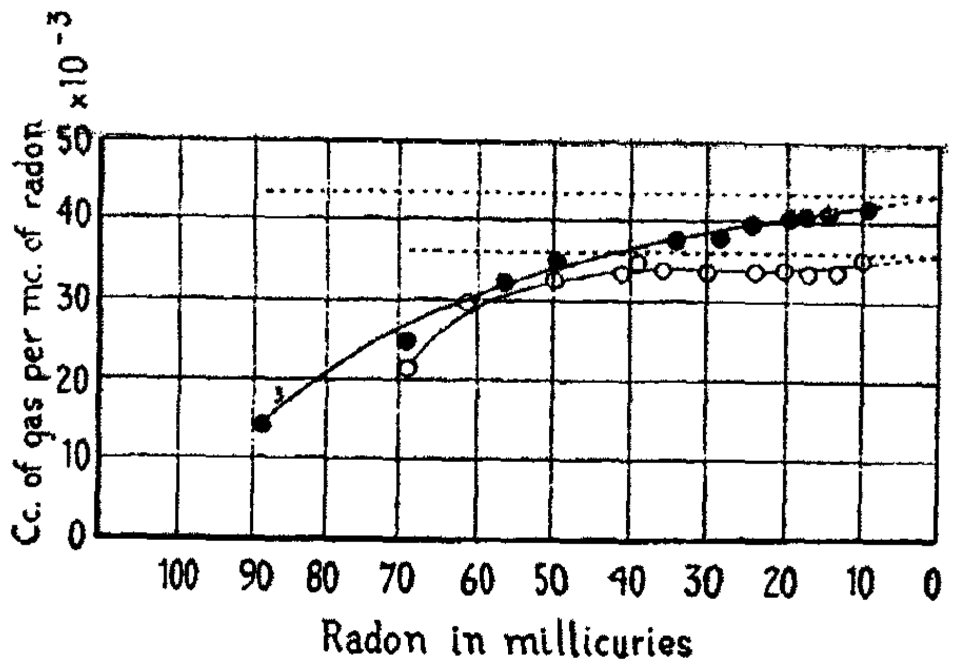

FIG. 5. CALIBRATION OF ALPHA-RAY BULB NO. 3 BY THE DECOMPOSITION OF WATER
● new bulb; ○ after the bulb had been refilled many times

In figure 5, the results of two experiments with the same alpha-ray bulb (No. 3, table 2) are shown. The agreement is fair except for the latter parts of the experiments. Here, the maximum variation is about 16 per cent, which is outside of the observational errors. The discrepancy may be due to the fact that the bulb had been filled with radon many times when the data for the lower curve was obtained. There may have been some mercury vapor or other substances condensed on the inside surface of the bulb which would give the effect of reducing the gas yield. In the course of the work it was noticed that small black deposits, probably some oxide of mercury, were visible on the bulbs. These bulbs were removed from the system and cleaned with nitric acid and water. This is a delicate process of manipulation and occasionally the bulbs were broken.

TABLE 2

Calibration of alpha-ray bulbs

BULB NO.	DIAMETER	DAYS	RADON E_0	V'	PER CENT OF TOTAL TRANSMISSION	PER CENT OF ALPHA-RAY TRANSMISSION
	millimeters		*millicuries*			
1	1.8	13.8	112.5	7.708	18.6	15.3
2	2.5	1.88	105.0	1.041	8.4	4.8
		1.60	31.4	0.359	10.8	
		7.73	12.3	0.449	11.5	
		1.87*	53.1	0.773	12.4	9.0
		1.25*	72.6	0.709	12.2	8.9
3	1.8	13.9†	69.1	2.239	8.7	5.0
		10.7	91.9	3.307	10.4	7.0

* Ferrous sulfate.

† The low per cent of transmission is probably due to mercury vapor condensing on the inside wall of the alpha-ray bulb.

A summary of the results on the irradiation of water with radon in alpha-ray bulbs is given in table 2. The per cents of total transmission and alpha-ray transmission are shown in columns 6 and 7, respectively. The total radiant energy includes not only alpha rays, but also beta and gamma rays. The gamma-ray energy, however, is negligible, since the whole of it is a small per cent of the total radiant energy, and only a small part is absorbed by the water. On the other hand, an appreciable part of the gas is produced by beta rays, since practically none of them are absorbed by the glass while a large portion is absorbed by the water. From Rutherford's (17) estimation of the distribution of the total radiant energy from radium in equilibrium between alpha, beta, and gamma rays, and from the assumption that the total alpha-ray energy is divided equally between the four sources, radium, radon, radium A, and radium C, it can be shown that approximately 4.1, 5.9, and 90.0 per cent of the total radiant energy from radon in equilibrium is possessed by the beta, gamma, and alpha rays, respectively. Since 0.383 cc. of $H_2 + O_2$ (Duane and Scheuer's value) is produced when all of the alpha rays from 1 mc. are absorbed in water, then 0.383/0.9, or 0.426 cc., is produced when all of the alpha, beta, and gamma rays are absorbed. The latter rays produce 0.025 cc., and therefore 0.401 cc. is produced by the beta and alpha rays. If this factor represents 100 per cent transmission of all beta and alpha rays through the glass wall of the alpha-ray bulbs, then a simple arithmetical calculation from the gas yields from various bulbs gives their per cent of total and their per cent of alpha-ray transmissions.

Unfortunately, the thinnest bulb, No. 1, was broken when the gaseous mixture was exploded in a second test of its wall thickness. At least six bulbs, in reaction vessels of gas volumes varying from 5 to 10 cc., and whose yields were larger than 0.06 cc. per millicurie of radon destroyed, were broken when the hydrogen and oxygen were removed by the electric spark. This yield represents a transmission of approximately 12 per cent of the alpha-ray energy, and is apparently the maximum allowable transmission without breaking the bulbs in the particular systems used in these experiments.

The experimental results lead to the conclusion that the variation of gas yield with radiation intensity is a result of the recombination of ions in the water before they become electrically neutral and pass to the gas phase. The liquid volume wherein the ions are produced is exceedingly small, and if large quantities of radon are contained in the bulbs, the ionic concentration is of the same order of magnitude as the molecular concentration of the water. The alpha-ray bulbs ranged in size from 1.5 mm. to 2.5 mm. in diameter. The range of the alpha rays in the water is not more than a few hundredths of 1 mm. Therefore, all of the ions are produced in a thin layer of water immediately surrounding the bulbs. The idea of recombination of ions is supported by the fact that when the molecules of a concentrated solution of ferrous sulfate offer another means of escape for some of the ions, then their chances of recombination are reduced, and more become neutralized and escape to the gas phase. If, in the experiments with ferrous sulfate, an amount of oxygen equivalent to the hydrogen which is produced, is added to the hydrogen, then the new gas yield assumes a value approximately equal to the gas yield from water for the lower intensities of irradiation. This fact was mentioned previously and is indicated by the crosses in curve 2 of figure 4.

The results of Duane and Scheuer in their first experiment indicate a slight departure from the law of Cameron and Ramsay, while their second and third do not. They apparently gave no significance to it, but it is interesting to note in connection with the more marked discrepancy observed here. In their first experiment, the capillary tube in which radon was used was approximately six times thicker than in the other two experiments. Therefore the range of the alpha particles was less, and, consequently, the region of ionization was smaller. Additional evidence that the ionic concentration may depend appreciably upon the range was observed here. One of the smallest bulbs and with the greatest wall thickness, gave results with the greatest variation from the general law.

The method of calibrating alpha-ray bulbs described in the preceding pages has some advantages over other methods commonly used. This is particularly true when the bulbs are used in systems where complete absorption is desired. Here, the calibration is determined in the chamber which is later used for other reactions. The transfer of bulbs from one system to another is eliminated. The bulbs may be filled several times with a new supply of radon, and one bulb may be used in several different experiments. The transmission is the average transmission for all parts of the bulbs, regardless of the non-uniformity of wall thickness. The thick spots at their tops and the thick portions around the steam are given their proper weight in the average value. One disadvantage is the relatively long time required for a careful determination of the transmission. The minimum time is about five days when 50 mc. of radon are used. This time, however, depends upon the capacity of the reaction chamber.

II. Oxidation of ferrous sulfate

The effects of alpha rays in solutions of ferrous sulphate in 0.8 normal sulfuric acid were studied by both the direct and indirect methods. Gas yields were determined. The procedure and the notation used in recording the results is the same as was used in the experiments on water. The solutions were stirred continuously and their temperature was kept constant. Furthermore, the quantity of ferrous sulfate changed was determined by electrometric titrations.

Three particular points of interest were investigated. It was desirable first, to study the behavior of the excess hydrogen during the course of an experiment; second, to determine the relationship between alpha-ray dosage and the per cent of ferrous sulfate changed; and third, to investigate the effects in solutions of different concentrations. These points will be discussed in the order named.

Some results of both methods are recorded in table 3. The course of the reaction is demonstrated in figures 6 and 7. The most marked difference in the gas yields from ferrous sulfate and the yields from water is the high percentage of gas left in the reaction chamber of the former when the gaseous mixture is exploded. This residual gas is assumed to be hydrogen alone; however, at the present time, no qualitative analysis of the gas has been made. If the assumption is correct, then near the end of the experiment described by figure 6 the gas is almost exclusively hydrogen and in figure 7 the gas consists of nearly 97 per cent hydrogen. The action of the alpha rays on the ferrous sulfate molecules is probably a secondary effect which results from the primary decomposition of the water. The oxygen from the decomposed water is used in the oxidation of the ferrous ion, and consequently, the only gas which escapes from the liquid is hydrogen.

TABLE 3

Gas yield in the oxidation of ferrous sulfate by radon

Direct method

0.0385 molar $FeSO_4$ in 0.8 *N* H_2SO_4

Solution volume = 15.0 cc.; gas volume = 4.99 cc.; initial quantity of radon = 24.4 mc.; ferrous sulfate changed = 25 per cent

DAYS	T_w	p_1	p_t	v_1	v_t	V	V_H	V'	PER CENT V_H	PER CENT RADON USED	$\frac{V'}{V_\infty} \times 100$
0	24.6		30.0		0.181						
0.47	24.4	88.7	87.7	0.535	0.528	0.353	0.347	0.527	98.3	8.3	9.2
1.03	24.8	128.9	127.9	0.775	0.769	0.601	0.589	0.895	98.0	17.0	15.9
2.41	24.6	255.0	255.0	1.536	1.536	1.367	1.355	2.044	99.1	35.3	35.8
3.14	24.6	301.0	300.0	1.813	1.813	1.644	1.632	2.460	99.8	43.2	43.1
4.52	24.2	376.0	377.0	2.267	2.267	2.098	2.085	3.141	99.8	55.8	55.0
5.49	23.8	424.0	424.0	2.561	2.561	2.392	2.380	3.582	99.8	62.8	62.7
7.14	24.0	485.0	485.0	2.927	2.927	2.758	2.746	4.131	99.8	72.0	72.3

Indirect method

0.0046 molar $FeSO_4$ in 0.8 *N* H_2SO_4

Solution volume = 16.0 cc.; gas volume = 9.97 cc.; initial quantity of radon = 40.3 mc.; ferrous sulfate changed = 99 per cent

DAYS	T_w	p_1	p_t	v_1	v_t	V	V_H	V'	PER CENT V_H	PER CENT RADON USED	$\frac{V'}{V_\infty} \times 100$
0	22.2		0.1		0.007						
1.01	22.2	28.0	24.6	0.339	0.298	0.332	0.291	0.472	87.6	16.4	15.6
2.10	22.4	53.4	53.4	0.647	0.647	0.681	0.640	1.001	93.9	31.6	33.2
3.68	22.0	81.6	81.6	0.990	0.991	1.024	0.983	1.515	96.0	48.1	50.2
5.19	22.2	93.2	93.2	1.131	1.131	1.165	1.123	1.726	96.4	60.5	57.2
7.00	22.2	120.0	119.0	1.456	1.444	1.490	1.436	2.208	96.5	71.5	73.2
9.65	22.0	134.3	132.3	1.631	1.607	1.677	1.600	2.477	95.4	82.1	82.1

Here, as in the experiments on water, the law of Cameron and Ramsay applies to the gas produced, since the points representing the per cent of completed reaction follow closely the decay curve of radon.

Several samples of ferrous sulfate of the same initial concentration were exposed to different doses of alpha particle irradiation. The results of six experiments with each method are indicated by the sets of points in figures

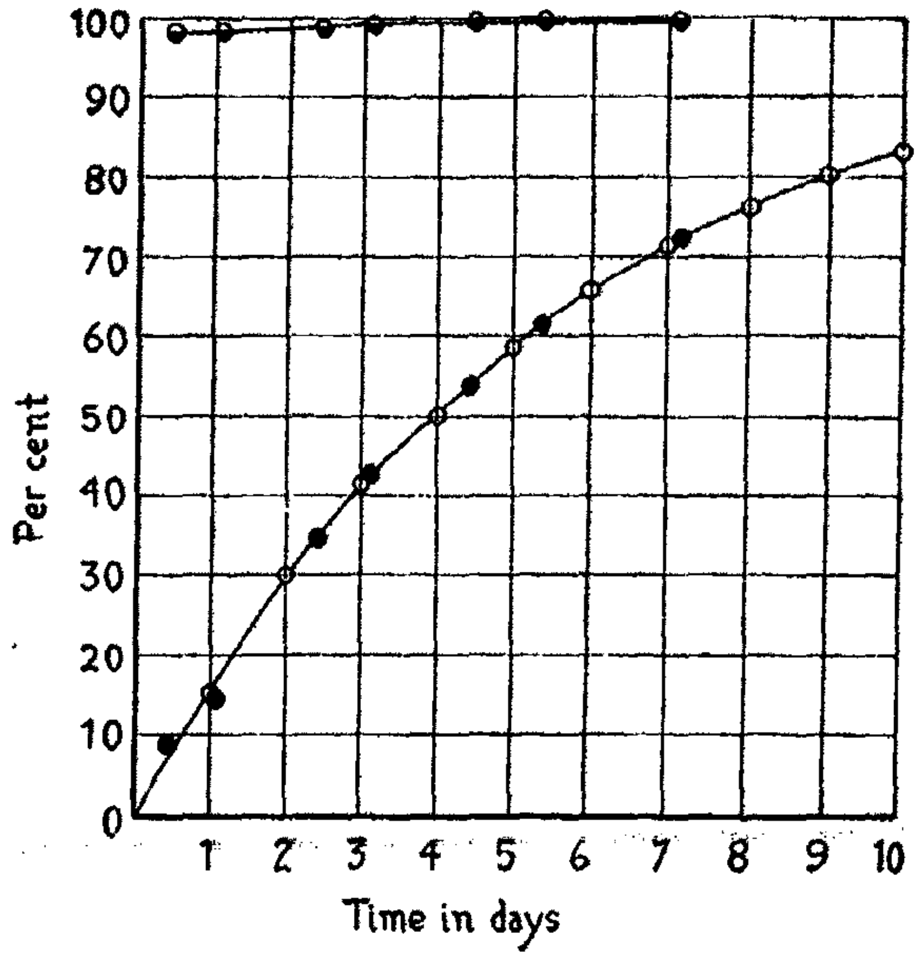

FIG 6. GAS YIELD IN THE OXIDATION OF FERROUS SULFATE BY RADON

Direct method; 0.0385 molar ferrous sulfate in 0.8 *N* sulfuric acid.

○ per cent of radon destroyed; ● per cent of completed reaction; ◒ per cent of excess hydrogen.

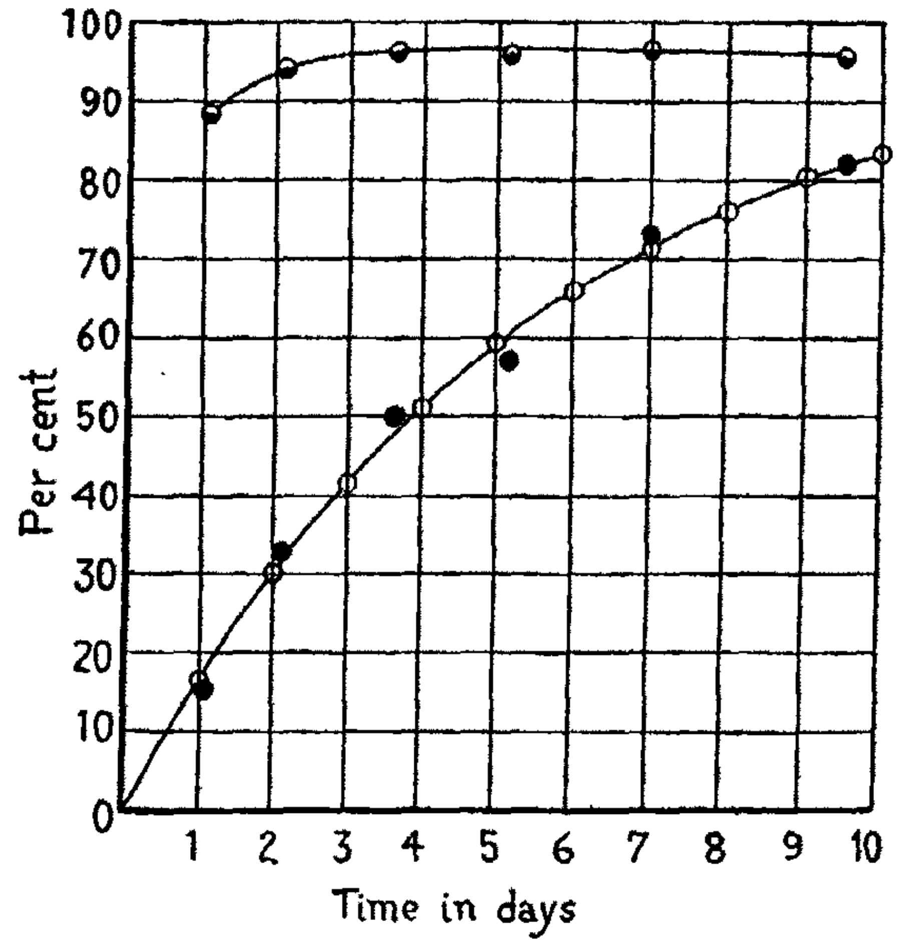

FIG. 7. GAS YIELD IN THE OXIDATION OF FERROUS SULFATE BY RADON

Indirect method; 0.0046 molar ferrous sulfate in 0.8 *N* sulfuric acid.

○ per cent of radon destroyed; ● per cent of completed reaction; ϙ per cent of excess hydrogen.

8 and 9. The liquid volumes were 20.3 cc. and 16.0 cc., and the gas volumes were 1.66 cc. and 10.0 cc. for the direct and indirect methods, respectively. The relationship between dosage and per cent of ferrous sulfate changed is linear when radon is dissolved in the solution, but when radon is in the alpha-ray bulb there is a slight deviation from the straight line. The linear relationship indicates equilibrium to be almost 100 per cent on the side of oxidation of the ferrous ion, while the curve in figure 9 may indicate some reduction of the ferric ions. The latter reaction has been observed in acid solutions (7) when irradiated with penetrating rays.

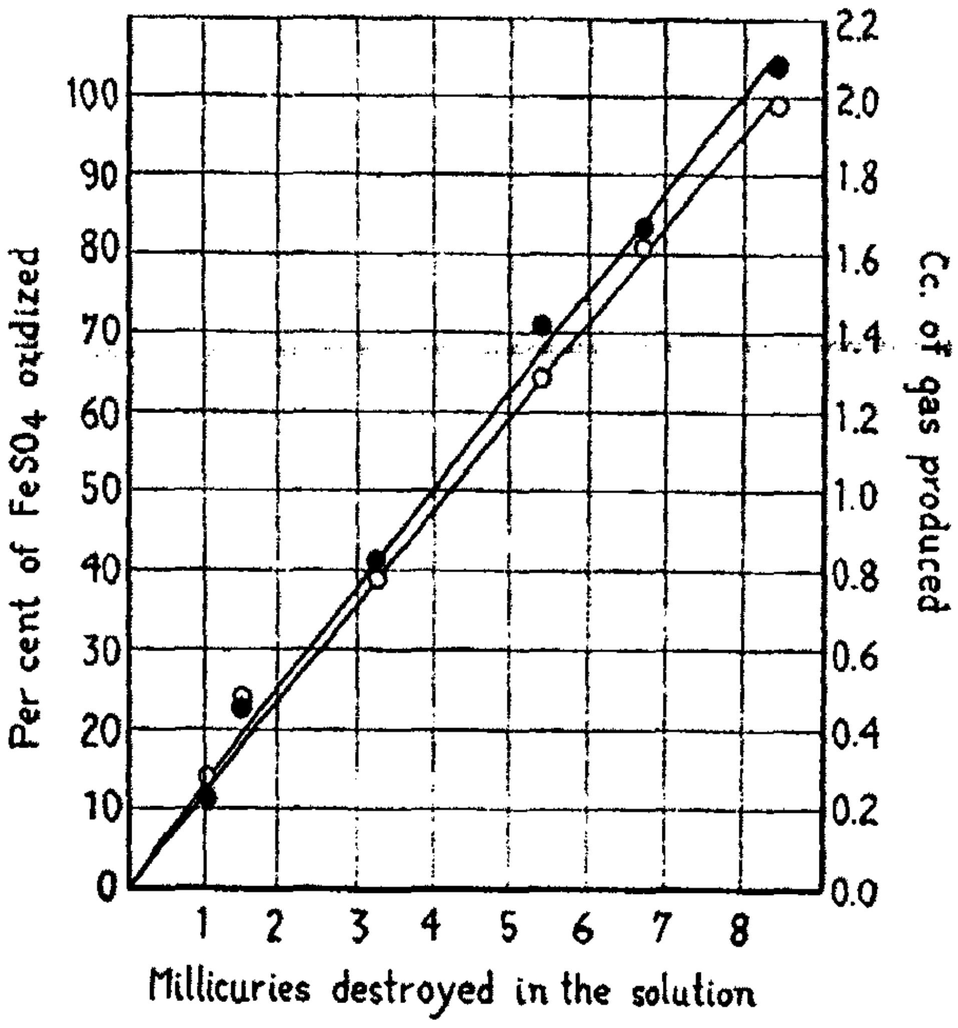

FIG. 8. OXIDATION OF FERROUS SULFATE BY RADON
Direct method; 0.0045 molar ferrous sulfate in 0.8 N sulfuric acid.
○ per cent of oxidation; ● gas yield.

Fricke and Morse (4) noted in one of their experiments on the irradiation of ferrous sulfate with x-rays an apparent reversal of the reaction when nearly all of the ferrous ions were oxidized. They concluded that x-rays are able to reduce the ferric ion.

The gas yields in the twelve experiments (figures 8 and 9) are indicated by the shaded circles. The separation of the lines in each figure has no significance other than its dependence upon the choice of scale. Since the gas was nearly 100 per cent hydrogen the correction due to the ionizing effects of the alpha particles in the gas is negligible. Furthermore, the quantity of hydrogen dissolved in the solution is small and was not added to the total gas yield unless it amounted to one or more per cent of the observed hydrogen volume.

In the six experiments whose results are recorded in figure 9, the initial quantity of radon was less than 50 mc., so that, as can be seen in figure 4, the gas yield per unit of energy absorbed was more constant than it would have been for greater quantities of radon. In other words, the recombination of ions, which may occur in very dilute solutions, was reduced to a minimum.

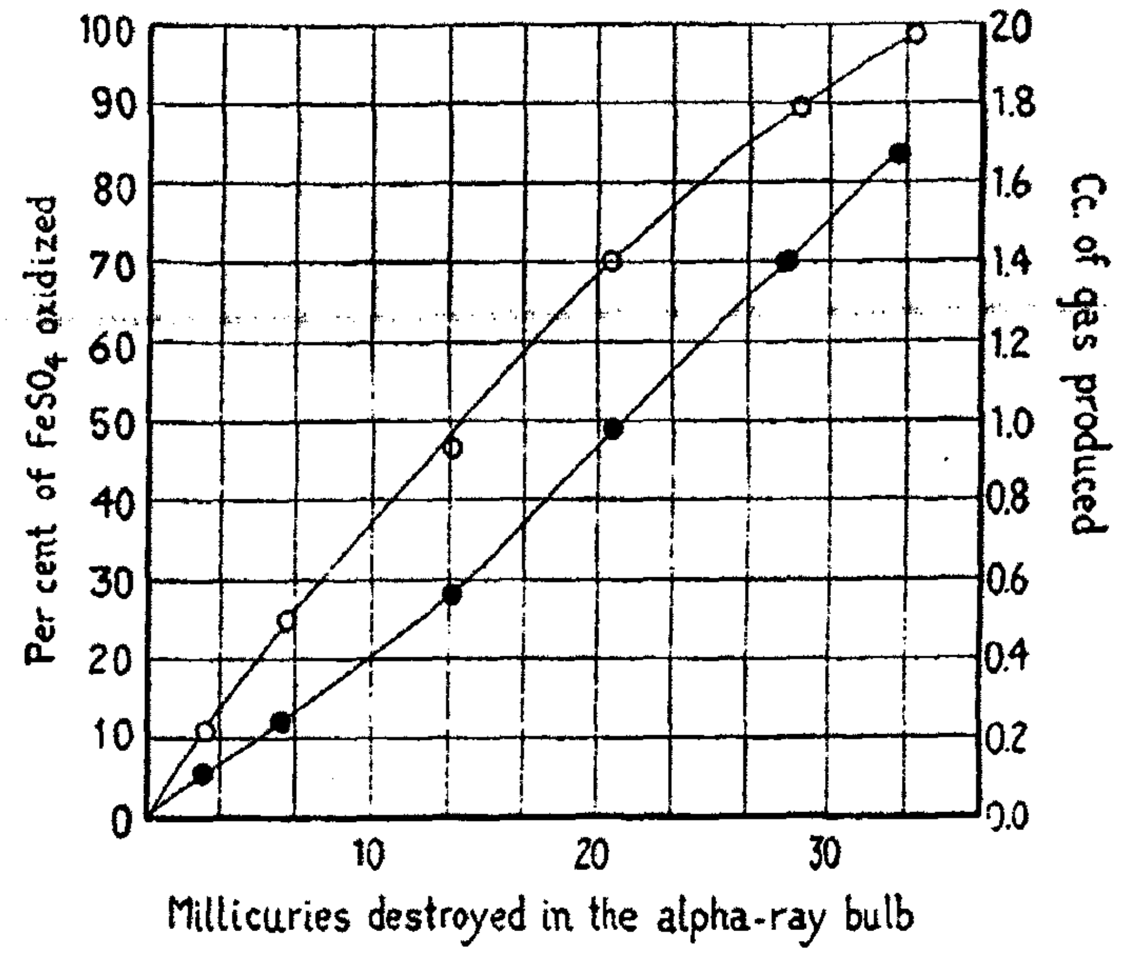

FIG. 9. OXIDATION OF FERROUS SULFATE BY RADON

Indirect method; 0.0046 molar ferrous sulfate in 0.8 N sulfuric acid.
○ per cent of oxidation; ● gas yield.

Solutions of ferrous sulfate of different concentrations were irradiated and the results are given in table 4. The concentration of each solution was determined at the beginning and the end of an experiment as described in the preceding pages. The absolute amount of ferrous sulfate transformed, expressed in milligrams per millicurie of radon decayed, is not constant, but increases as the initial concentrations of the solutions are increased from 0.00048 to 0.5 molar. This may at first seem to disagree with the results plotted in figure 7, for in figure 7 the solutions do have their ferrous ion concentration reduced; however, the yield per millicurie remains constant. Close inspection of table 4, however, shows that the numerical values in column 4 seem to approach a constant value as the solution concentration is reduced; and furthermore, the range of concentrations in the experiments of figure 8 is either equal to or less than the minimum concentration of table 4. The irradiation of solutions of initial concentrations less than 0.00048 molar might have added more information in regard to this point; however, they are difficult to study, since small quantities of radon produce large percentages of transformation. Consequently, the end point of the titration curve is not distinct. Moreover, the gas yield is too small to measure accurately with the apparatus employed.

The chemical action of the alpha rays in the ferrous sulfate solutions is expressed in terms of the ionization of the rays in the last two columns of table 4. M_{FeSO_4} denotes the number of ferrous sulfate molecules transformed and is equal to $\frac{m \times 6.06 \times 10^{23}}{277.9 \times 1000}$, where m denotes ferrous sulfate transformed in milligrams, 6.06×10^{23} is Avogadro's number, and 277.9 is the molecular weight of $FeSO_4 \cdot 7H_2O$. N denotes the number of ion pairs formed in water by the absorption of a quantity of radiant energy equal to that absorbed by the solutions. The factors in the calculation of N were described previously. The ratio M_{FeSO_4}/N in both methods decreases with concentration, but not linearly. It seems to approach a constant value for dilute solutions. The number of molecules of hydrogen which are produced per ion pair is expressed by the ratio M_{H_2}/N. The

TABLE 4

Oxidation of ferrous sulfate by radon in solutions of different concentrations

CONCENTRATION	PER CENT OXIDIZED	RADON USED	MILLIGRAMS CHANGED PER MC. OF RADON	VOLUME OF H_2	PER CENT OF H_2	$\frac{M\ FeSO_4}{N}$	$\frac{M_{H_2}}{N}$
Direct method							
molar		*millicuries*					
0.5000	2.3	8.04	12.4	2.067	99.2	3.13	0.80
0.0498	30.4	12.5	5.52	3.342	99.5	1.40	0.83
0.0333	7.2	5.90	4.01	1.438	94.2	1.01	0.74
0.0045	39.6	3.33	3.02	0.947	94.7	0.78	0.88
Indirect method							
0.4100	4.4	15.2	3.80	0.534	100.0	8.10	0.91
0.0460	12.8	14.9	1.27	0.762	94.5	2.75	1.32
0.0046*	37.4	6.87	0.81	0.372	95.9	1.70	1.41
0.0045†	37.4	10.6	0.75	0.500	92.0	1.68	1.33
0.00048	57.9	1.33	0.70	0.095	78.0	1.64	1.85

* Alpha-ray bulb No. 2.
† Alpha-ray bulb No. 3.

ratios, M_{FeSO_4}/N and M_{H_2}/N, are in most cases nearly 50 per cent greater in the indirect method than in the direct method. It was at first thought that the difference in yields might be partially due to errors in the determination of the transmission of the alpha-ray bulb. However, the results obtained with two different bulbs (Nos. 2 and 3, table 2) agree and so it is unlikely that the M/N values of the two methods differ owing to errors in transmission determinations.

DISCUSSION OF RESULTS

The increase of M_{FeSO_4}/N without a corresponding increase of M_{H_2}/N when solutions of greater concentrations of ferrous sulfate are used complicates the reaction beyond expectation. When the work began, it was thought that the reaction would most likely be a simple oxidation of the ferrous ions to ferric ions by the oxygen of the decomposed water. If the activated water molecules or the ions resulting from the dissociation of the water molecules simply oxidized the ferrous ion and no other reaction is present, then M_{H_2}/N would be some constant multiple, most likely two, of M_{FeSO_4}/N; that is, M_{FeSO_4}/M_{H_2} would be equal to 2. The experimental results do not verify this conclusion, and, therefore, other reactions must be present. Whatever the side reactions may be, they must proceed with the oxidation of ferrous ions without liberating hydrogen. Chemical analyses of the reaction products have not as yet been studied and therefore no definite statement about their nature can be made. It is interesting to note that if there be added to M_{H_2} (table 4) the number of molecules of oxygen contained in a volume equivalent to the hydrogen volume, then $\frac{M_{H_2} + M_{O_2}}{N}$ would have a value near to that for pure water.

Fricke and Morse (9) irradiated aqueous solutions of ferrous sulfate in 0.8 N sulfuric acid with x-rays from a water-cooled tungsten tube. They obtained for solutions whose concentrations varied from 0.00878 to 0.0000406 gram-molecules in 1000 g. of solution, a linear relationship between the x-ray dosage and the per cent of ferrous sulfate transformed up to the arbitrary dose 29. Beyond 29, the relation is linear, but the line describing it has a different slope. They attribute the sharp break in their curve as occurring when all of the dissolved oxygen in the solution is consumed. Moreover, they find that M_{FeSO_4}/N, where M_{FeSO_4} has the same meaning as is defined in the preceding pages, and N is the number of ion pairs formed in air by the absorption of the same amount of x-rays as is absorbed in their solutions, is equal to 5.7 when the solution contains oxygen and is equal to 2.8 when the solution does not contain oxygen. These values are within the range of variation of M_{FeSO_4}/N given in table 4. However, the latter are obtained after the dissolved gases in the solution were partially removed, and, therefore, the higher yields cannot be attributed to dissolved oxygen alone. Furthermore it is difficult to understand why the consumption of oxygen should end so suddenly as is indicated by the sharp break in the slope of their curves.

SUMMARY

1. Two methods, called the direct and indirect, of irradiating liquids with alpha-rays from radon are described, and the errors and their corrections in the direct method are discussed.

2. The decomposition of water by alpha rays is suggested as a method for the determination of the transmission of alpha-ray bulbs. The gas yields are shown to deviate somewhat, owing to recombination of ions in the water, from the general law of Cameron and Ramsay.

3. Aqueous solutions of ferrous sulfate were irradiated by both methods. The gas yield is nearly 100 per cent hydrogen. Equilibrium lies almost 100 per cent on the side of oxidation of the ferrous ions to ferric ions.

4. Milligrams of ferrous sulfate changed per millicurie of radon destroyed increase when the initial concentration of ferrous sulfate is increased from 0.00048 molar to 0.5000 molar.

5. The ratios M_{FeSO_4}/N and M_{H_2}/N vary with the concentration of ferrous sulfate. Furthermore, M_{FeSO_4}/M_{H_2} is not equal to two and therefore reactions other than the oxidation of the ferrous ions by the decomposition products of water are present.

6. Dissolved oxygen alone does not account for the yield of oxidized ferrous sulfate.

The author wishes to express his appreciation to Professor Wilhelm K. Stenström for his active coöperation and interest throughout the course of this study. He also thanks Professor S. C. Lind of the Chemistry Department of the University of Minnesota for his interest and helpful suggestions; and he is grateful to the Department of Physiology and to the Cancer Institute of the University Hospitals, who have made the work possible by their generous supply of the necessary apparatus.

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THE EFFECT OF ULTRA-VIOLET RAYS ON THE ULTRA-VIOLET ABSORPTION SPECTRUM OF AQUEOUS METHYLENE BLUE SOLUTIONS

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In 1912 Lasareff (7) observed that methylene blue was bleached by sunlight if it were spread on thin plates in the form of a gelatin solution. The bleaching of the visible spectrum of methylene blue has been reported also by Gebhard (1) and Krestownikoff (6). Iimori and Kitaoka (4) found that methylene blue was decolorized by exposure to the rays of the mercury arc. Hill (3) has used the fading of solutions of methylene blue in 30 per cent acetone to measure the ultra-violet intensity in the "physiologically active" region of the spectrum. Stenström and Lohmann (9), in an investigation of the fading action of Roentgen rays on various colored solutions, found that aqueous methylene blue solutions were faded by the rays. In this paper we shall report the changes in the ultra-violet absorption spectrum of aqueous methylene blue solutions following irradiation with ultra-violet rays.

The accurate determination of absorption bands by the visual selection of points of equal density on a photographic plate is made more difficult by the uncontrollable variations in the intensity of the light source. Some of the errors of this method are eliminated by the use of the Judd Lewis (8) sector photometer, manufactured by Adam Hilger, London, since, by the use of this instrument, simultaneous and adjacent spectra of the light passing through both photometer and solution are obtained.

In this laboratory, we use an under-water tungsten spark of the type recommended by the Bureau of Standards (2) as a source of light. The advantage of such a source lies in the fact that the resulting spectrum is continuous and relatively free from intense emission lines. Light from this source is split by the lens system of the apparatus into two parallel beams. The upper of the two beams passes through the solution whose absorption bands are being determined, while the lower one passes through a variable sector photometer and, if it is desired, through the pure solvent used in making the solution. (We have always taken the precaution of placing either the pure solvent or distilled water in the lower beam.) The two beams pass through the lens system of a quartz spectrograph and are then brought together on a photographic plate, the image of the upper one lying just above that of the lower. The light source previously has been carefully adjusted so that the two images are equally intense when the photometer is opened completely and when no solution is placed in either beam. A series of photographs is then made on one plate. The customary method is to take the first exposure with the photometer set at 0.1 (on the lower of the two photometer scales), the second exposure with the photometer set at 0.2, and so on, the last exposure being made when the photometer is set at 1.5. In order to keep constant the density of the spectrum on the photographic plate produced by the light passing through the sectors, it is necessary to use a different time of exposure for each sector setting. The time of each exposure is calculated conveniently by means of the formula,

$$\text{Exposure time} = A\frac{J'}{J}$$

where A is a constant and where J'/J is the ratio of the light intensity before the light enters the photometer to that after it has passed through the photometer. The constant, A, is easily determined by experiment. The ratio, J'/J, is the antilogarithm of the lower scale reading of the photometer scale. After the plate is developed (which process requires no special care, since the pairs of spectra are both exposed and developed simultaneously and under identical conditions), the points of equal density on each of the pairs of spectra are determined by using a suitable ocular and are marked with India ink. The extinction coefficients (5) can then be calculated by means of the relation,

$$K = \frac{1}{L}\log_{10}\frac{J'}{J}$$

where K is the extinction coefficient, L is the length (in centimeters) of the absorption chamber used, and $\log_{10} J'/J$ (slight corrections, found in the directions furnished by Hilger, must be applied), the logarithm of the ratio of the light intensity before the beam enters the photometer to that after it leaves it, is the lower reading of the photometer scale. A wave length scale is provided with the spectrograph; two images, one at the bottom and one at the top of the series of exposures, are recorded on the photographic plate by means of 15-second exposures with a 40-watt electric lamp. The wave length corresponding to each India ink dot is determined by placing a straight edge across the two wave length scales and moving it until the edge passes through the center of the dot. By plotting the extinction coefficient as a function of the wave length, the absorption bands can be illustrated in graphic form.

EXPERIMENTAL

A standard solution of methylene blue, containing 0.1 mg. of dye per cubic centimeter was made by dissolving recrystallized methylene blue in distilled water. From this stock solution, working solutions were prepared by dilution. By preliminary experiments, it was found that 0.008 mg. per cubic centimeter represented the correct concentration to show photographically the ultra-violet absorption bands when a 2-cm. absorption chamber was used. Accordingly this concentration was used in all our experiments.

As a source of ultra-violet light for the irradiation of the methylene blue solutions, we used a Victor mercury arc lamp. All the solutions irradiated were placed at a distance of 30 cm. from the center of the lamp bulb. The operating voltage of the lamp varied between 65 and 70 volts. In all cases except one (where distilled water was used as the solvent) the time of exposure was 2 hours.

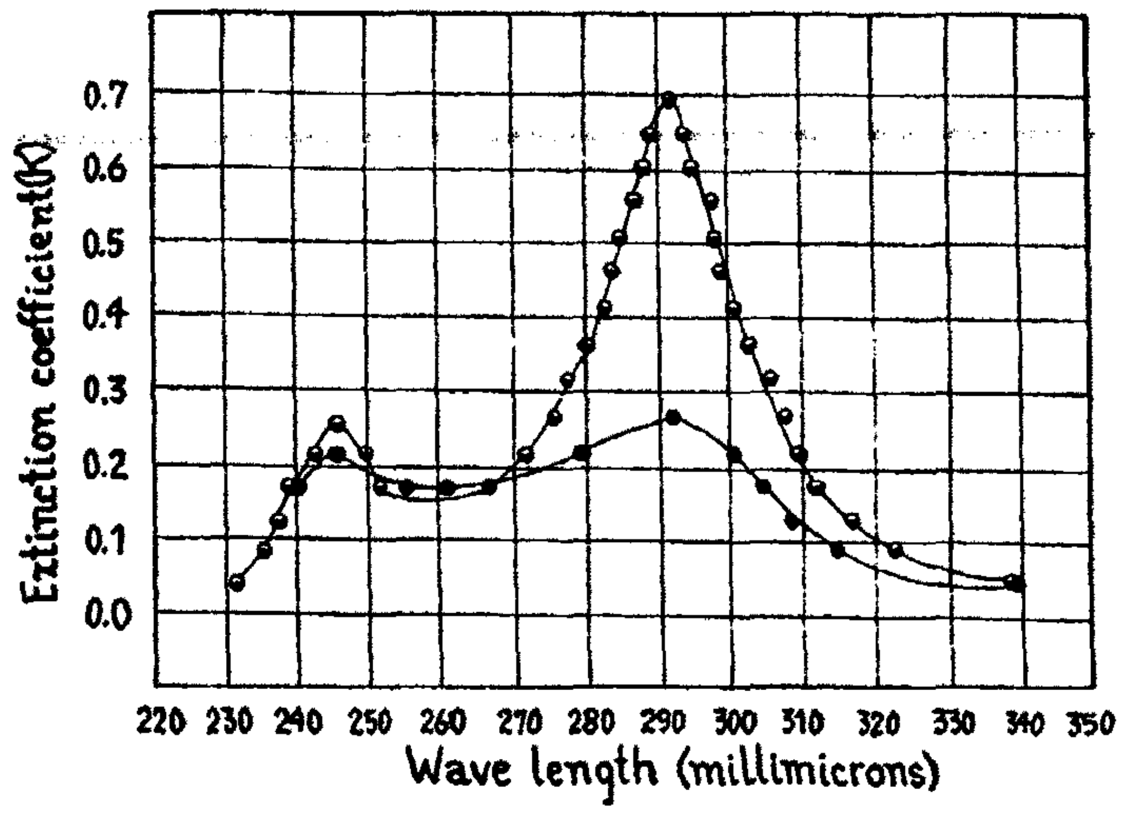

FIG. 1. ULTRA-VIOLET ABSORPTION SPECTRA OF METHYLENE BLUE IN DISTILLED WATER

⊖ before irradiation; ● after irradiation

Figure 1 shows the absorption curve of methylene blue in distilled water, both before and after irradiation. A 20-cc. sample of the solution was placed in a small Petri dish (forming a layer of solution 0.8 cm. thick) and exposed to the rays. After a period of one hour, fading had become so marked that irradiation was stopped. The ultra-violet absorption curve shows that a very definite decrease in absorption had occurred in the ultra-violet region of the spectrum. The transmission at 670 millimicrons (point of maximum absorption of visible light by methylene blue (9)), as

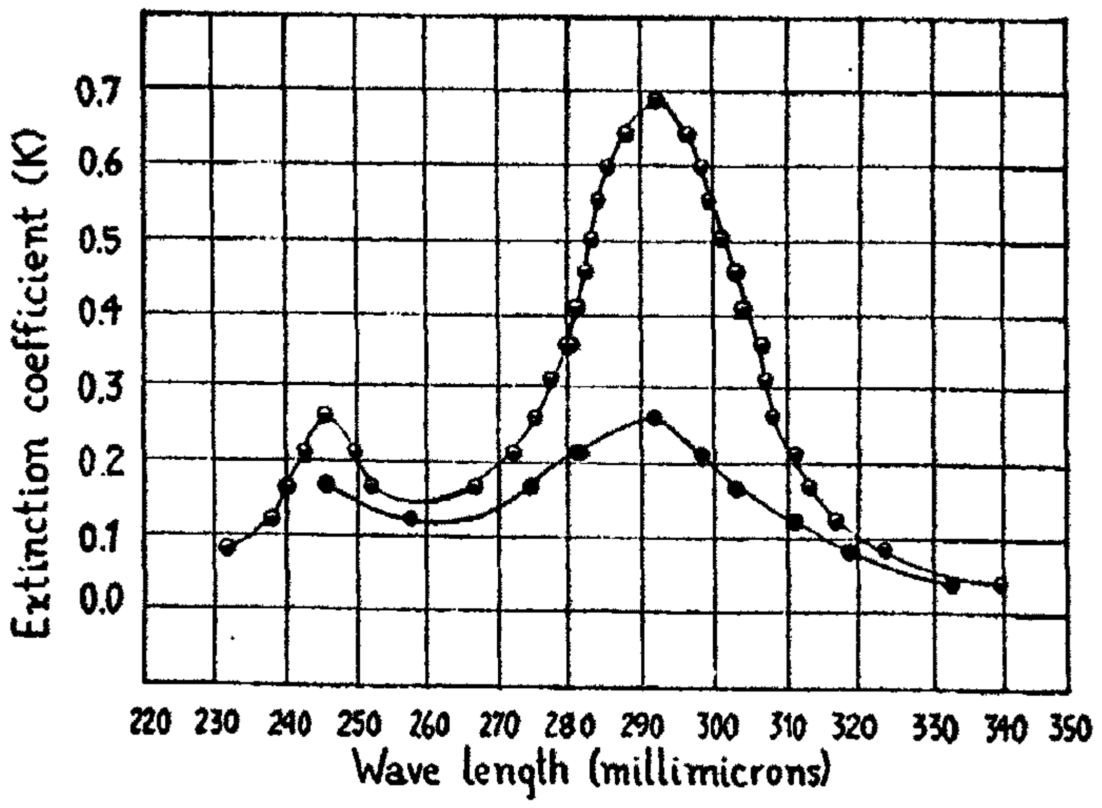

FIG. 2. ULTRA-VIOLET ABSORPTION SPECTRA OF METHYLENE BLUE IN HYDROCHLORIC ACID-POTASSIUM CHLORIDE SOLUTION (pH 2.19)

◒ before irradiation; ● after irradiation through quartz

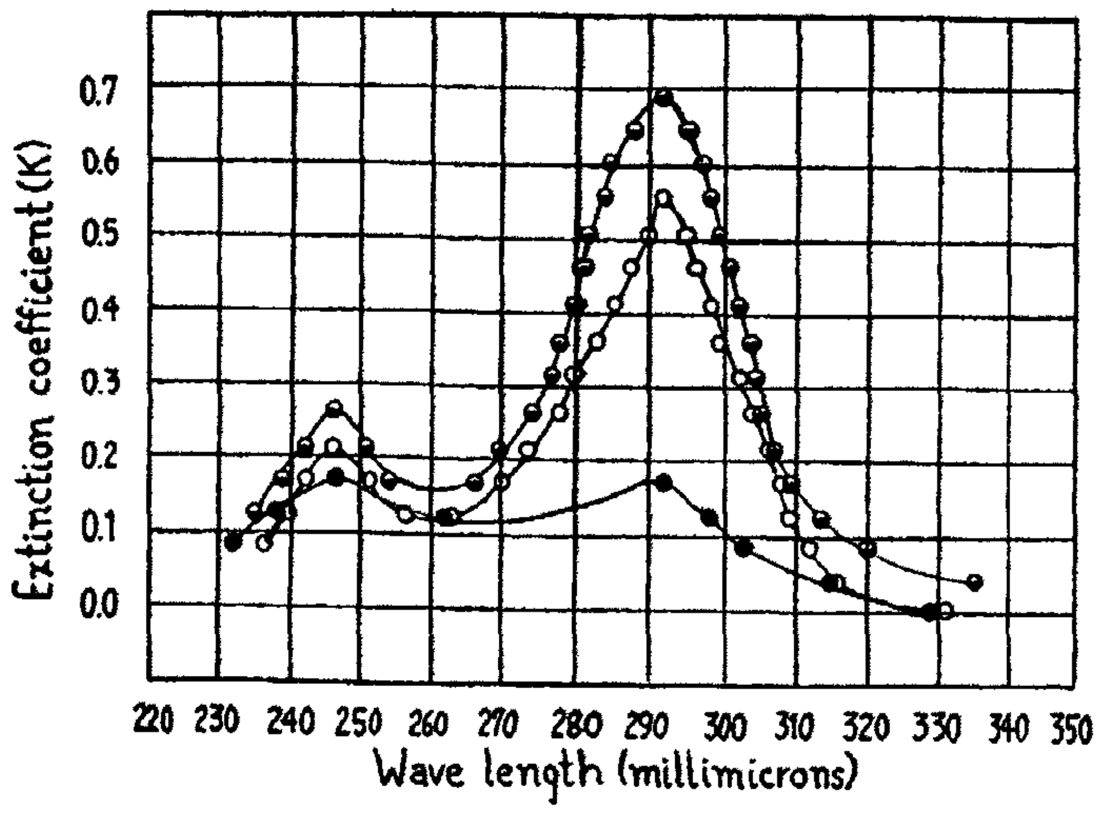

FIG. 3. ULTRA-VIOLET ABSORPTION SPECTRA OF METHYLENE BLUE IN PHOSPHATE SOLUTIONS (pH 6.69)

◒ before irradiation; ● after irradiation through quartz filter; ○ after irradiation through Blue-purple Corex A filter.

determined by a Bausch and Lomb spectrophotometer, increased from 0.0008 to 0.478 as a result of the irradiation.

In order to be sure that the observed fading was caused by the ultra-violet rays and not by the heat produced by the lamp, two experiments were performed. Some of the same solution used above was irradiated under conditions identical with those described, except that it was protected by a thin sheet of ordinary window glass. No change in either visible or ultra-violet regions of the spectrum occurred. In addition, some of the same solution was boiled for several minutes, the beaker being covered with a watch glass to prevent evaporation. In this case, also, the methylene blue spectrum was not altered.

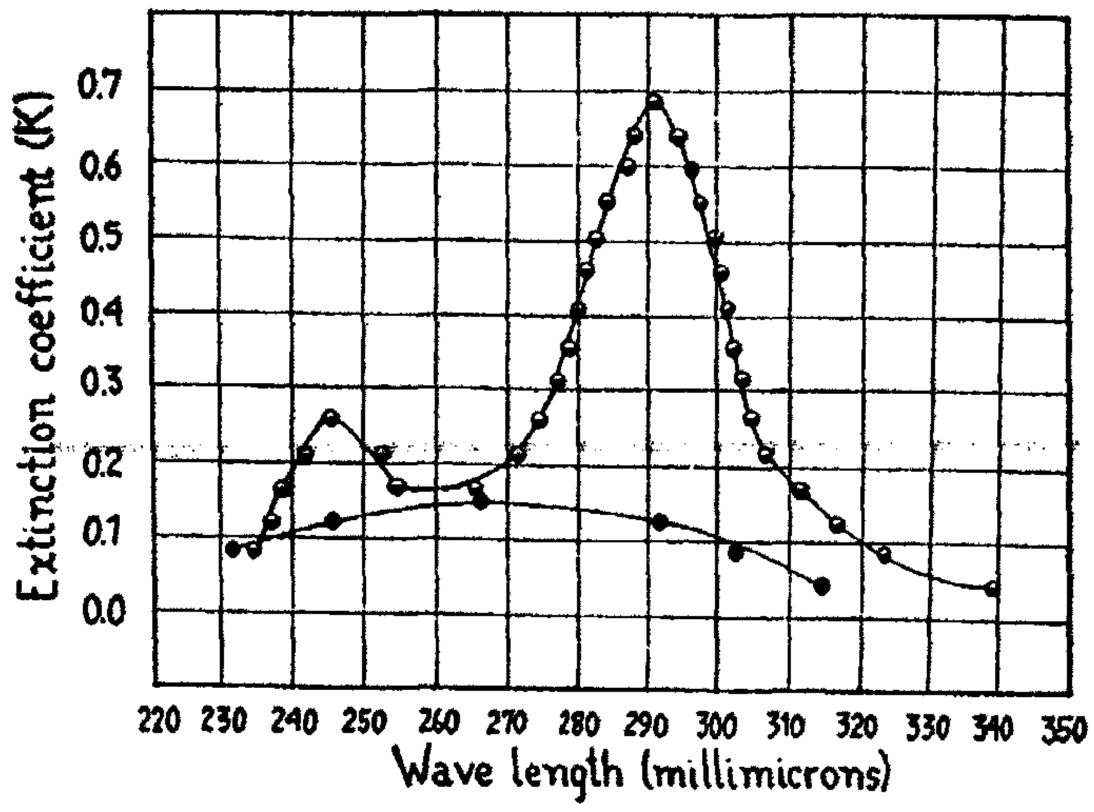

FIG. 4. ULTRA-VIOLET ABSORPTION SPECTRA OF METHYLENE BLUE IN SODIUM BORATE SOLUTION (pH 9.08)

⊖ before irradiation; ● after irradiation through quartz filter

TABLE 1

SOLVENT	FILTER	pH		$J:J'$ (670 MILLIMICRONS)	
		Before irradiation	After irradiation	Before irradiation	After irradiation
HCl–KCl buffer	Quartz	2.19	2.18	0.0007	0.125
Sodium borate buffer	Quartz	9.08	9.07	0.0008	0.699
Phosphate buffer	Quartz	6.69	6.68	0.0008	0.660
Phosphate buffer	Blue-purple Corex A	6.69	6.70	0.0008	0.005

The work of Stenström and Lohmann (10) has brought out the fact that pH apparently has little or no effect on the visible absorption spectrum of methylene blue solutions before exposure to Roentgen rays, but that during exposure greatest fading takes place in solutions of highest pH. Our experiments have shown this to be true also in the case of ultra-violet irradiation. The effect of pH is illustrated by figures 2, 3, and 4 and by table 1. The pH of the solutions was measured potentiometrically.

In an attempt to determine which wave lengths were most effective, several filters—including window glass, Vita glass, Clear Corex D, Blue-purple Corex A, and quartz—were used. In the case of all the filters except quartz, the following procedure was adopted: 20c c. of the methylene blue solution was placed in a small Petri dish, after which the dish was covered with the filter. Irradiation was carried out as described above. In order to eliminate any possible effects due to ozone formation, irradiations in which the quartz filter was used were carried out by placing the solution in a small, completely closed quartz vessel. Ultra-violet transmission curves of the filters were determined by means of a quartz spectrograph in combination with a microphotometer. The curves for the particular samples of Blue-purple Corex A and quartz used are given in figure 5. The transmission curve for the quartz was taken through the quartz vessel mentioned above and represents, therefore, the transmission of a filter of twice the thickness actually used. Figure 4 and table 1 show that the decrease in absorption produced when the Blue-purple Corex A filter was used was slight as compared with that produced with the quartz filter. Since the transmissions of the other filters were less than that of the Blue-purple Corex A glass, their transmission curves are not included here. It appears that the wave lengths most active in decreasing the absorption bands of methylene blue are shorter than 270 millimicrons. For this

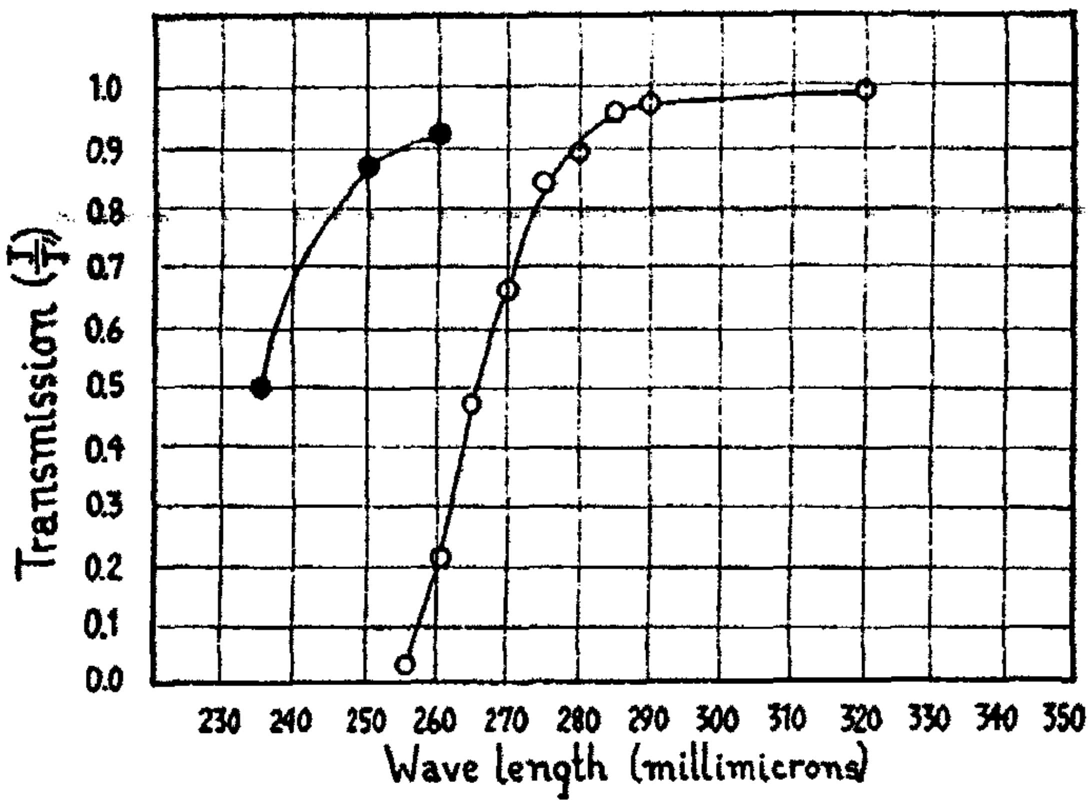

FIG. 5. ULTRA-VIOLET TRANSMISSION CURVES FOR FILTERS
● quartz; ○ Blue-purple Corex A

reason we do not believe that the change in aqueous solutions of methylene blue produced by ultra-violet rays can be used for the purpose of measuring the radiation intensity between 290 and 310 millimicrons (the "physiologically active" region of the spectrum).

SUMMARY

1. The method of using the Judd Lewis sector photometer in combination with the quartz spectrograph is briefly described.

2. The ultra-violet spectrum of methylene blue is included. Maximum absorption occurs at 292 millimicrons and at 246 millimicrons.

3. Exposure of methylene blue solutions to ultra-violet rays causes a decrease in the absorption bands in both visible and ultra-violet regions of the spectrum.

4. pH has no effect on the ultra-violet spectrum of methylene blue solutions, but irradiation with ultra-violet light causes greatest change in solutions which have highest pH.

5. The wave lengths most active in decreasing the absorption bands of methylene blue solutions are shorter than 270 millimicrons.

The authors wish to express their gratitude to Dr. W. K. Stenström who suggested the problem and whose coöperation has made this investigation possible.

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AN APPROACH TO AN EXPLANATION OF THE SURFACE WORK FUNCTIONS OF PURE METALS

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Up to six or seven years ago the developments in the field of metal surface work functions had resulted in the recognition of the following principles (2, 4, 5, 8, 9):

1. Each metal has an intrinsic potential that is characteristic of the pure metal. (These characteristic potentials are the origins of the volta effect, the photoelectric effect, thermionic emission, and electromotive force.)

2. A characteristic potential can be represented diagrammatically as a surface barrier, or a condenser on the surface of the metal.

3. Part of each barrier is the work performed by an emitted electron against the attraction of the electric image.

4. Emitted electrons are subject to the image forces only when they are outside of a distance which is characteristic of the metal.

These are the older principles that are very useful at the present time.

In the last seven years there has been developed a concept of metals which is based on the behavior of the electrons in metals according to the Pauli exclusion principle, with the valence electrons exhibiting the Fermi-Dirac distribution of velocities. As a result of the great and increasing usefulness of this new theory, several additional principles concerning electron emission must be recognized (6, 7, 10).

1. If there are a number of free electrons comparable to the number of atoms in a metal, then the electrons will obey the Fermi statistics and behave as a degenerate gas. (All of the distinctly metallic substances fall in this category.)

2. The electrons on the interior of metals are credited with possessing considerable kinetic energy even at absolute zero. (The energies are as great as from 5 volts to 15 volts.)

3. The total surface barrier must be four or five times the net or external surface work function. The net surface work function is just the difference between the total surface work function, W_a, and the maximum kinetic energy of the electrons, which is equal to U_0 at 0°K.

In its gross outline the problem which the author is attacking is the explanation of the existence of the total surface work function, W_a, which serves as a barrier to the escape of the electrons of a metal. Using the above principles and the results of the work of Bartlett and Waterman, a simple analysis shows that the total barrier of pure metals is made up of three parts (figure 1): (1) the space charge potential energy, (2) the image potential energy, and (3) the potential energy due to the different initial and final electrostatic environments.

The first of these divisions has been treated by Bartlett and Waterman (1, 13). The results of their calculations show that "space charge" effects will account for the reduction of the kinetic energy of the electrons from their enormous Fermi energies to their classical $(3/2)kT$ energy. Or, giving a probable broad meaning to these results, a "space charge" barrier surrounds a metal surface to the extent that this part of the barrier contributes nothing to the net surface work function but merely balances the 0°K. kinetic energy of the electrons, so that without the existence of the other two divisions of the barrier it would be possible to draw electrons out of metals using only slight external fields under any condition of temperature or radiation.

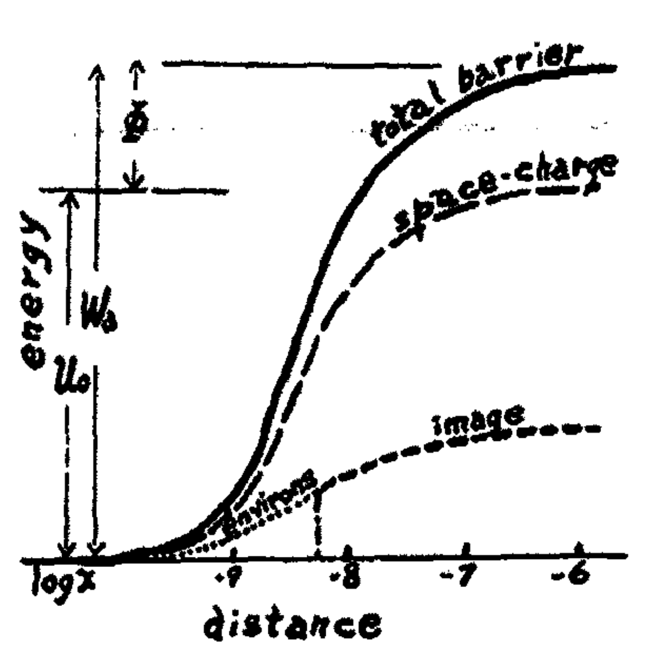

FIG. 1

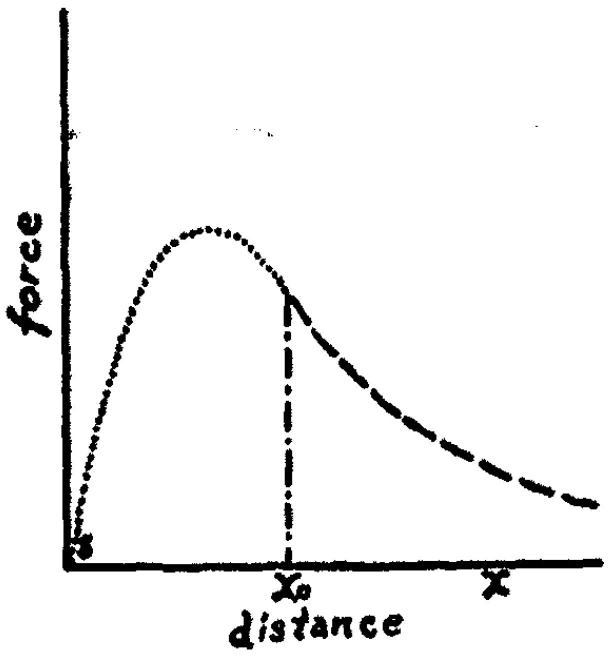

FIG. 2

The second of these divisions is well understood from the standpoint of classical electrostatics. Its nature is such that it must be included in the net work function part of the total barrier. The problem involved in understanding the image forces is only the determination of how close to the metal surface they are effective. It has been popular in the past to consider this problem along with those connected with the third division of the barrier, and this treatment has been found quite effective by the author.

The above discussion of the first two divisions of the barrier concentrates the burden of the explanation of metal surface work functions on to the solution of the problem concerning the third division, the work done by the electrons in emerging far enough from their local electrostatic environment so that the image furnishes the environment. Consequently the main discussion of this paper suggests a hypothesis to serve as a basis for this division of the potential barrier.

The most acceptable classical approach to an understanding of metal surface work functions is the Langmuir modification of the Schottky principle (5). According to this theory the change in the force acting on an electron is proportional to the displacement of the electron from its initial equilibrium position. At a distance x_0 (figure 2) the parabolic force-distance curve merges into the hyperbolic force–distance curve of the image forces. The surface work function is inversely proportional to this distance x_0. This modification of Langmuir's is arbitrary because the postulations of other shapes for the curve inside distance x_0 will account for some of the phenomena of surfaces to the same extent. However the general shape of this curve is admitted to be quite logical in terms of our present knowledge of cohesive and repulsive forces. It might be pointed out also that the equation which the author will use later could serve as a first approximation of some more complicated functional relationship.

All of the theories have stalled at this point. Distance x_0 was identified with the distance between the ions in the crystal, which varied considerably with the temperature. Φ is inversely proportional to x_0; consequently Φ should vary considerably with the change in temperature. This is not so. The photoelectric threshold of a metal not only changes very slightly with change in temperature but its change is quantitatively predicted by Fowler's theory, which is based on the change in the kinetic energy of the electrons in the metal at elevated temperatures in accordance with the Sommerfeld theory of metals. Necessarily the correct hypothesis to explain the net work function must account for its being independent of the temperature, aside from its change predicted by the Maxwell-distribution-law tail to the Fermi-Dirac distribution of the electron velocities in metals.

The following principles are used by the author as guides for his approach to an explanation of the net work function: (1) The electrons should be considered as more or less in condition of equilibrium in a field of force characteristic of the crystal. (2) The Langmuir modification of the Schottky principle should be useful providing x_0 is identified with some quantity other than the distance between the atoms. (3) The net work functions should be independent of the temperature. (4) The hypothesis should allow the calculation of the Φ's for the various metals.

A study of these principles leads to this hypothesis. *The slope of the force–distance parabola is identified with the lattice energy of the metal crystal and can be assumed to be equal to a constant times the electrostatic potential energy of the crystal.*

There are two sources from which one can obtain the values of the electrostatic potential energy constants for metals. One source requires the complete knowledge of the crystal structure of the metals and involves lengthy calculations. The other source is readily available and the calculations are very simple, although indirect. These calculations involve starting from the compressibilities of the metals, using the principles developed by J. J. Thomson (12), and calculating the linear potential energy constants of the various metals.

If

$$K \text{ (the bulk modulus of compressibility)} = C\left(\frac{\Delta}{M}\right)^{4/3}$$

$$P \text{ (the potential energy constant)} = \frac{C}{4.5}\left(\frac{\Delta}{M}\right)^{1/3}$$

or

$$P = k'''' K \frac{M}{\Delta}$$

The formula for the parabola in the force-distance curve is

$$y = \frac{k'x}{x_0^3} - \frac{k''x^2}{x_0^4}$$

When $x = 0$,

$$S = \frac{dy}{dx} = k' \frac{1}{x_0^3}$$

or

$$x_0 = \frac{k'''}{S^{1/3}}$$

Since

$$S = c'P$$

and also

$$\Phi = \frac{c''}{x_0}$$

then

$$\Phi = c'''\left(\frac{KM}{\Delta}\right)^{1/3}$$

(The *k*'s and *c*'s are constants)

Using the last equation the author has calculated the values of the intrinsic potentials of a large number of metals. The value of the constant was evaluated from the experimental values of the potentials. The values of the compressibilities and densities were taken from the International Critical Tables. With one exception the largest of the accepted values for compressibilities of metals was used. The calculated values are compared with the arbitrary experimental values which were used to evaluate the constant and other values which were largely taken from a collection made by Hughes and DuBridge (3) in table 1.

TABLE 1

METALS USED FOR COMPARISON	CALCULATED VALUES (J.F.C.)	ARBITRARY EXPERIMENTAL VALUES	VALUES ACCEPTED AS GOOD	HENNING CONTACT POTENTIALS	RICHARDSON PHOTO-ELECTRIC THRESHOLD	MISCELLANEOUS		
						Photo-electric*	Photo-electric*	Thermionic values†
K..........	2.06	1.99* (Iv)‡				1.99 (Iv) 2.1 (S)	1.9 (Ho) 2.2 (Ol)	
Na..........	2.11	2.1* (Ri)			2.1	2.2 (P & P)	1.8 (Mi)	
Li..........	2.07	2.2* (Mi)				2.3 (Ol)	2.3 (Mi)	
Ca..........	3.00	3.0* (Ri)			3.0	2.8 (We)	3.08 (Ha)	
Mg..........	3.11	3.2* (Ri)		2.63	3.2			
Al..........	3.58	3.57* (R)	3.57	3.06	2.8	3.57 (R)	3.4 (H & K)	
Zn..........	3.64*	3.68* (R)	3.5	3.46	3.4	3.69 (R)	3.57 (D)	
Sn..........	3.86	3.78c (H)	4.50 4.38	3.78	3.6	4.38 (G)	4.50 (G)	
Cu..........	3.88	3.85* (W & S)	4.38		4.1	3.85 (W & S)	4.1 (H & K)	4.38 (G)
Fe..........	4.18	4.2* (R)	4.72	3.86		4.2 (R)	4.72 (C) 4.1 (H & K)	
Co..........	4.20	4.25† (C)	4.25 4.12			4.0 We		4.25 (C) 4.12 (C)
Ni..........	4.22	4.12* (R)	5.01			4.12 (R) 5.01 (G)	4.1 (Ha) 4.1 (We)	
Ag..........	4 33	4.30* (S)	4.68 4.56	4.05		4.30 (S) 3.85 (R)	3.8 (Wer) 4.58 (Wi)	4.08 (G)
Pd..........	4.67	4.96*† (DB)	4.96			4.4 (Wer)	4.96 (DB)	4.99 (DB)
Au..........	4.71	4.72* (Mo)	4.72			4.72 (Mo)	4.82 (Mo)	4.42 (G)
Mo..........	5.02	4.41† (D)	4.41			4.33 (R)	3.22 (Ma)	4.41 (D) 3.48 (Ma)
Ta..........	5.00	4.07† (D)	4.07 4.05			3.92 (R)	4.05 (C)	4.07 (D) 4.31 (L)
Pt..........	5.34	5.45* (W)	6.30		4.3	4.40 (R) 4.62 (S)	6.30 (DB)	6.27 (DB)
W..........	5.67	5.45* (Hag)	4.52			4.52 (R) 4.58 (Wer) 5.4 (Hag)	4.80 (Wer) 4.50 (D & G)	4.52 (L) 4.52 (D)

* See columns 3, 7, and 8.

† See columns 3 and 9.

‡ C = Cardwell; D = Dushman; DB = DuBridge; G = Goetz; H & K = Henning and Kadesch; H = Hennings; Ha = Hammer; Hag = Hagenow; Ho = Hamleck; Iv = Ives; L = Langmuir; Mi = Millikan; Ma = Martin; Mo = Morris; Ol = Olpin; P & P = Pohl and Pringsheim; R = Roy; Ri = Richardson; S = Suhrman; We = Welch; Wi = Winch; Wer = Warner.

A careful study of the table will show any one familiar with the field that the agreement between the calculated and the experimental values is better than the experimental results demand in order to show the probable validity of the relationships. In fact the agreement between the calculated values and the experimental values obtained when the best of outgassed conditions were not present is nothing short of remarkable. The author's equation predicts that Φ is practically independent of the temperature. K/Δ shows very little variation with the variation of the temperature; the value of K/Δ is greater than one; consequently the cube root of K/Δ is practically independent of the temperature. The useful (useful when applied to pure metals) Schottky principle is maintained intact. In addition the requirement of Tamm and Schubin (11) is met. In short, the author's theory with its subordinate hypotheses seems to be a tool of considerable usefulness.

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RHYTHMIC PRECIPITATION WITH ORGANIC PRECIPITANTS[1]

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As a result of many investigations (6) since Liesegang's discovery (8) of rhythmic precipitation there is considerable belief (1, 2, 7, 9) that it is a general phenomenon and may occur under suitable conditions with any pair of substances that form a fairly insoluble precipitate.

When precipitation occurs in gels Hedges (5) distinguishes four types of structures that may appear: (a) precipitates of continuous structure very finely divided, as with silver chloride; (b) discrete structures frequently containing well-formed crystals of significant size; (c) cellular structures; and (d) periodic structures with definite bands or rings. In view of these different possibilities it seemed of interest to determine the type of structure produced in a gel by precipitates formed with certain organic compounds that are finding increasing use in analytical chemistry. Precipitates such as nickel dimethylglyoxime are very voluminous in character.

EXPERIMENTAL WORK

Materials

Gels of silicic acid or agar were used, the former being prepared from sodium silicate and the latter from an American product. Salts were of "reagent" quality and organic compounds were used as purchased.

Procedure

As preliminary experiments showed that solutions of the organic precipitants did not diffuse well into the gels, in most cases these compounds were put in the gels and the solutions of the salts on top. Agar gels were prepared by dissolving 1 g. of agar in about 80 ml. of hot water, adding 10–20 ml. of a solution of the organic compound, diluting the mixture to 100 g., and filtering through glass wool into test tubes which had been previously coated with gelatin (3) to assist the gel in sticking to the tube. In preparing gels of silicic acid, sodium silicate was dissolved in water to give a solution of approximately 1.06 specific gravity. The alkalinity of the

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[1] Taken from Part I of a dissertation presented by J. E. Heck to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

TABLE 1

Data for silica gels

GEL						DIFFUSING SOLUTION		STRUCTURE
Precipitant			Sodium silicate					
Material	Volume	Concentration	Volume	Specific gravity	Reaction	Salt	Concentration	
	ml.		*ml.*					
1[*]	13.0	Satd. soln. 0.96 *N* AcOH	8.0	1.06	b[†]	$CuSO_4$	1.0 *N*	GB
1	14.0	"	8.0	1.06	a	"	1.0 *N*	FB (364)
1	13.0	"	8.0	1.06	b	$Cu(NH_3)_4SO_4$	1.0 *N*	FB
1	14.5	"	8.0	1.06	a	"	1.0 *N*	FB
2, 4	10.6	"	10.0	1.08	a	$CuSO_4$	1.0 *N*	PB, PB
2, 4	14.8	"	8.0	1.06	a	$FeCl_3$	1.0 *N*	PB, NP
2	14.8	"	8.0	1.06	a	$CuSO_4$—20 ml. AcONa—1 g.	1.0 *N*	PB
3	10.0	"	10.0	1.08	a	$Ni(NO_3)_2$	1.0 *N*	NP
3	13.6	"	8.0	1.06	b	$CuSO_4$	1.0 *N*	PB
3	13.6	"	8.0	1.06	b	KOH—2 drops $Cu(NH_3)_4SO_4$	10 per cent 1.0 *N*	DS
3	10.0	"	10.0	1.08	a	"	1.0 *N*	DS
3	13.6	"	8.0	1.06	b	KOH—2 drops NH_4Cl—3 ml. $Ni(NH_3)_4(NO_3)_2$	10 per cent 10 per cent 1.0 *N*	DS
3	10.0	"	10.0	1.08	a	KOH—2 drops $Ni(NH_3)_4(NO_3)_2$	10 per cent 1.0 *N*	NP
4, 8	10.6	"	10.0	1.08	a	$CoCl_2$	1.0 *N*	NP, CS
4, 8	14.8	"	8.0	1.06	a	"	1.0 *N*	NP, FB
5	10.3	2.5 g. per liter 0.97 *N* AcOH	10.0	1.08	a	$ZnSO_4$	1.0 *N*	PB
5	10.3	"	10.0	1.08	a	$CdSO_4$	Saturated	CS
5	11.3	"	10.0	1.08	a	"	1.0 *N*	PB
5	11.3	"	10.0	1.08	a	$CuSO_4$	1.0 *N*	PB
5	12.3	"	10.0	1.08	a	$Al_2(SO_4)_3$	1.0 *N*	PB
6	13.0	6.0 g. per liter 0.96 *N* AcOH	10.0	1.08	a	KNO_3	1.0 *N*	F (344)
6	16.0	3.0 g. per liter 0.96 *N* AcOH	8.0	1.06	a	"	1.0 *N*	F (347)
6	11.0	"	10.0	1.08	a	"	1.0 *N*	F (351)
7	9.6	Satd. soln. 0.96 *N* AcOH	10.0	1.08	n	$CoCl_2$	1.0 *N*	PB

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[*] In the column headed "Material" the numbers refer to the following precipitants: 1, α-benzoin oxime; 2, cupferron; 3, dicyandiamidine sulfate; 4, dinitrosoresorcinol; 5, 8-hydroxyquinoline; 6, nitron; 7, nitroso-β-naphthol; and 8, phenylthiohydantoic acid.

[†] The reaction of the gels is indicated as follows: a, acidic, b, basic, and n, neutral.

TABLE 1—*Concluded*

GEL						DIFFUSING SOLUTION		STRUCTURE
Precipitant			Sodium silicate					
Material	Volume	Concentration	Volume	Specific gravity	Reaction	Salt	Concentration	
	ml.		*ml.*					
7	10.6	Satd. soln. 0.96 *N* AcOH	10.0	1.08	a	$CoCl_2$	Saturated	CS
7	9.6	"	10.0	1.08	n	H_2O_2—15 ml. $COCl_2$—50 ml.	3 per cent 1.0 *N*	FB
7	10.6	"	10.0	1.08	a	"	3 per cent Saturated	CS
7	10.6	"	10.0	1.08	a	$FeCl_3$	1.0 *N*	CS
8	10.6	"	10.0	1.08	a	$CdSO_4$	1.0 *N*	PB
8	10.6	"	10.0	1.08	a	$HgCl_2$	Saturated	GB (335)
8	13.8	"	8.0	1.06	n	"	"	FB
8	13.8	"	8.0	1.06	n	$CoCl_2$	1.0 *N*	FB
8	13.0	"	8.0	1.06	b	"	Saturated	FB
8	14.0	"	8.0	1.06	a	"	"	FB
8	13.8	"	8.0	1.06	n	$CdSO_4$	1.0 *N*	FB
8	14.8	"	8.0	1.06	a	$Pb(NO_3)_2$	1.0 *N*	CS
8	13.0	"	8.0	1.06	b	"	Saturated	PB
8	14.0	"	8.0	1.06	a	"	"	PB
8	13.0	"	8.0	1.06	b	$CuSO_4$	"	GB (353)
8	15.0	"	8.0	1.06	a	"	1.0 *N*	PB

solution was determined by titration with an acid, using phenolphthalein as the indicator. Based on this, acetic acid containing the precipitant was added to give an acidic, neutral, or basic gel, as indicated in table 1. After the gels set (within an hour) normal or saturated solutions of the different salts were placed over them in the tubes. For each mixture three tubes were prepared, one of which was kept in the dark in order to determine the effect of light on the formation of the precipitates.

Data

Tables 1 and 2 give the composition of the different gels and the diffusing solutions, together with an indication of the types of precipitation observed. Figures 1 to 4 show the characteristics of some of the more striking structures. The types formed are indicated in the tables as follows: GB, good bands; FB, fair bands; PB, poor bands; CS, continuous structure; DS, discrete structure; F, fern-like structure; and NP, no precipitate.

For the tubes shown in figure 1 certain variations were made so that they are considered separately. The gel in tube 14 was basic, being made from sodium silicate, hydrochloric acid, and alcoholic dimethylglyoxime. The

TABLE 2

Data for agar gels

PRECIPITANT IN GEL		DIFFUSING SOLUTION		STRUCTURE
Material	Concentration	Concentration	Salt	
α-Benzoin oxime	10.0 g. per liter 95 per cent ethanol	1.0 *N*	$CuSO_4$	FB
"	"	1.0 *N*	$Cu(NH_3)_4SO_4$	FB
Cupferron	Satd. aq. soln.	1.0 *N*	$CuSO_4$	PB
"	"	1.0 *N*	$CuSO_4$ in 0.05 *N* HCl	PB
"	"	1.0 *N*	$FeCl_3$	NP
"	"	1.0 *N*	$AgNO_3$	CS
Dicyandiamidine sulfate	40 g. per liter 50 per cent ethanol	1.0 *N*	$Ni(NO_3)_2$	NP
"	"	1.0 *N*	$Ni(NH_3)_4(NO_3)_2$	DS
"	"	1.0 *N*	$CuSO_4$	NP
"	"	1.0 *N*	$Cu(NH_3)_4SO_4$	NP
Dimethylglyoxime	10 g. per liter 95 per cent ethanol	1.0 *N*	$Ni(NO_3)_2$	DS
Dinitrosoresorcinol	Satd. aq. soln.	1.0 *N*	$CoCl_2$	NP
"	"	1.0 *N*	$CuSO_4$	NP
"	"	1.0 *N*	$FeCl_3$	NP
8-Hydroxyquinoline	10 g. per liter 95 per cent ethanol	1.0 *N*	$MgSO_4$	NP
"	"	5 per cent 1.0 *N*	NH_4OH—5 ml. $MgSO_4$—95 ml. AcONa—2 g.	CS
"	"	1.0 *N*	$ZnSO_4$	GB
"	"	1.0 *N*	$Al_2(SO_4)_3$	FB
"	"	1.0 *N*	$AlCl_3$	PB
"	"	1.0 *N*	$CdSO_4$	GB (121)
"	"	10 per cent 1.0 *N*	AcOH—2 ml. $CdSO_4$—98 ml. AcONa—2 g.	GB (99, 125)
"	"	1.0 *N*	$CuSO_4$	GB (137)
"	"	10 per cent 1.0 *N*	AcOH—2 ml. $CuSO_4$—98 ml. AcONa—2 g.	PB
"	"	1.0 *N*	$CdSO_4$—100 ml. AcONa—2 g.	GB (123)
"	"	1.0 *N*	$ZnSO_4$—100 ml. AcONa—2 g.	GB (133)
Nitron	5 g. per liter 95 per cent ethanol	1.0 *N*	KNO_3	F
"	"	1.0 *N*	KNO_3 in 0.13 *N* AcOH	DS

TABLE 2—*Concluded*

PRECIPITANT IN GEL		DIFFUSING SOLUTION		STRUCTURE
Material	Concentration	Concentration	Salt	
Nitroso-β-naphthol*	4 g. per liter 60 per cent ethanol	1.0 *N*	$CoCl_2$	CS
"	"	1.0 *N*	$Ni(NO_3)_2$	PB
Phenylthiohydantoic acid	Satd. aq. soln.	1.0 *N*	$CoCl_2$	FB (169)
"	"	1.0 *N*	$Ni(NO_3)_2$	DS (172)
"	"	1.0 *N*	$CuSO_4$	CS
"	"	1.0 *N*	$Pb(NO_3)_2$	CS

* This gel consisted of 1 g. of agar dissolved in 20 g. of the solution of the precipitant and 80 g. of water. All others contained the same amount of agar, but 10 g. of the solution of precipitant and 90 g. of water.

diffusing solution was nickel nitrate. Tube 18 was the same except for being neutral. Tube 30 was similar to tube 14 except that the diffusing solution and precipitant were interchanged in position. Tube 34 contained a gel made slightly basic from sodium silicate, acetic acid, and potassium nitrate. Tube 41 was the same except for being acidic. The diffusing solution in both cases was nitron in 1.0 *N* acetic acid. Tube 55 is the familiar cupric chromate in agar.

DISCUSSION OF RESULTS

It is evident from the data presented that the precipitates formed in gels with organic precipitants show several types of structure. In many cases for which photographs are not shown these were not as well defined as the ones selected but they were distinctly evident.

Under the conditions studied salts of α-benzoin oxime, 8-hydroxyquinoline, and phenylthiohydantoic acid gave the best bands. Some of these are shown in tubes 99, 125, 137, 169, 335, 353 and 364. Cupferron and nitroso-β-naphthol gave noticeable bands in a few cases but they were so close together and the gels so dark that clear photographs were unobtainable. These two compounds seemed to decompose readily giving dark gels. In some cases no precipitate was obtained with dicyandiamidine sulfate or dinitrosoresorcinol. If one was formed it generally assumed a discrete structure (4), although in a few cases there was a slight indication of bands. The nickel salt of phenylthiohydantoic acid shown in tube 172 illustrates a discrete structure. Tubes 14, 18, and 30 show that bands of nickel dimethylglyoxime form with the organic compound either in the gel or above it. All other organic precipitants failed to give this type of structure if in the solution diffusing into the gel.

Nitron nitrate was the only precipitate not giving noticeable bands in at least one type of gel. Tubes 344, 347, and 351 show the fern-like

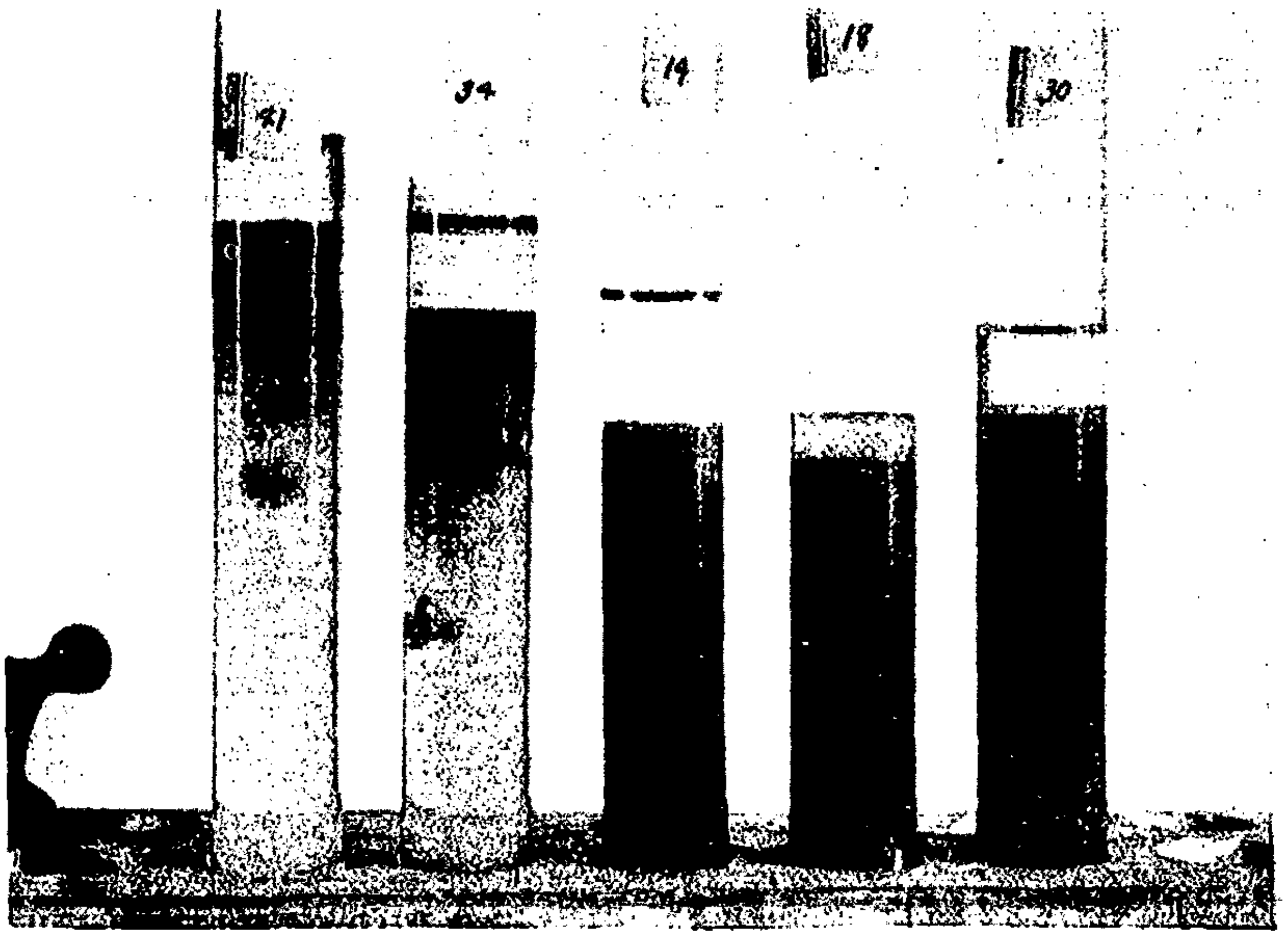

FIG. 1. RHYTHMIC PRECIPITATION WITH NITRON NITRATE AND NICKEL DIMETHYLGLYOXIME

Tubes 41 and 34, nitron nitrate; tubes 14, 18, and 30, nickel dimethylglyoxime

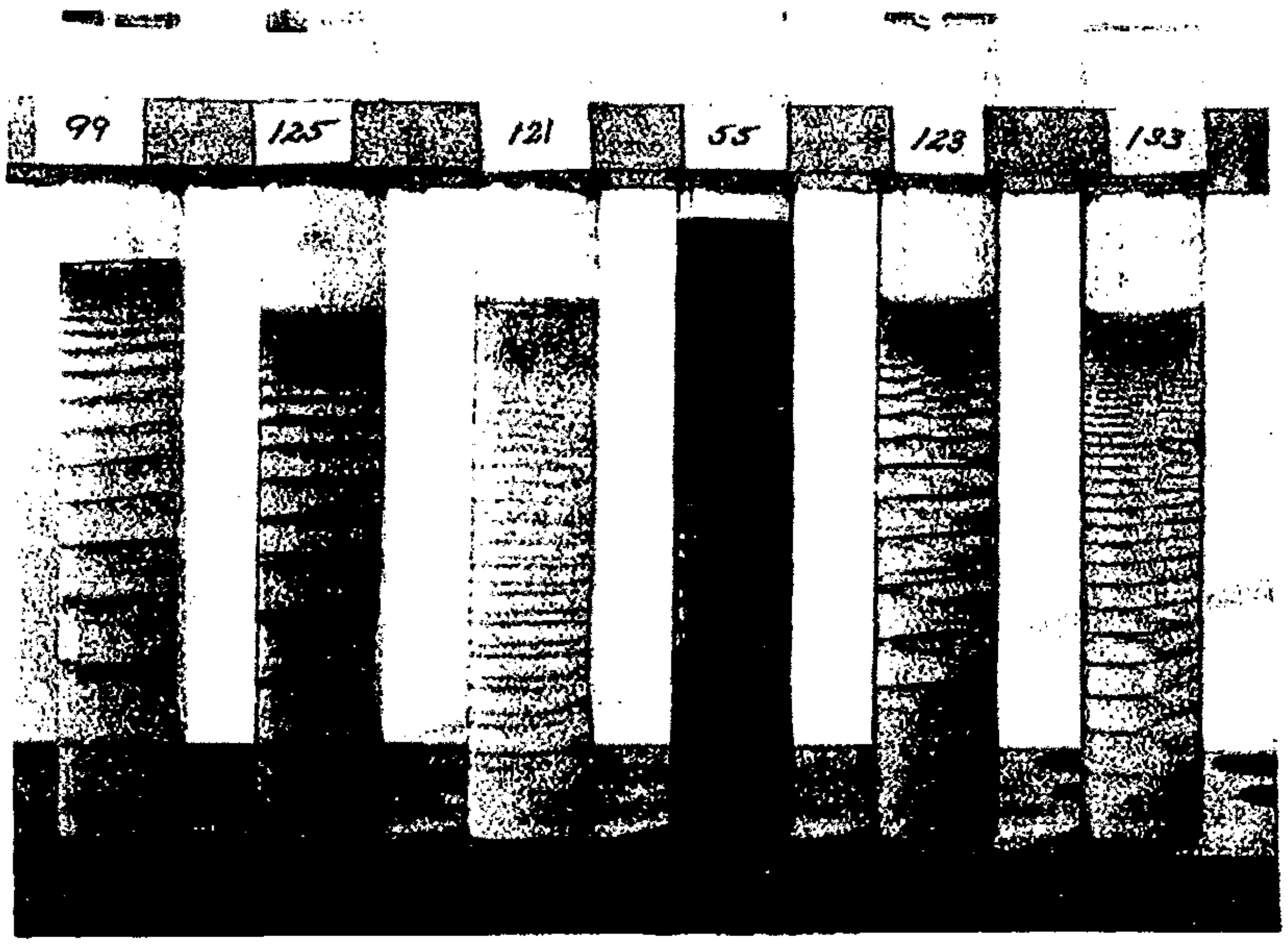

FIG. 2. RHYTHMIC PRECIPITATION WITH 8-HYDROXYQUINOLINE

Tube 99, cadmium salt of 8-hydroxyquinoline (kept in the dark); tube 125, cadmium salt of 8-hydroxyquinoline (kept in the light); tube 121, cadmium salt of 8-hydroxyquinoline; tube 55, cupric chromate; tube 123, cadmium salt of 8-hydroxyquinoline; tube 133, zinc salt of 8-hydroxyquinoline.

structures obtained. The more basic the gel the larger the crystals grew. Tubes 34 and 41 also show this precipitate, but in this case the solution of nitrate was added to the gel. Here the resulting structure is more moss-like in appearance and extends only a short distance below the surface of the gel. A well-formed, isolated crystal is shown in tube 41.

Tubes 123 and 133, containing respectively the cadmium and zinc salts of 8-hydroxyquinoline, show a helicoid variation from bands not frequently encountered. Also twin bands are shown in tube 121.

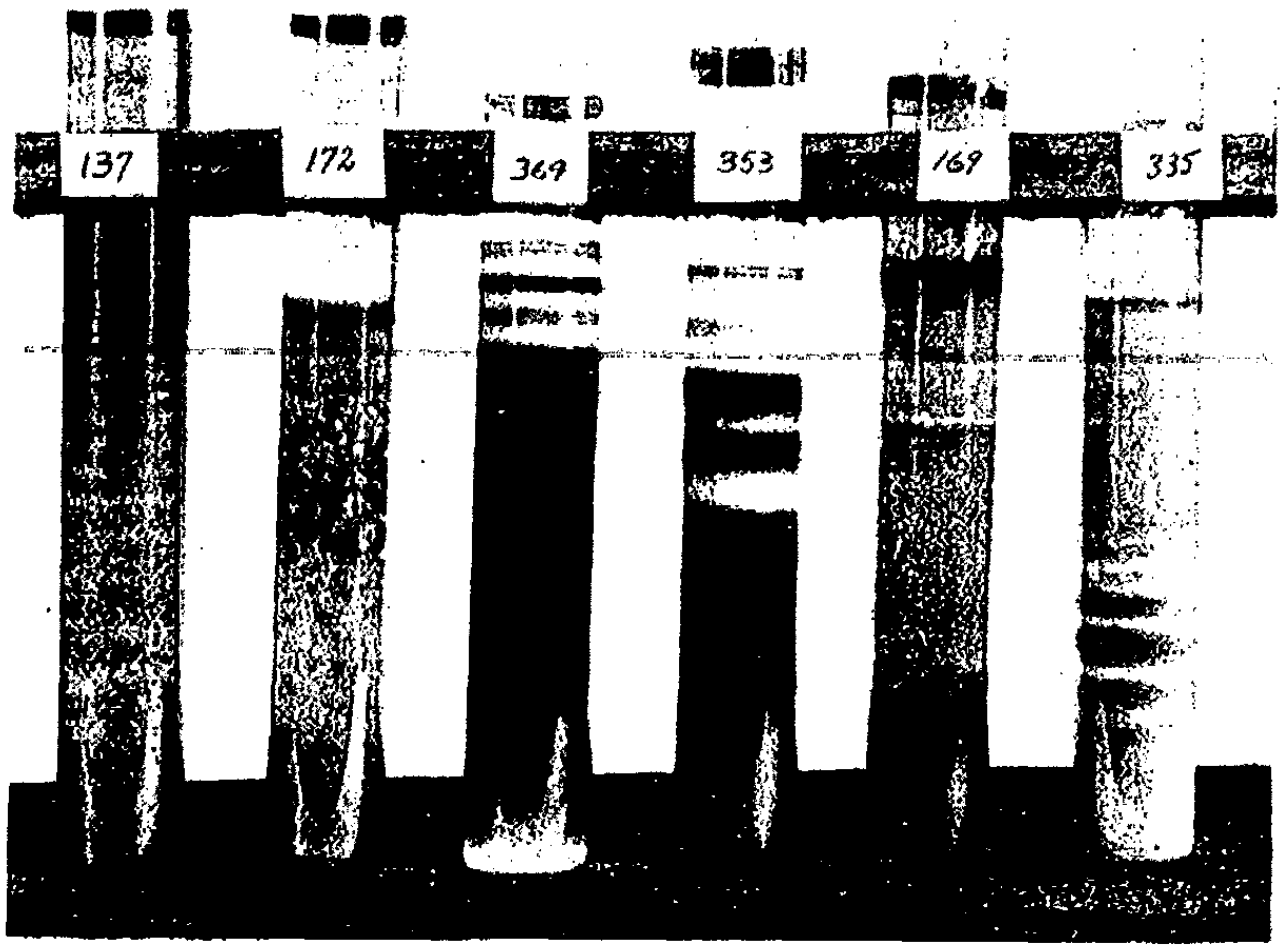

Fig. 3. Rhythmic Precipitation with Various Organic Precipitants

Tube 137, cupric salt of 8-hydroxyquinoline; tube 172, nickel salt of phenylthiohydantoic acid; tube 364, cupric salt of α-benzoin oxime; tube 353, cupric salt of phenylthiohydantoic acid; tube 169, cobalt salt of phenylthiohydantoic acid; tube 335, mercuric salt of phenylthiohydantoic acid.

Although the silica gels were made from both a commercial liquid water glass and from solid sodium silicate, no particular difference was evident in the structures obtained. With the exception of 8-hydroxyquinoline, the precipitants producing banded precipitates did so equally well in the different gels. This one reagent gave the best bands in agar. Keeping one set of tubes in the dark did not yield structures differing appreciably from those formed in the light. For the latter an occasional precipitate indicated some sensitivity to light resulting in some darkening.

No explanation is offered for the fact that different types of structures were obtained for different combinations, nor for the variation in quality of bands. Duplicate tubes did not always show equally good results.

Altogether several hundred tubes were prepared with considerable variation in conditions, such as acidity, concentration, and kind of gel, and the data presented were selected as being representative of all that available.

Fig. 4. Precipitation with Nitron Nitrate

SUMMARY

As a result of a study of the formation in gels of precipitates with certain organic compounds, the following conclusions were reached:

1. Different types of structures were obtained in different cases.
2. Of the combinations forming bands not all were equally good. Nitron nitrate showed no noticeable bands.
3. The best results were obtained with the precipitant in the gel.
4. Bands were obtained in both agar and silicic acid gels. 8-Hydroxyquinoline gave better bands in agar.
5. Several good spirals and twin bands were obtained.
6. Light produced no apparent effect on the type of structure obtained.

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A QUANTITATIVE SPECTRO-PHOTOELECTRIC ANALYTICAL METHOD APPLIED TO SOLUTIONS OF CHLOROPHYLLS *a* AND *b*

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The accurate photoelectric method for comparison of low light intensities, described by Zscheile, Hogness, and Young (3), has been used to obtain quantitative analytical data for chlorophyll components *a* and *b* and their mixtures in 90 per cent acetone solution (10 per cent water). This solvent was chosen because extracts of the green and yellow plant pigments from fresh leaf material are easily obtained in aqueous acetone solution.

The absorption spectra of components *a* and *b* in ether solution (figure 1) were measured from λ 3950–7800 A. U. with an accuracy of 2.0 per cent (1.0 per cent at the absorption maxima).[2] Comparison of figure 1 with the first graphs of figures 3 and 4 shows that the absorption spectra of *a* and *b* in 90 per cent acetone solution are very similar to those in ether solution. The maxima of the principal bands are shifted 25 A. U. toward the red when the solvent is changed from ether to 90 per cent acetone. These data were useful in the choice of wave lengths for analysis of mixtures.

According to Lambert's law, the amount of radiant energy absorbed in a homogeneous medium is expressed by the equation:

$$I_x = I_0 \times 10^{-\beta x}$$

or

$$\log \frac{I_0}{I_x} = \beta x$$

In this equation,

I_0 = intensity of light transmitted by solvent-filled cell.
I_x = intensity of light transmitted by solution-filled cell.
x = thickness of absorption cell in centimeters (4.25 cm.).
β = specific light absorption coefficient.

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[1] National Research Fellow in the Biological Sciences.

[2] Details of the absorption spectra measurements and of the preparation of components *a* and *b* are presented in reference 2.

When β is proportional to the concentration, c (in grams per liter), Beer's law is obeyed and

$$\beta = \alpha c$$

Then,

$$\log \frac{I_0}{I_x} = \alpha c x$$

or

$$\alpha = \frac{\log \frac{I_0}{I_x}}{c x}$$

The logarithm is to the base 10. The absorption coefficient, α, is expressed in liters per gram centimeter.

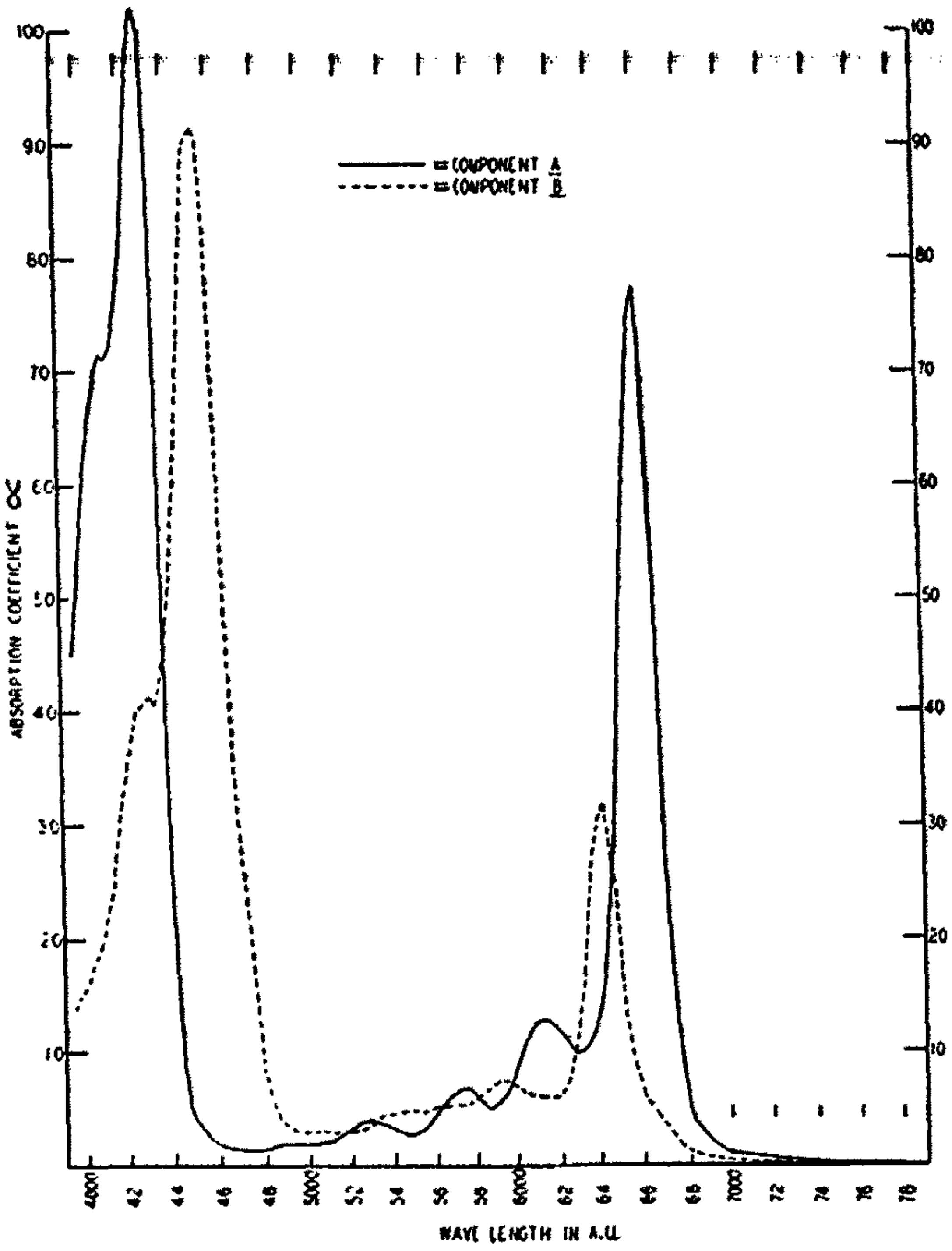

FIG. 1. ABSORPTION SPECTRA OF CHLOROPHYLLS *a* AND *b* IN ETHER

ACCURATE ANALYSIS OF MIXTURES OF CHLOROPHYLLS *a* AND *b*

For spectro-photoelectric analysis of mixtures of chlorophylls *a* and *b* for which neither the total chlorophyll ($a + b$) concentration nor the ratio of *a* to *b* is known, it is necessary to know the values of α at two carefully chosen wave lengths. The wave length 4400 A. U. was chosen for total chlorophyll ($a + b$) determination because the light absorption coefficient is the same for both components at this wave length (see figure 3, first graph). For determination of the ratio, *a* to *b*, two wave lengths, 4100 and 4270 A. U., were selected in the spectral region where there is a great difference in the absorption coefficients of *a* and *b*. Determinations at these two wave lengths serve as checks upon each other. These wave lengths were chosen in the violet rather than in the red region (where the absorption difference is also great), because narrower spectral regions may be isolated by the monochromator at the shorter wave lengths. The width of the spectral regions used in these measurements was 7 A. U. or less.

Chlorophylls *a* and *b* were isolated in the pure state and weighed samples of the best preparations of these were dissolved in ether to form solutions of known concentrations. Aliquots of these solutions were measured volumetrically and mixtures of the components *a* and *b* were made, having the following compositions: 5, 10, 25, 50, 75, 90, and 95 per cent *a*. The ether was evaporated in a stream of dry nitrogen and the chlorophyll was dissolved in 90 per cent acetone, measured volumetrically. Such dilutions were made that the values of $\frac{I_0}{I_x}$ were approximately 2.00 at the wave lengths employed. The accuracy of the concentration values was 1.0 per cent, or better.

Before each measurement of light intensity, the electrometer vane (3) was returned to the zero position by a closing of the shutter between the photocell and the second slit of the monochromator. I_0 was measured before and after I_x and the measurements were averaged for the final value of I_0. The average of two determinations of $\log \frac{I_0}{I_x}$ was used as a final value. Measurements of I_0 and $\log \frac{I_0}{I_x}$ have precisions of better than 0.5 per cent and 1.0 per cent, respectively.

When very accurate data are desired, the absorption cells should be tested at least once daily in regard to their relative light transmissibilities at the wave lengths employed. Both cells are cleaned, filled with solvent, and the intensities of light transmitted by them are measured. Those used in these experiments differ by 1.5 to 4.0 per cent. This difference varies according to the wave length and the position of the cell. Suitable corrections are made on all values of I_0 so that the effect of this difference between the cells is cancelled.

In figure 2, the experimental values of α, determined from the mixtures of known composition and from solutions of the pure components, are plotted against composition. It is evident that the values of α for any one wave length fall on a straight line and therefore that Beer's law is valid for light of these three wave lengths at the concentrations employed (0.0010 to 0.0030 g. per liter).

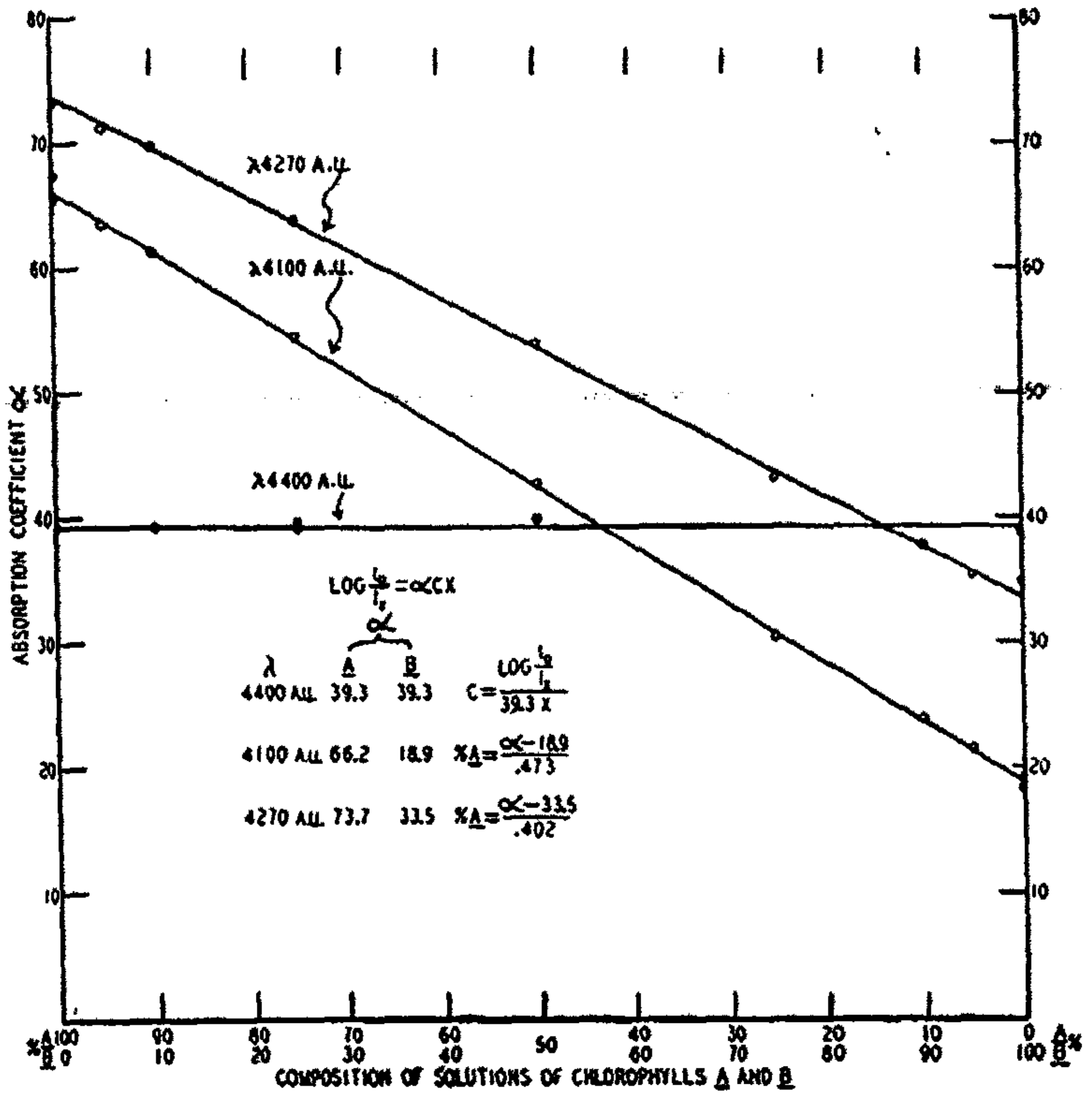

FIG. 2. QUANTITATIVE SPECTRAL ANALYSIS OF MIXTURES OF CHLOROPHYLLS *a* AND *b* IN 90 PER CENT ACETONE

The α values at λ4400 A. U. lie on a horizontal line and are independent of composition. The final values of α for pure *a* and *b* were taken from the intersections of these straight-line curves with the ordinate axes, and are thus more accurate than single observations on the pure components. In the table of figure 2 are the final values of α for *a* and *b* at the wave lengths 4400, 4100, and 4270 A. U. and equations (of the straight-line curves of figure 2) for calculation of total chlorophyll ($a + b$) concentration and percentage component compositions of unknown solutions of a and b.

Using the final values of α at λ4100 and 4270 A. U., the percentage compositions of all the mixtures were calculated from the experimental data. These are presented in table 1. The greatest deviation from the true composition is 1.2 per cent. When the analyses for both wave lengths are averaged, the deviation is only 1.0 per cent.

TABLE 1

Spectral analysis of chlorophylls a and b in 90 per cent acetone

$$\log \frac{I_0}{I_x} = \alpha c x$$

WAVE LENGTH	α		COMPOSITION IN TERMS OF a								
			Knowns $a + b$							Unknowns $a + b$	
	a	b	5 per cent	10 per cent	25 per cent	50 per cent	75 per cent	90 per cent	95 per cent	Example	
										1	2
A.U.											
4100	66.2	18.9	5.50	10.5	24.3	50.3	75.3	89.9	94.2	65.3	63.5
4270	73.7	33.5	4.73	10.4	24.1	50.7	75.6	90.3	93.8	66.7	65.0
Average per cent composition.......			5.11	10.45	24.2	50.5	75.45	90.1	94.0	66.0	64.25

ANALYSIS OF UNKNOWNS

Two unknown mixtures of a and b (neither total concentration nor composition known) were analyzed and the results are presented in table 1. Determinations at the two wave lengths agree within 1.5 per cent. Thus, it is possible to analyze mixtures of chlorophylls a and b by this spectro-photoelectric method with great accuracy and to obtain the percentage composition with an error of less than 1.0 per cent.

SUPPLEMENTARY ANALYTICAL METHOD

To estimate, with considerable accuracy, the amount of one component present as an impurity in a preparation of the other, the following supplementary method is useful.

For the same mixtures that were used in the absolute determination of α, the absorption curves were measured in the blue and red regions of the spectrum (λ4200–4800 A. U. and λ6300–6700 A. U.) where the absorption differs most for the two components. Determinations of $\frac{I_0}{I_x}$ were made with an accuracy of 1.5 per cent at intervals of 25 A. U. These curves are presented in figures 3 and 4. In the first graphs of figures 3 and 4, are the curves of the pure components, *a* and *b*. The dotted curve of pure *a* is repeated in each graph of figure 3 for comparison with the mixture curves. Similarly, the dotted curve of pure *b* is repeated in figure 4.

The region of λ4200–4800 A. U. is useful for detection of impurities of *b* in preparations of *a* (fig. 3). Five per cent of *b* may be detected easily by the appearance of the 4560 A. U. band of *b*. As the percentage of *b* increases to 50 per cent, the 4560 A. U. band becomes more prominent and the intensity of the 4300 A. U. band of *a* decreases.

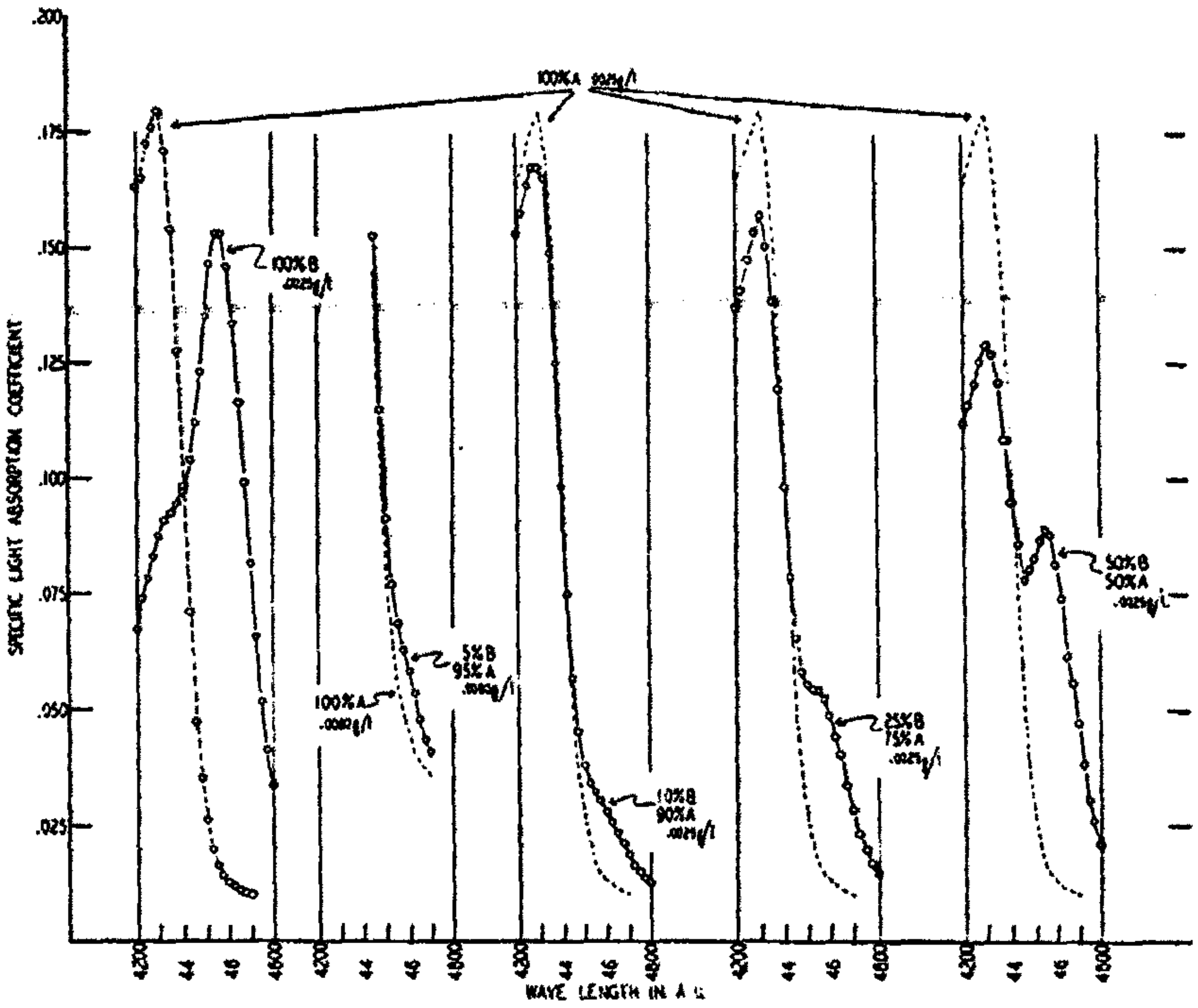

FIG. 3. LIGHT ABSORPTION OF MIXTURES OF CHLOROPHYLLS *a* AND *b* IN 90 PER CENT ACETONE

To detect impurities of component *a* in preparations of *b*, the region of λ6300–6700 A. U. may be used to best advantage (figure 4). The spectrum is appreciably changed in this region when 5 per cent *a* is present and the deviation from the spectrum of pure *b* becomes greater as the percentage of *a* increases.

The concentration of the solution need not be known accurately for detection of considerable contamination of one component by another. This fact makes the supplementary method useful in following the purity of a preparation through the various steps of the isolation procedure.

Ghosh and Sen-Gupta (1) measured the molecular extinction coefficients of chlorophylls *a* and *b* (prepared by Stoll) and their mixtures in acetone solution with a König-Marten spectrophotometer. Since their method of light intensity comparison was visual, it would not have the precision and accuracy of the photoelectric method over a wide range of wave lengths. In such a visual method, the monochromatic quality of the light could not be so high as in the photoelectric method used above. Their measurements were taken at such great intervals of wave length, especially in the blue region of the spectrum, that small differences in the absorption bands could not be detected. For this reason, and particularly because of the improved preparative methods of chlorophyll component separation (2), the purity of their components is questionable.

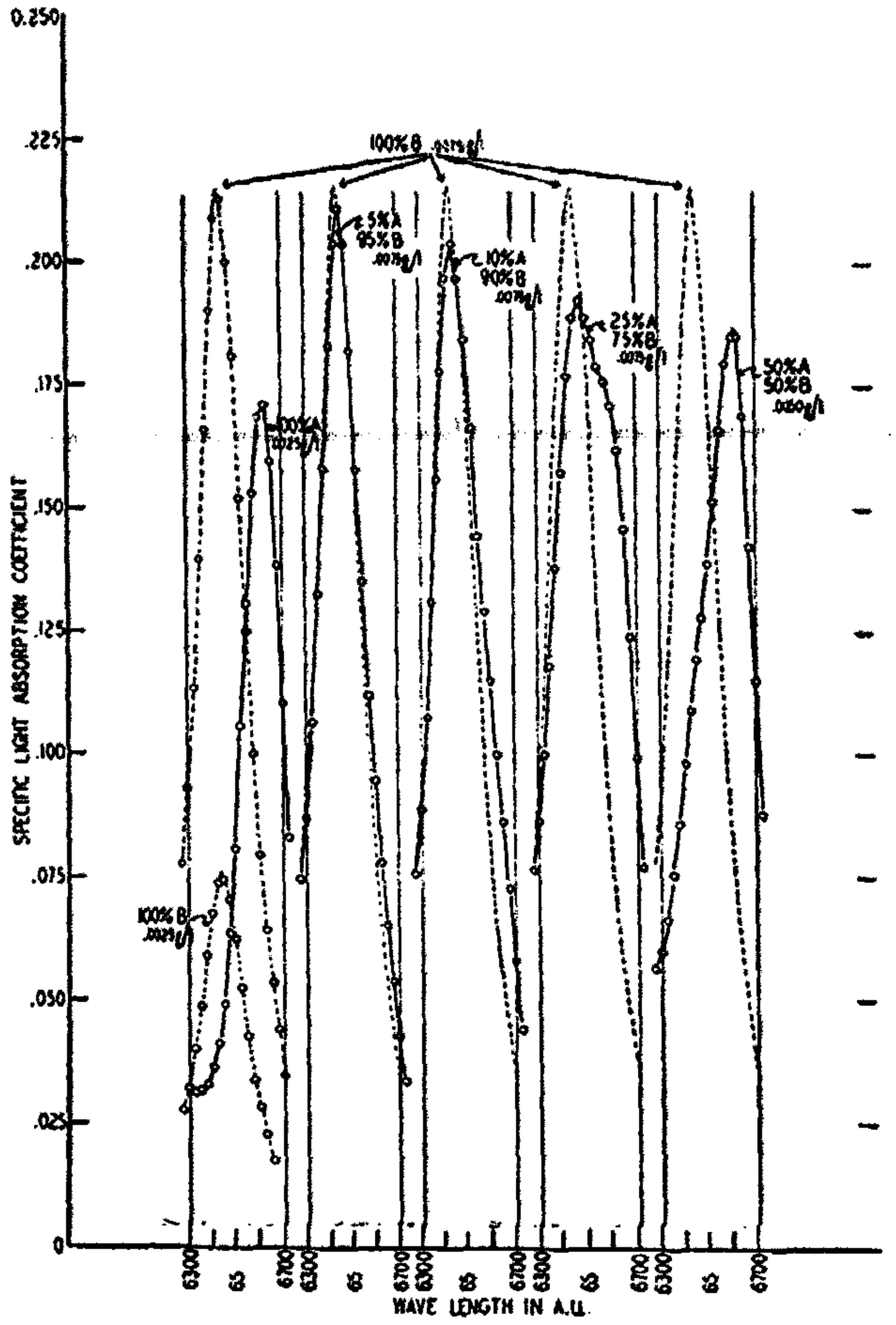

FIG. 4. LIGHT ABSORPTION OF MIXTURES OF CHLOROPHYLLS *a* AND *b* IN 90 PER CENT ACETONE

The spectro-photoelectric analytical method, as demonstrated here, undoubtedly has a wide field of usefulness, particularly in certain problems of biochemistry. By extension of the method into the ultra-violet region, as is possible with the particular monochromator and photocell used in this work, the purity of preparations of hormones, vitamins, enzymes, and other colorless compounds which are difficult to isolate in the pure state, could probably be quickly followed during preparative processes. The method will also be useful in identification of such compounds whose formulas are unknown. Mixtures of colored substances whose solutions obey Beer's law may be analyzed quickly and easily.

Similar studies on the yellow plant pigments are now in progress. It is hoped that this work, when completed, may be combined with the results reported in this paper to make possible a simpler quantitative analysis for all of the yellow and green pigments of the leaf.

SUMMARY

1. By an accurate spectro-photoelectric method, quantitative light absorption data were obtained for pure chlorophylls *a* and *b* and their mixtures. The percentage composition of unknown mixtures of components *a* and *b* were determined with an accuracy of better than 1.0 per cent.

2. From light absorption measurements at λ4400 A. U., the total chlorophyll ($a + b$) concentration is calculated. The ratio of *a* to *b* is calculated from measurements at λ4100 or 4270 A. U.

3. Experimental details are discussed which are essential for a high degree of accuracy.

4. It is shown that Beer's law is valid for chlorophyll solutions in 90 per cent acetone over a narrow range of concentrations.

5. A supplementary analytical method, accurate to 5 per cent, is useful for estimation of mixture compositions.

The writer is thankful to Dr. T. R. Hogness for suggestions given during the development of this method.

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STUDIES ON GLASS. VIII

The Coefficient of Thermal Expansion of Boron Trioxide

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For these studies on glass, which are now being carried on at Stanford University, boron trioxide was selected a few years ago as a typical inorganic, glass-forming material. The results of an extensive study of its heat capacity have been presented in an earlier paper by Thomas and Parks (4). With increasing temperatures, the specific heat at constant pressure was found to undergo an increase of more than 60 per cent between 215° and 270°C. Below this transition region the boron trioxide was a hard glass with a mean atomic heat of 3 to 4 calories, depending upon the temperature and the previous heat treatment of the material; above the transition it was an extremely viscous liquid with an atomic heat approximating the Dulong-Petit value.

In view of these interesting results a number of other physicochemical properties of boron trioxide are now being investigated in this laboratory. In the present paper we shall give some of the data which have been obtained in a study of the cubical coefficient of thermal expansion over the temperature range 100° to 320°C.

METHOD AND APPARATUS

The samples of boron trioxide used in this investigation were prepared from Merck's c. p. anhydrous B_2O_3 (impurities guaranteed to be less than 0.01 per cent). This material was always heated in a platinum crucible for one to two hours at a temperature of about 1200°C. in order to drive off the last traces of water and to eliminate gas bubbles. The molten oxide was next poured into a small cylindrical mold, made out of copper foil, and permitted to cool to room temperature in a desiccator containing phosphorus pentoxide. The copper foil was then stripped from the boron trioxide glass and the latter was smoothed down a little in a lathe. These small cylinders usually contained from 5.5 to 7.5 gm. of oxide, equivalent to 3 or 4 cc. in volume.

A simple dilatometer, with mercury as the dilatometric fluid, was em-

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[1] Holder of the Shell Research Fellowship at Stanford University for the academic year 1932–1933.

ployed in the determinations of the coefficient of thermal expansion. It was made entirely out of "tool" steel and consisted essentially of a stout cylindrical can of about 2.0 cm. diameter and 6 cc. capacity. A top fitted into this can by means of a tapered, vacuum-tight joint and was held firmly in position by an adjustable nut. A steel capillary tube, welded through the top, projected upward for a distance of 15 cm. and ended in a small horizontal nozzle; it served as a means of ejecting the excess mercury as the dilatometer was heated to successively higher temperatures and the contents of the steel can underwent expansion.

The large, electrically-heated copper block which Thomas and Parks (4) developed for their specific heat measurements was employed in the present investigation as an adjustable thermostat. The can of the dilatometer was placed within the central cavity of this block with the steel capillary passing upwards through a hole so that the exit nozzle was in the outside air. A small glass weighing bottle then served to collect the mercury droplets as they were expelled at this nozzle during the heating of the copper block between successive steps in temperature.

Measurements of the temperatures were made with calibrated thermocouples in conjunction with a White double-combination potentiometer. A chromel-alumel thermocouple, having one junction fastened to the outside wall of the dilatometer can and the other imbedded in the copper block, served to tell when the dilatometer was at the same temperature as its surroundings. A platinum-platinrhodium thermocouple with one junction on the outside of the dilatometer and the other at 0°C. was used for measuring the actual temperatures to 0.01°C.

The procedure in filling the dilatometer for the expansion measurements was extremely simple. A prepared cylinder of the boron trioxide glass was first placed in position in the dilatometer can, the top was fitted on, and the whole instrument was evacuated to 0.01 mm. by a "Cenco-megavac" oil pump. Clean, freshly heated mercury was then caused to flow into the free space of the dilatometer by raising the level of a mercury reservoir which was connected to the side tube of the evacuating and filling system. The dilatometer and contents were next heated under reduced pressure to over 300°C. in order to remove any possible air bubbles within the instrument, and afterwards a small amount of mercury was introduced as the dilatometer was quickly cooled down to room temperature by quenching in a water or alcohol bath.

After such preparations the dilatometer was placed within the copper block and the latter was heated electrically from 100°C. up to about 300° or 325°C. in seven to ten steps. These steps often covered temperature intervals as large as 32°C., where the boron trioxide was either a hard glass or a very viscous liquid and the expansion coefficient was not changing greatly. On the other hand, the temperature steps within the range

210° to 270°C. were usually kept between 15° and 20°C., as here the coefficient was increasing rapidly. Since boron trioxide is a very poor conductor of heat, it was important to allow sufficient time to elapse at each step for complete equalization of temperature within the sample. Accordingly, in some cases the temperature in the copper block was maintained constant for periods as long as two and a half hours.

The calculation of the coefficient of expansion of the boron trioxide from the weights of the mercury ejected between successive temperatures was simple. At an initial temperature, T_1, the volume of the mercury in the dilatometer plus the volume of the oxide sample was equal to the volume of the dilatometer itself; or in equation form we have

$$\left(\frac{1}{d_1}\right)W_1 + V_{1(\text{oxide})} = V_{1(\text{dilatometer})} \qquad (1)$$

where d_1 and W_1 represent, respectively, the density and weight of the mercury in the dilatometer. At a higher temperature, T_2, we may similarly write

$$\left(\frac{1}{d_2}\right)W_2 + V_{2(\text{oxide})} = V_{2(\text{dilatometer})} \qquad (2)$$

The weight of mercury which is ejected from the dilatometer in heating from T_1 to T_2 is, of course, $W_e = W_1 - W_2$. By making use of this fact and subtracting the first equation from the second, we then obtain

$$\Delta V_{\text{oxide}} = \Delta V_{\text{dilatometer}} - \left(\frac{1}{d_2} - \frac{1}{d_1}\right)W_1 + \frac{W_e}{d_2} \qquad (3)$$

The volume increase of the dilatometer over the temperature ranges of this study was first determined in two independent series of measurements, which were carried out in the absence of a boron trioxide sample. The necessary data for the density of mercury at the various temperatures were taken from the Landolt-Börnstein "Tabellen" (2).

From the values of ΔV_{oxide} (obtained by equation 3) the cubical coefficient of expansion, α, may be evaluated. By definition

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

However, for the rather small temperature steps employed in the present investigation $\frac{\Delta V_{\text{oxide}}}{\Delta T}$ approaches $\left(\frac{\partial V}{\partial T}\right)_p$; and accordingly we have employed here the approximation

$$\alpha = \frac{2}{V_2 + V_1}\left(\frac{\Delta V_{\text{oxide}}}{T_2 - T_1}\right) \tag{4}$$

which will not involve us in any great error.

EXPANSION DATA

Expansion determinations were made upon several different boron trioxide samples in the course of our investigation, but naturally a number of these measurements were rather preliminary in character. In the present connection we shall restrict ourselves for the purposes of brevity to a consideration of the data for the last two samples studied.

TABLE 1

The cubical coefficient of expansion of boron trioxide

UNANNEALED		PARTIALLY ANNEALED		CAREFULLY ANNEALED	
Sample 1, under various conditions					
degrees C.	α	*degrees C.*	α	*degrees C.*	α
113.1	0.41 (10^{-4})	122.1	0.48 (10^{-4})	123.7	0.52 (10^{-4})
139.7	0.37 (10^{-4})	156.9	0.55 (10^{-4})	157.4	0.60 (10^{-4})
166.7	0.17 (10^{-4})	188.1	0.55 (10^{-4})	184.4	0.83 (10^{-4})
193.7	−0.17 (10^{-4})	213.3	0.83 (10^{-4})	204.4	1.08 (10^{-4})
217.8	−0.73	234.8	3.98	222.8	3.45
234.9	2.19	256.6	5.70	247.5	5.61
251.1	5.84	286.5	6.25	275.7	6.05
269.1	6.00				
290.3	6.16				
310.0	5.84				
Sample 2, under various conditions					
122.1	0.40 (10^{-4})	120.6	0.56 (10^{-4})	114.2	0.54 (10^{-4})
152.3	0.19 (10^{-4})	152.9	0.59 (10^{-4})	143.4	0.49 (10^{-4})
180.4	−0.19 (10^{-4})	177.8	0.71 (10^{-4})	171.8	0.59 (10^{-4})
204.9	−1.07 (10^{-4})	198.3	0.85 (10^{-4})	199.6	1.18 (10^{-4})
229.4	0.55 (10^{-4})	217.1	1.62 (10^{-4})	226.9	4.35 (10^{-4})
250.2	4.10	233.1	4.64 (10^{-4})	250.0	6.13
270.0	6.22	249.1	6.64 (10^{-4})	270.0	5.92
293.8	6.35				

Sample 1 contained 6.3 g. of the oxide. After its installation in the dilatometer it was first heated to about 325°C. and then quickly cooled by quenching the dilatometer in water. The results of a series of expansion measurements made upon the material in this condition are given in the first part of table 1 under the heading "unannealed." The sample was next cooled from 300°C. down to room temperature at the rate of about 5°C. per hour. The subsequent series of expansion measurements appears in the first section of table 1 under the heading "carefully annealed." Finally, the sample was cooled from 300°C. to room temperature at the rate of 25°C. per hour, after which the data for the "partially annealed" material were obtained.

Sample 2 was very similar to the preceding one, although it had been prepared from a different batch of boron trioxide. In this case the expansion coefficients for the unannealed condition were obtained after the dilatometer and contents had been heated to 325°C. and quenched in a large beaker of ethyl alcohol. The heat treatments of the sample prior to the "carefully annealed" and "partially annealed" determinations were practically the same as in the case of sample 1. All these data appear in table 1.

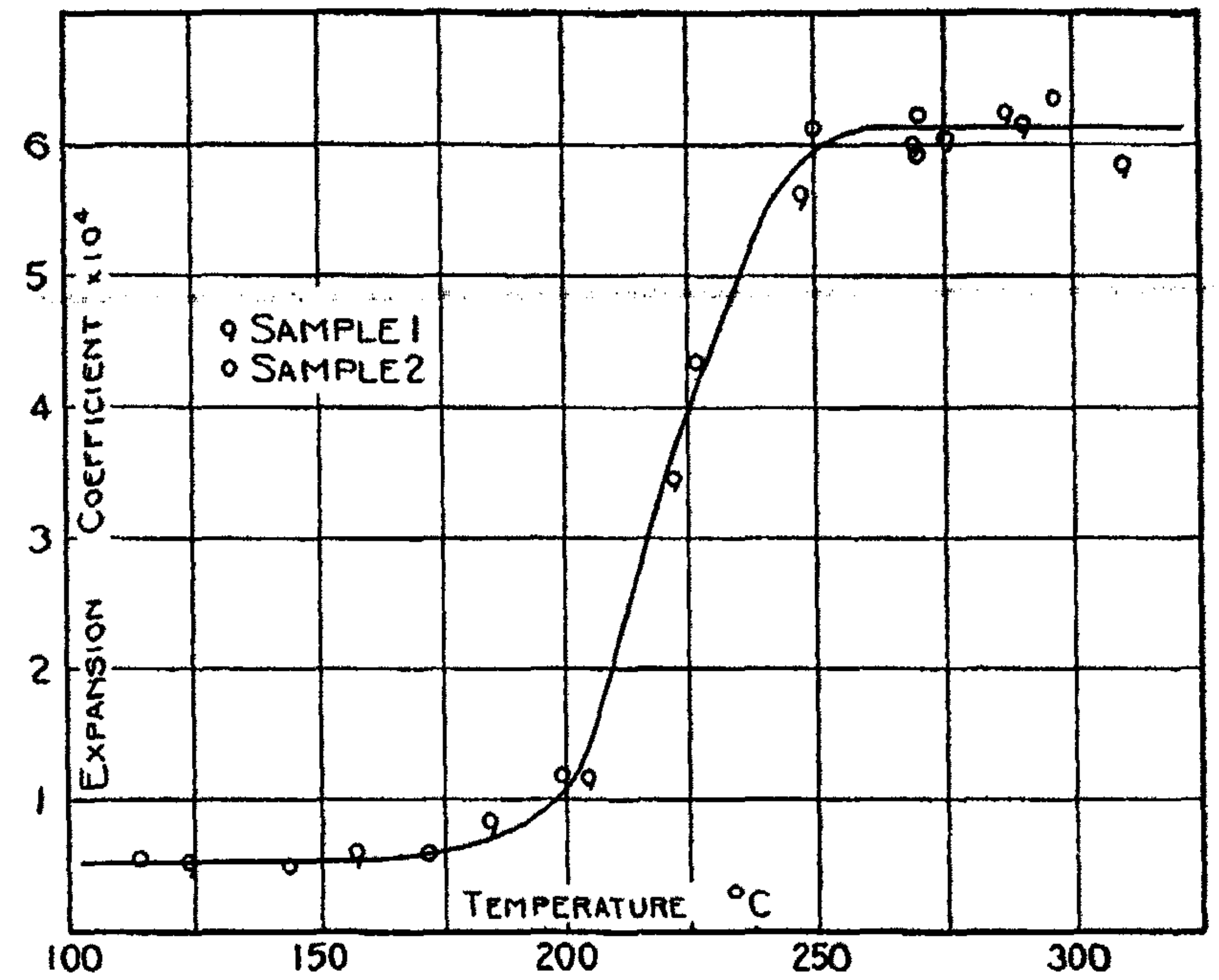

FIG. 1. SHOWING THE EXPANSION DATA FOR THE TWO SAMPLES IN THE CAREFULLY ANNEALED CONDITION

In our judgment the experimental error incidental to our method of measuring the coefficient of expansion should be under 5 per cent in all cases. Any deviations between different series of data which appreciably surpass this figure should be attributed to differences in the heat treatment of the samples either prior to or during the measurements. A comparison of our various results therefore serves to bring out the great variability of the boron trioxide in the region below 260°C., where, as it cools, the oxide begins to change over from an extremely viscous liquid[2] to a hard, glassy condition.

The glasses, after they have been "carefully annealed," undoubtedly represent fairly close approaches to internal equilibrium and accordingly the expansion coefficients obtained in this connection for the two samples are in good agreement. Likewise, the influence of strains and previous thermal history is relatively unimportant in the viscous liquid above 270°C., and so in this region the results of all determinations, regardless of previous treatment, are practically within the limits of experimental error. These findings are represented graphically in figure 1.

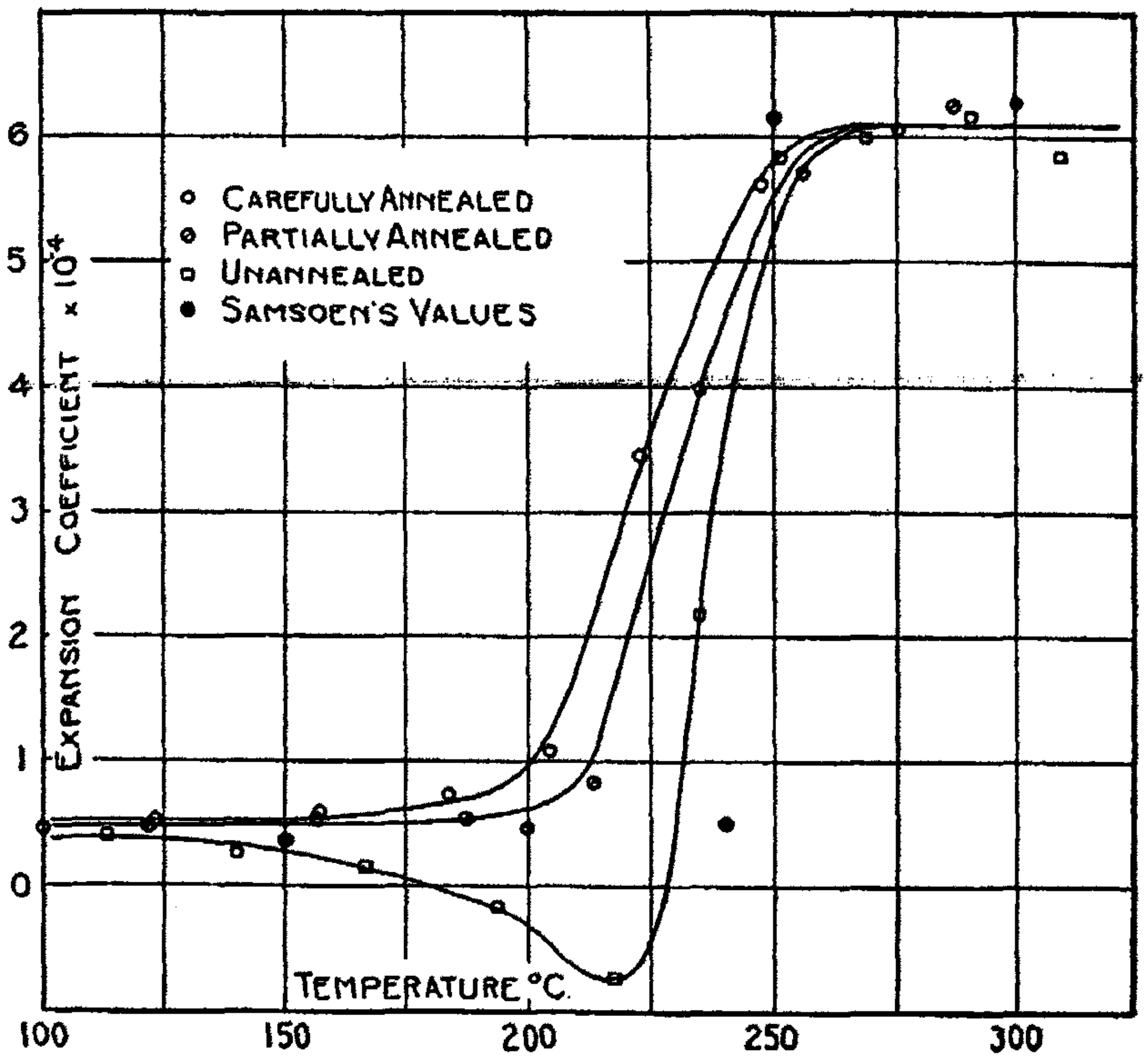

Fig. 2. Showing the Expansion Data Obtained for Sample 1 Following Various Degrees of Annealing

On the other hand, the glasses in the "unannealed" and "partially annealed" conditions yielded results of poorer reproducibility below 260°C. In particular, the coefficients of expansion for the unannealed glasses run decidedly below those for the carefully annealed and even assume various

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[2] We have been able to make viscosity measurements upon boron trioxide down to 267°C., at which temperature $\eta = 2\ (10^{11})$ poises.

negative values between 180° and 230°C. In other words, there is actually a decrease in the volume of the glass sample within this range. Such behavior, of course, makes the subsequent rise as the viscous-liquid condition is approached even more rapid than in the case of a carefully annealed glass. The data for the "partially annealed" glasses, as might have been expected, generally lie between those for the "unannealed" and "carefully annealed" conditions. Curves for the three sets of data thus obtained in the case of sample 1 are shown in figure 2.

Some measurements of the coefficient of thermal expansion of boron trioxide within this temperature range have also been made by Samsoen (3). The values reported by him have been included for comparative purposes in figure 2 where they are represented by the solid dots. His results below 200°C. and above 260°C. are in good agreement with some of our determinations. However, between these two temperatures he obtains a much sharper transition in the expansion coefficient than we have ever found in any of our samples.

DISCUSSION

The results of this study show that for boron trioxide the cubical coefficient of thermal expansion in the viscous-liquid state is more than ten times that for the glass and that between these two states there is a transition[3] extending over a temperature range of about 50°C. Thus these expansion phenomena parallel those found by Thomas and Parks (4) in their study of the specific heats of this substance. They are also in thorough agreement with the results of some expansion measurements of an optical glass reported by Berger (1). In view of such findings it seems to us quite clear that a glass must be considered in a separate category from the undercooled viscous liquid from which it is formed.

The very marked influence of the rate of cooling from the liquid to the glassy states is also a noteworthy feature. Probably no actual glass can be considered as being in a condition of true thermodynamic equilibrium at a temperature much below its softening region; the attainment of such an equilibrium might require the lapse of almost infinite time. However, our boron trioxide glasses which were formed by careful annealing were probably not greatly removed from a condition of internal equilibrium or, in other words, they represent a good approach to stable glasses. On the other hand, the glasses which were produced by quenching the dilatometer in water or alcohol represent substances which are in a state of great strain or, we might say, which are greatly removed from the condition of internal equilibrium at lower temperatures. It is interesting to

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[3] It must be realized that the coefficients of expansion reported here are mean values over temperature intervals. Such values tend to smooth out the curve and to decrease the sharpness of the change.

note that the volumes of such glasses are appreciably larger than those for the annealed, as the comparative data (table 2) for the volumes of the two samples under various conditions show.

The volumes of the unannealed glasses at room temperature are almost as great as those of the carefully annealed at a temperature within the transition region. Thus in the unannealed glass there must be a tendency for the material to undergo internal changes in the direction of a smaller volume. Nevertheless, the effects of such a tendency cannot become very noticeable at temperatures far below the softening region of the glass because the velocity of the shift toward the equilibrium point is bound to be extremely low where molecular translation is infrequent. However, as the temperature of the unannealed glass approaches the softening region and the frequency of translational motion of the molecules in the structure increases markedly, this tendency of the internal equilibrium to shift towards a smaller volume predominates for a time over the general expansion tendency of the material and produces the negative values of the coefficient of expansion between 180° and 230°C.

TABLE 2

The volume of the glass samples at room temperature

CONDITION	SAMPLE 1	SAMPLE 2
	cc.	cc.
Unannealed	3.419	3.425
Partially annealed	3.384	3.379
Carefully annealed	3.373	3.366

SUMMARY

By use of a small dilatometer with mercury as the dilatometric fluid the coefficients of thermal expansion of two samples of boron trioxide have been measured between 100° and 325°C. with a probable experimental error of less than 5 per cent. The coefficient for the viscous liquid was found to be more than ten times that for the glassy state. The character of the expansion coefficient–temperature curves below 260°C. depended greatly upon the extent of the annealing during the initial formation of the glass.

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THE THERMODYNAMICS OF THE ELECTROCAPILLARY CURVE. I

The General Equations

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I. Introduction

If a difference of electric potential $\mathfrak{E}$, varying from 0 to about 1.5 volts is applied to the electrodes of a system such as

$$\mathrm{Hg}\left|\begin{array}{l}\text{aqueous KNO}_3\text{ solution}\\ \text{of any concentration}\end{array}\right|\begin{array}{l}\text{any constant nonpolarizable}\\ \text{reference electrode}\end{array}$$

making the $Hg|KNO_3$ solution end the cathode, the surface tension σ at the $Hg|KNO_3$ solution boundary varies in a regular way. The measurement of σ for various values of $\mathfrak{E}$ is best carried out in the Lippmann electrometer (1). The curve obtained by plotting σ as ordinate and $\mathfrak{E}$ as abscissa is called the electrocapillary curve of the system. In practice the system may be varied by replacing the mercury by an amalgam or by some other liquid metal such as gallium, and the potassium nitrate solution by aqueous or organic solutions of any electrolytes whose cations are sufficiently electropositive not to be deposited upon the metallic phase to any appreciable extent within the range used; the electrolyte must therefore in particular be as free as possible of the ions of those metals constituting the metallic phase.

Since its discovery (2), two thermodynamic theories of the electrocapillary curve have been advanced. The first, due chiefly to Lippmann, Helmholtz and Planck (3), is that of the so-called "perfectly polarizable electrode." The second, usually referred to as the "Gibbs theory," and due chiefly to Gibbs, Thomson, Warburg, Gouy and Frumkin (4), consists in the direct application of Gibbs' adsorption theorem to the polarized electrode.

The two theories start from independent, apparently unrelated assumptions, but both lead to the same result, verified by experiment (5), that the slope of the electrocapillary curve is equal to the surface density of electric charge on the surface of the mercury in contact with the solution. Together the two theories give a good account of most of the facts of electrocapillarity (6). Nevertheless they are unsatisfactory in at least two respects:

1. The theory of the "perfectly polarizable electrode" does not give an account of the variation of the electrocapillary curve with the composition of the two phases involved.
2. The "Gibbs theory," although it does take account of the composition, rests on the assumption, among others, that the mercury surface is always in equilibrium with Hg_2^{++} and Hg^{++} ions in the solution adjacent to it in the capillary. This assumption is open to question because, except for the lowest part of the ascending branch of the curve,[1] the solution in the capillary never contains an appreciable concentration of mercury salt; the values of $C_{Hg_2}{}^{++}$ calculated from the potentials applied along by far the greater part of the curve lie between 10^{-8} and 10^{-60}. This means that any Hg_2^{++} or Hg^{++} ions at all, which happen to diffuse into the neighborhood of the mercury surface in the capillary, are immediately and violently removed from the solution by electrolysis, so that actually there is anything but equilibrium with respect to these ions.[2] That in spite of this assumption the "Gibbs theory" leads to a correct result, suggests that the error is partly or wholly counterbalanced by the other assumptions, difficult to verify individually, on which that theory rests.

In short, the first theory seems to be incomplete, and the second one at least partly wrong—a situation which explains the disconcerting existence of two apparently unrelated theories leading to one correct result.

The following is an attempt to give a complete theory starting from only one special assumption, which is sufficiently realized in the Lippmann electrometer.

II. THE THEORY

A. THE ASSUMPTIONS

1. The perfectly polarizable system

Let A, figure 1, represent a system of two electrically conducting liquid phases, α and β, separated by a plane inhomogeneous boundary layer B, of finite thickness (lightly shaded portion of figure). The external surface of A is to be looked upon as bounded by a container of some nonconducting and chemically inert material. It is furthermore assumed that the interior of the system is electrically neutral as a whole. This means that any closed surface, D, in the interior, extending into the homogeneous regions

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[1] For this part of the curve to be sure, where $C_{Hg_2}{}^{++}$ may reach values as high as 10^{-3}, the equilibrium $Hg \mid Hg_2^{++}$ does obtain, as shown by A. Frumkin and A. Obrutschewa (Z. physik. Chem. **136A**, 248 (1928) and K. Bennewitz and K. Küchler (Z. physik. Chem. **153A**, 443 (1931)).

[2] The author is indebted to Professor E. Lange for calling his attention to this difficulty.

of both α and β and cutting the boundary layer B perpendicularly everywhere, can contain no appreciable excess electric charge—a condition which is fulfilled by all conducting two-phase systems in equilibrium at ordinary temperatures.

Finally, the system is assumed to have the following special property: *Somewhere within the inhomogeneous boundary layer B and parallel to it, there exists a thin layer C′* (heavily shaded portion of figure 1), *which is impermeable in both directions to charged particles (ions, electrons) of any sort.* The word "thin" in this statement means that the barrier to charged particles may be thin compared with the entire inhomogeneous layer B. The barrier C′ is evidently the layer in which the general properties of the medium change relatively abruptly from those of a metal to those of an aqueous or other solution: on one side of C′ the system, although still inhomogeneous, has entirely metallic properties; on the other side, although also inhomogeneous, it has entirely nonmetallic properties.

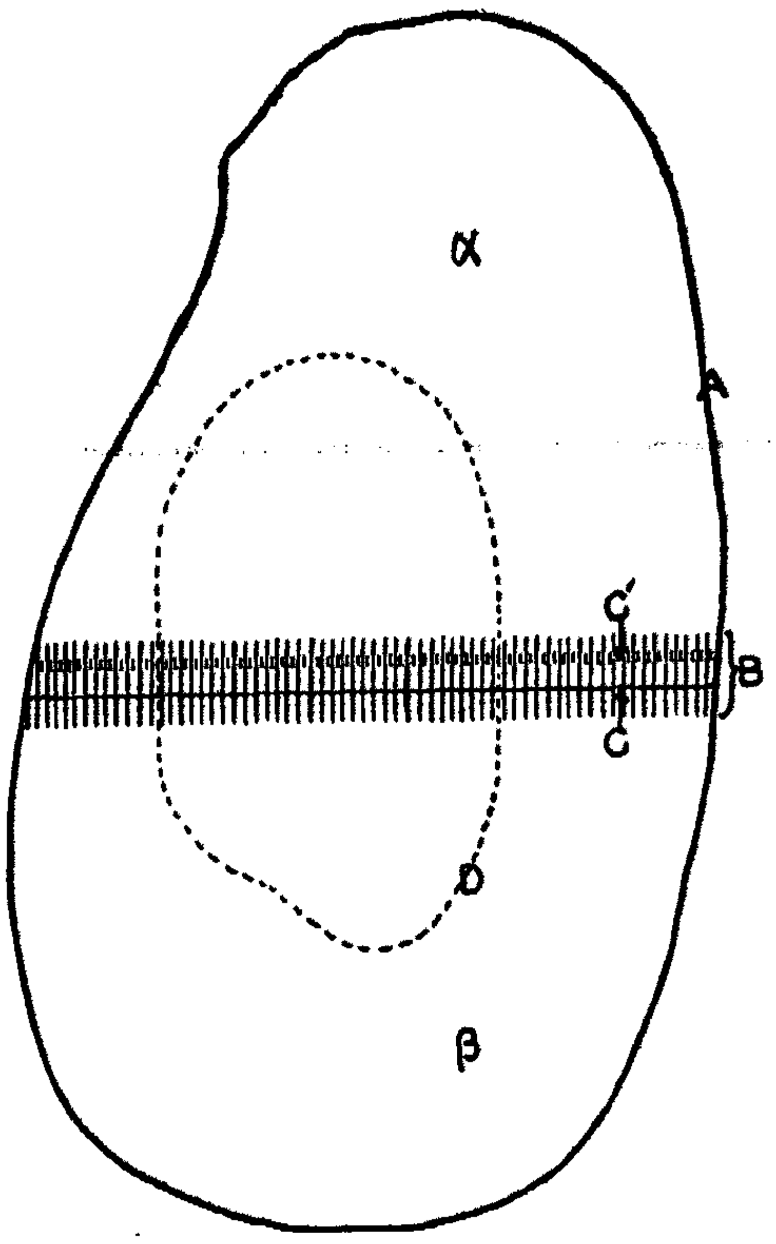

FIG. 1. SCHEMATIC REPRESENTATION OF PERFECTLY POLARIZABLE SYSTEM
B = boundary layer between phases α and β; C′ = barrier impermeable to charged particles; C = fictitious Gibbs surface; D = fictitious closed surface in interior.

A necessary condition for the above special property is the following: of all the species of electrically charged particles (formed by dissociation of any of the components) present in one of the phases, say α, none may be present to any appreciable extent in the other phase β, and vice versa. This condition implies the complete absence of electrochemical equilibrium. The condition is, however, not sufficient, because its fulfillment does not preclude all electrolysis (e.g., the formation of gaseous hydrogen on a copper cathode in a solution containing H^+ but no Cu^+ or Cu^{++}, due to passage of electrons from the metal into the solution). Since electrolysis can always be brought about by applying a sufficient E.M.F. in the proper direction, a given system can possess the property mentioned only within a certain range of $\mathfrak{E}$.

A discussion of the definition and properties of the "perfectly polarizable electrode" of Planck (3) would be inexpedient here. Suffice it to say that the assumption of the above property leads to all the consequences necessary for an exact treatment of the "perfectly polarizable electrode." The property in question will therefore be designated as that of *perfect polarizability*, and any system possessing it as a *perfectly polarizable system*. The physical significance of this name lies in the impossibility of electrolysis and the attendant absence of electrochemical equilibrium. The perfectly polarizable system evidently constitutes a case intermediate between that of two conducting phases in electrochemical equilibrium as regards one or more charged species, and that of a conducting phase in contact with a dielectric.

2. Relation of the perfectly polarizable system to the electrocapillary curve

If to the electrodes of the system Hg | aqueous KNO_3 solution | 1 *N* KCl | Hg_2Cl_2 | Hg potentials $\mathfrak{E}$ are applied making the Hg | KNO_3 side the cathode, practically no electrolysis will take place as long as $0 \leq \mathfrak{E} \leq 1.3$ volts, because (1) the potassium nitrate solution contains no Hg_2^{++} or Hg^{++}, (2) K^+ is too electropositive to be deposited in appreciable amount (7), and (3) even after the deposition potential of hydrogen gas at atmospheric pressure ($\mathfrak{E}$ = about 0.7 volts in the example quoted) is exceeded, overvoltage keeps the hydrogen from being formed to any appreciable extent. Similar considerations apply to the other systems giving rise to electrocapillary curves in the Lippmann electrometer. The perfectly polarizable system thus constitutes an idealization which is closely approached by the real systems in question. Consequently a thermodynamic theory of perfectly polarizable systems will at the same time be a general theory of the electrocapillary curve. Any discrepancy between such a theory and the facts will be due to a deviation of the system from perfect polarizability.

But of such deviation there exists a very direct measure; it is the density of the "depolarization current" which flows upon applying the potential $\mathfrak{E}$.

If there were no depolarization current, the system would be perfectly polarizable. In a Lippmann electrometer containing alkali salt solution, the current density (at the small electrode) is very small, of the order of 10^{-4} to 10^{-3} ampere $\times \text{cm}^{-2}$.

B. THE COMPOSITION OF THE SYSTEM

1. Three definitions concerning composition

(1a) *Charged components.* In a system containing electrically charged species it is possible to regard the latter as components in the thermodynamic sense. For such "charged components," as for the electrically neutral components of a system, the chemical formulas assumed are to some extent arbitrary, the *number* of components alone being fixed. Let any system in equilibrium be bounded by a non-conducting chemically inert container of variable volume. Then the number of charged components is the number of electrically charged species, the *total* amount of which within the container may be varied *independently*. Thus, the system: aqueous H_2SO_4 solution | vapor has three charged components, which may be taken as H^+, OH^-, $SO_4^=$, or H_3O^+, OH^-, $SO_4^=$, or H^+, OH^-, HSO_4^-, etc. In a binary alloy there are three charged components: the ions of the two metals and electrons.

(1b) *Electrolyte components.* No matter in what proportions the charged components are present in any system as a whole, including its inhomogeneous boundary regions, all phase interiors will remain electrically neutral, because excess charges always collect in boundary layers. The interiors of the conducting phases of a system may therefore be regarded as containing a certain number of neutral components capable of dissociation, of which the charged components are dissociation products. These neutral but dissociating components will henceforth be referred to simply as "electrolyte components," whether they are electrolytes in the ordinary sense or not. Thus the system Tl amalgam | aqueous KCl solution, which contains two electrolytes in the ordinary sense, potassium chloride and water, contains four electrolyte components, which may be taken as thallium, mercury, potassium chloride, and water.

The chemical formulas assigned to the electrolyte components are to some extent arbitrary, only the number of these components in a given system being fixed. Thus, for a system consisting of a single phase and its boundary layers, and containing p^α charged components, the number of electrolyte components is in general $p^\alpha - 1$.[3]

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[3] Owing to electroneutrality the amounts of only $p^\alpha - 1$ of the p^α species can be varied independently in the phase interiors. This means that the presence of p^α charged components *in the system* demands the presence of $p^\alpha - 1$ (corresponding) components for the phase interior. But whether these $p^\alpha - 1$ components of the interior are taken to be electrically charged species, or neutral species giving rise to

(2) *Neutral components.* Any uncharged components which do not dissociate appreciably into charged species will be referred to simply as "neutral components."

The point of these definitions lies in the fact that whereas at constant temperature and pressure the state of a *system as a whole* depends upon the amounts of the neutral components and of the charged components, the state of *all the phase interiors*[4] may be regarded as depending only upon the amounts of neutral components and of the electrolyte components, that is, the electrolyte components are convenient alternatives to the charged components in the description of phase interiors apart from boundary layers.

2. *Description of the composition of the perfectly polarizable system*

Since both phases α and β of the system, figure 1, are electrically conducting, they will both contain charged components. Let p^α be the number of charged components in α, p^β the number in β, and p the total number of charged components of the system. Then, since α and β may have no charged components in common,

$$p = p^\alpha + p^\beta \tag{1}$$

Let q^α be the number of electrolyte components in α, q^β the number in β, and q the total number of electrolyte components of both phase interiors. Then, since the perfectly polarizable system behaves, as regards its charged components, like two entirely separated single phases,

$$q^\alpha = p^\alpha - 1 \tag{2.1}$$

$$q^\beta = p^\beta - 1 \tag{2.2}$$

$$q = q^\alpha + q^\beta = p - 2 \tag{3}$$

Let r^α be the number of neutral components in α, r^β the number in β, and r the total number of neutral components of the system. Then, since there is theoretically no restriction on the number or nature of the neutral components, so that the two phases may have a certain number, $r^\alpha + r^\beta - r$, in common,

$$r \leq r^\alpha + r^\beta \tag{4}$$

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the charged species by dissociation, or some of each, is immaterial, because only the number of the components is significant. Thus, if a one-phase system contains the charged components K^+, Na^+, Cl^-, NO_3^-, the amounts of only three of these ions can be varied independently in the phase interior, and so there are only three electrolyte components, KCl, KNO_3, $NaNO_3$, or KCl, $NaCl$, $NaNO_3$, etc.

[4] By the state of a phase interior is meant the totality of the factors affecting any events that might be caused to take place in the phase interior.

In practice one of the two phases is always metallic, so that the r neutral components will practically always be restricted to one phase, the nonmetallic one, i.e., if α denotes the metallic phase, then:

$$r = r^{\beta} \tag{5}$$

The treatment will, however, proceed on the more general assumption (equation 4).

The total number, J, of components of the *system* is given by

$$J = p^{\alpha} + p^{\beta} + r = p + r \tag{6.1}$$

$$= q^{\alpha} + q^{\beta} + r + 2 = q + r + 2 \tag{6.2}$$

and the number, K, of components of the *two phase interiors* is given by

$$K = p^{\alpha} + p^{\beta} + r - 2 = p + r - 2 \tag{7.1}$$

$$= q^{\alpha} + q^{\beta} + r = q + r \tag{7.2}$$

so that, for the perfectly polarizable system,

$$K = J - 2 \tag{8}$$

In what follows, the subscript i will refer to the charged components, j will refer to the electrolyte components, and k will refer to the neutral components. In accordance with this notation, the (charged) species representing the charged components of the system will be designated by X_i^{α}, X_i^{β} or, without allocation to phase, by X_i; the electrolyte components by X_j^{α}, X_j^{β}, or by X_j; and the neutral components by X_k^{α}, X_k^{β}, or by X_k.

C. GENERAL EQUATIONS OF THE PERFECTLY POLARIZABLE SYSTEM

1. *The extensive properties of the boundary layer*

The values of the extensive properties such as energy, entropy, or the amount of a component, may be defined according to Gibbs for any boundary layer as follows. Imagine a geometrical surface C, lying parallel to the boundary layer B (figure 1) at an arbitrary level. This level, being arbitrary, may be regarded as defined by a variable x, denoting the distance from C to any parallel fixed level, say that of a certain mark on the containing wall of the system A. If G is the value of an extensive property such as energy, entropy, etc., for the entire space (matter filled) enclosed by the surface D (figure 1), then the corresponding value G^{ω} for the boundary layer is defined by:

$$G = G^{\alpha} + G^{\beta} + G^{\omega} \tag{9}$$

where G^{α} denotes the energy, entropy, etc., which the space bounded by C and that part of D which lies in α *would have if* the matter contained in it remained homogeneous up to C, and G^β denotes the same for β. Any G^ω thus defined evidently depends upon the position of the fictitious surface C, and is therefore a function of x. In a perfectly polarizable system the only G^ω values of much physical interest are those for which the surface C is placed within the physical barrier C′ separating the metallic from the nonmetallic media. The exact definition of this level, which will be designated as the physical dividing surface of the system, and which, for a given state of the boundary layer, is characterized by a constant value of x, $x = x'$, is given on p. 124. From p. 124 on, all G^ω values will definitely and finally be referred to the physical dividing surface $x = x'$, but until then x will be regarded as arbitrary.

It may be noted that according to the above definition

$$V = V^\alpha + V^\beta \tag{9.1}$$

where V denotes the volume of the space within D (figure 1). As a result the volume of the boundary layer, V^ω, is always zero, and thus occupies a special position among the extensive properties G^ω.

2. *The charge of the double layer*

The space bounded by the fictitious surface C and that part of D which lies in α in general contains a certain net electric charge carried by charged particles accumulated near C; denote this charge by θ^α. If Ω is the area cut out of C by the closed surface D, the surface density of the charge in question is θ^α/Ω; set $\theta^\alpha/\Omega = \epsilon^\alpha$. Quantities θ^β and $\epsilon^\beta = \theta^\beta/\Omega$ may be similarly defined. θ^α, θ^β and ϵ^α, ϵ^β are regarded as the charges and charge densities, respectively, of the two sides of the double layer, *referred to the arbitrary surface* C; since these quantities are so referred, they are, like the G^ω, functions of x, of greatest physical interest for $x = x'$.

3. *The electroneutrality of the double layer*

From the initial assumption (p. 112) that the space bounded by the closed surface D is electrically neutral as a whole, it follows that if this space is divided into two parts by any surface whatever, as, for instance, C, the excess charges in the two parts are equal and opposite. Hence

$$\theta^\alpha + \theta^\beta = 0 \tag{10.1}$$

$$\epsilon^\alpha + \epsilon^\beta = 0 \tag{10.2}$$

i.e., the double layer as a whole is electrically neutral.

This condition of electroneutrality can be obtained in a different form as follows. Let n_i denote the number of *equivalents* of any charged component, X_i, contained within D. Then, by equation 9:

$$n_i = n_i^\alpha + n_i^\beta + n_i^\omega \tag{11}$$

Furthermore let the quantity w_i be defined by

$$w_i = \frac{z_i}{|z_i|} \tag{12}$$

where z_i denotes the valence of X_i with sign included (e.g., $z_{Ca^{++}} = 2$, $z_{SO_4^{=}} = -2$); w_i is evidently equal to $+1$ for each positively charged component and to -1 for each negatively charged component. If equation 11 is multiplied by w_i and the sum taken over all p charged components, the result is

$$\sum_{i=1}^{p} w_i n_i = \sum_{i=1}^{p} w_i n_i^{\alpha} + \sum_{i=1}^{p} w_i n_i^{\beta} + \sum_{i=1}^{p} w_i n_i^{\omega} \tag{13}$$

The term on the left vanishes because the space within D is electrically neutral as a whole, and so do the first two terms on the right because the phase interiors are electrically neutral; this leaves

$$\sum_{i=1}^{p} w_i n_i^{\omega} = 0 \tag{14.1}$$

expressing the electroneutrality of the double layer. The introduction of the surface densities of the X_i (in equivalents per unit area) defined by $\Gamma_i = n_i^{\omega}/\Omega$ into equation 14.1, gives the alternative form

$$\sum_{i=1}^{p} w_i \Gamma_i = 0 \tag{14.2}$$

4. In a perfectly polarizable system the charge of the double layer can be varied independently of the state of the interiors of the two phases

If this proposition is true for θ^{α}, θ^{β} referred to the physical dividing surface $x = x'$, it is obviously true for any other value of x. Its truth for $x = x'$ is evident from the following. Suppose there were in contact with the phase α a series of electrodes, one for each of the X_i^{α}, permitting its addition to or removal from the system. Suppose the same for β. Now through an electrode in contact with α cause Δn_i^{α} equivalents of X_i^{α} with an electric charge of $w_i^{\alpha} F \Delta n_i^{\alpha}$ (F = Faraday's equivalent) coulombs to enter the system, simultaneously introducing an equal number of equivalents Δn_i^{β} of some oppositely charged component X_i^{β} into β. Since no electrolysis can take place, the result will be that an electric charge of $w_i^{\alpha} F \Delta n_i^{\alpha}$ will distribute itself (1) along the α side of C, (2) along the free surface of α, and that an equal and opposite charge, $w_i F \Delta n_i^{\beta}$, will distribute itself similarly in β.[6] Moreover, although only one of the X_i^α be originally introduced into each phase, all of them will in general take part in this distribution (cf. equations 14.1 and 14.2). Consequently the concentrations of the X_j^α, X_j^β in the phase interiors will in general be changed by the introduction of the charges $w_i^\alpha F \Delta n_i^\alpha$, $w_i^\beta F \Delta n_i^\beta$. Finally, owing to shifting of the absorption equilibria of the X_k by the change in charge density at the double layer and at the free surfaces, the concentrations of the X_k in the phase interiors will also be changed. But the concentrations of the X_j and X_k in the phase interiors may be restored to their original values, leaving the charge of the double layer at a new value, $\theta^\alpha + \Delta\theta^\alpha$, $\theta^\beta + \Delta\theta^\beta$.

Such a process can be carried out only in the absence of electrochemical equilibrium, because otherwise electrolysis will always take place. In systems *with* electrochemical equilibrium, the state of the boundary layer including θ^α, θ^β is always *completely* determined by the state of the adjacent phase interiors.

The process described is essentially the one taking place in a Lippmann electrometer when a potential is applied, except that in the electrometer it is not necessary artificially to restore the concentrations in the phase interiors to their original values, the concentration changes produced being insignificant as long as deviations from perfect polarizability remain small.

5. *Deduction of the fundamental equations for the boundary layer and for the surface tension*

A "fundamental equation" of the Gibbsian type for the energy of the boundary layer E^ω (defined according to equation 9), will express E^ω as a function of the entropy of the boundary layer S^ω, the extent of the surface Ω, and the amounts of the various components adsorbed. In order to obtain this equation, consider the change in the total energy E of the region bounded by the fictitious surface D, figure 1, when the system as a whole is subjected to any infinitesimal change whatever, in which equilibrium is preserved. The energy change in question can be due only to (1) the heat absorbed or evolved by the system, (2) the mechanical work done on or by the system through changes in the volumes V^α, V^β and in the area Ω, (3)

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[6] The charges $\Delta\theta^\alpha$ and $\Delta\theta^\beta$ added to the two sides of the double layer will by equation 10.1 be equal and opposite. Hence the charges added to the free surfaces of α and β will also be equal and opposite; they will furthermore in general be numerically much smaller than $\Delta\theta^\alpha$, $\Delta\theta^\beta$ because charges of opposite sign tend to come as close together as possible. Therefore, the condition

$$|\Delta\theta^\alpha| = |w_i^\alpha F \Delta n_i^\alpha| = |w_i^\beta F \Delta n_i^\beta| = |\Delta\theta^\beta|$$

will be very nearly fulfilled in most cases.

the change in energy due to changes in the amounts, n_i and n_k of the components X_i and X_k respectively. Consequently

$$dE = TdS - P^\alpha dV^\alpha - P^\beta dV^\beta + \sigma d\Omega + \sum_{i=1}^{p} \eta_i dn_i + \sum_{k=1}^{r} \mu_k dn_k \tag{15}$$

P^α and P^β are the pressures of the phases α and β respectively,[6] σ is the surface tension at the boundary layer B, η_i the electrochemical potential[7] per *equivalent* of X_i, and μ_i the chemical potential per *mole* of X_k, n_i, and n_k being measured in equivalents and moles respectively. Equation 15 contains the general condition for chemical equilibrium, namely, that a particular η_i or μ_k has the same value in all the parts of the system—i.e., both in the homogeneous phase interiors and in the boundary regions—in which the corresponding component is present to an appreciable extent. Since a given X_i is appreciably present in only one of the two phases, each of the η_i refers to only one phase; the same applies to the μ_k of any X_k present in only one of the two phases.

In order to obtain from equation 15 an expression for E^ω, the following relations, all special cases of equation 9, are necessary:

$$dE = dE^\alpha + dE^\beta + dE^\omega \tag{17}$$

$$dS = dS^\alpha + dS^\beta + dS^\omega \tag{18}$$

$$dn_i = dn_i^\alpha + dn_i^\beta + dn_i^\omega \tag{19}$$

$$dn_k = dn_k^\alpha + dn_k^\beta + dn_k^\omega \tag{20}$$

and also the following equations for the energy change that each phase would undergo if it remained homogeneous up to the arbitrary surface C:

$$dE^\alpha = TdS^\alpha - P^\alpha dV^\alpha + \sum_{i=1}^{p} \eta_i dn_i^\alpha + \sum_{k=1}^{r} \mu_k dn_k^\alpha \tag{21}$$

$$dE^\beta = TdS^\alpha - P^\beta dV^\beta + \sum_{i=1}^{p} \eta_i dn_i^\beta + \sum_{k=1}^{r} \mu_k dn_k^\beta \tag{22}$$

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[6] In general, P^α and P^β are related according to

$$P^\alpha - P^\beta = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{16}$$

where r_1, r_2 are the principal radii of curvature of the boundary layer. It follows that in the special case of a plane boundary layer ($r_1 = r_2 = \infty$) represented in figure 1, $P^\alpha = P^\beta$. Equation 15 and the equations deduced from it hold independently of whether the boundary layer is curved or plane, as long as r_1, r_2 are large compared with the thickness of the boundary layer.

[7] The electrochemical potentials η_i play exactly the same rôle for the charged components of a system as the chemical potentials μ_k do for the neutral components; they were first defined by E. A. Guggenheim (J. Phys. Chem. 33, 842 (1929)). For further discussion of the electrochemical potential, see reference 8.

The substitution of equations 17 to 22 inclusive into equation 15 gives:

$$dE^\omega = TdS^\omega + \sigma d\Omega + \sum_{i=1}^{p} \eta_i dn_i^\omega + \sum_{k=1}^{r} \mu_k dn_k^\omega \tag{23}$$

Equation 23 was derived for any change at all in which equilibrium is preserved and hence is generally true. Since the preservation of equilibrium includes that of electroneutrality, the quantities n_i^ω in equation 23 cannot all vary independently but only subject to the electroneutrality condition (equation 14.1):

$$\sum_{i=1}^{p} w_i n_i^\omega = 0 \tag{14.1}$$

Aside from this restriction, however, the variables n_i^ω are all independent, and so are S^ω, Ω, n_k^ω. The number of independent variables of which E^ω is a function is thus $p + r + 1 = J + 1$[8] (cf. equation 6.1).

The simultaneous equations 23 and 14.1 constitute a general thermodynamic solution of the problem of the perfectly polarizable system.

This solution may be obtained in the form of a single equation by solving equation 14.1 for one of the n_i^ω, say n_1^ω:

$$n_1^\omega = -\sum_{i=2}^{p} \frac{w_i}{w_1} n_i^\omega \tag{24}$$

and substituting this in equation 23, giving

$$dE^\omega = TdS^\omega + \sigma d\Omega + \sum_{i=2}^{p} B_i dn_i^\omega + \sum_{k=1}^{r} \mu_k dn_k^\omega \tag{25}$$

where

$$B_i = \eta_i - \frac{w_i}{w_1} \eta_1 \tag{26}$$

It may be noted that, since the variables whose differentials appear on the right side of the "fundamental equation" (equation 25) are all independent,

$$\left(\frac{\partial E^\omega}{\partial S^\omega}\right)_{\Omega,\, n_i^\omega,\, n_k^\omega} = T \tag{27.1}$$

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[8] A proof of the theorem that in the perfectly polarizable system any extensive variable G^ω is in general a function of $J + 1$ independent variables will be given in a subsequent communication.

$$\left(\frac{\partial E^{\omega}}{\partial \Omega}\right)_{s^{\omega},\, n_i^{\omega},\, n_k^{\omega}} = \sigma \tag{27.2}$$

$$\left(\frac{\partial E^{\omega}}{\partial n_i^{\omega}}\right)_{s^{\omega},\, \Omega,\, n_{i'}^{\omega},\, n_k^{\omega}} = B_i,\; i = 2, \ldots p \tag{27.3}$$

$$\left(\frac{\partial E^{\omega}}{\partial n_k^{\omega}}\right)_{s^{\omega},\, \Omega,\, n_i^{\omega},\, n_{k'}^{\omega}} = \mu_k \tag{27.4}$$

where the subscripts $n_{i'}^{\omega}$ and $n_{k'}^{\omega}$ mean that all the variables n_i^{ω} $(i = 2, \ldots p)$ and n_k^{ω} are kept constant except the one with respect to which the differentiation is carried out.

The application of the general equations, 23 and 14.1, or 25, to the problems arising in practice is facilitated by transformation into the Gibbs-Duhem type of equation. The independent variables in equation 25 are all extensive quantities, so that E^{ω} is a homogeneous function of the first order in these variables. Hence, by Euler's theorem

$$E^{\omega} = TS^{\omega} + \sigma\Omega + \sum_{i=2}^{p} B_i n_i^{\omega} + \sum_{k=1}^{r} \mu_k n_k^{\omega} \tag{28}$$

Differentiation of equation 28 and subtraction of the result from equation 25 yields the desired relation of the Gibbs-Duhem type:

$$0 = S^{\omega}\mathrm{d}T + \Omega\mathrm{d}\sigma + \sum_{i=2}^{p} n_i^{\omega}\mathrm{d}B_i + \sum_{k=1}^{r} n_k^{\omega}\mathrm{d}\mu_k \tag{29}$$

The most convenient form of this equation is that obtained by solving for $\mathrm{d}\sigma$:

$$\mathrm{d}\sigma = -\,s^{\omega}\mathrm{d}T - \sum_{i=2}^{p} \Gamma_i\mathrm{d}B_i - \sum_{k=1}^{r} \Gamma_k\mathrm{d}\mu_k \tag{30}$$

in which

$$s^{\omega} = \frac{S^{\omega}}{\Omega},\quad \Gamma_i = \frac{n_i^{\omega}}{\Omega},\quad \Gamma_k = \frac{n_k^{\omega}}{\Omega} \qquad (31.1, 31.2, 31.3)$$

It may be mentioned that of the $p + r + 1 = J + 1$ variables whose differentials appear in equation 30, J are independent[9] if the curvature of the boundary layer is regarded as variable,[10] so that σ may in general be regarded as a function of the J variables T, B_i $(i = 2, \ldots p)$, μ_k. The decrease in the number of independent variables from $J + 1$ to J in passing from equation 25 to equation 30 is due to the fact that the variables whose differentials appear in equation 25 are extensive, whereas those whose differentials appear in equation 30 are intensive.

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[9] Proof in a subsequent communication.

[10] Cf. footnote [6], p. 121.

Finally, it is to be noted that the substitution of equation 26 into equation 30 shows that just as equation 25 is equivalent to the simultaneous equations 23 and 14.1, so is equation 30 equivalent to the simultaneous equations

$$d\sigma = -s^{\omega}dT - \sum_{i=1}^{p} \Gamma_i d\eta_i - \sum_{k=1}^{r} \Gamma_k d\mu_k \tag{32}$$

$$\sum_{i=1}^{p} w_i \Gamma_i = 0 \tag{14.2}$$

Equation 32 together with the electroneutrality condition in the form of equation 14.2 or 10.2 furnishes the best starting point for the special applications of the theory.

The fundamental equation for E^{ω} having been obtained, it is of course possible to develop the theory of the perfectly polarizable system further along Gibbsian lines, obtaining expressions for the other characteristic functions of the system. This is, however, not particularly necessary, because from the foregoing it is already evident that all the equations will be of the form of the general Gibbsian equations for any boundary layer, with electroneutrality conditions attached, the simultaneous equations obtained by keeping the electroneutrality conditions explicit (e.g. equations 23, 14.1 and equations 32, 14.2) being more symmetrical than the corresponding equations with the electroneutrality conditions implicit (e.g., equations 25 and 30).

6. *Specialization of the general equations*

(1) *Introduction of the physical dividing surface.* The general equations of the perfectly polarizable system have so far been deduced with no special assumptions as to the position of the arbitrary dividing surface C, figure 1, with respect to which the extensive properties G^{ω} and the charge of the double layer are defined. From now on all equations will be limited to the one case of physical interest, mentioned on p. 118, in which the fictitious surface C is placed within the physical barrier C′, characteristic of the perfectly polarizable system. The exact level, $x = x'$ at which C is to be placed within C′ is defined as that in which the following equations, expressing the impermeability of the barrier to charged particles,

$$\epsilon^{\alpha} = F \sum_{i=1}^{p^{\alpha}} w_i^{\alpha} \Gamma_i^{\alpha} \tag{33.1}$$

$$\epsilon^{\beta} = F \sum_{i=1}^{p^{\beta}} w_i^{\beta} \Gamma_i^{\beta} \tag{33.2}$$

are most nearly fulfilled. Γ_i^α, Γ_i^β are the surface densities (in equivalents per unit area) of X_i^α, X_i^β with respect to the level in question, and ϵ^α, ϵ^β are the corresponding charge densities of the double layer.

In order to introduce the condition (equations 33.1 and 33.2) into the general equation (32), it is expedient formally to split up the electrochemical potentials (per equivalent) of the charged components X_i^α, X_i^β as follows:

$$\eta_i^\alpha = \mu_i^\alpha + w_i^\alpha F \varphi^\alpha \tag{34.1}$$

$$\eta_i^\beta = \mu_i^\beta + w_i^\beta F \varphi^\beta \tag{34.2}$$

μ_i^α, μ_i^β are the chemical potentials of X_i^α, X_i^β, and φ^α, φ^β are the absolute electric potentials in the two phase interiors.[11] Writing equation 32 in the form

$$\mathrm{d}\sigma = -s^\omega \mathrm{d}T - \sum_{i=1}^{p^\alpha} \Gamma_i^\alpha \mathrm{d}\eta_i^\alpha - \sum_{i=1}^{p^\beta} \Gamma_i^\beta \mathrm{d}\eta_i^\beta - \sum_{k=1}^{r} \Gamma_k \mathrm{d}\mu_k \tag{35}$$

and substituting equation 34.1, equation 34.2 gives

$$\mathrm{d}\sigma = -s^\omega \mathrm{d}T - \sum_{i=1}^{p^\alpha} \Gamma_i^\alpha \mathrm{d}\mu_i^\alpha - \sum_{i=1}^{p^\beta} \Gamma_i^\beta \mathrm{d}\mu_i^\beta - F \sum_{i=1}^{p^\alpha} w_i^\alpha \Gamma_i^\alpha \mathrm{d}\varphi^\alpha - F \sum_{i=1}^{p^\beta} w_i^\beta \Gamma_i^\beta \mathrm{d}\varphi^\beta$$
$$- \sum_{k=1}^{r} \Gamma_k \mathrm{d}\mu_k \tag{36}$$

into which equations 33.1 and 33.2 may now be introduced, along with the electroneutrality condition (equation 10.2), giving

$$\mathrm{d}\sigma = -s^\omega \mathrm{d}T - \sum_{i=1}^{p^\alpha} \Gamma_i^\alpha \mathrm{d}\mu_i^\alpha - \sum_{i=1}^{p^\beta} \Gamma_i^\beta \mathrm{d}\mu_i^\beta - \sum_{k=1}^{r} \Gamma_k \mathrm{d}\mu_k - \epsilon^\alpha \mathrm{d}(\varphi^\alpha - \varphi^\beta) \tag{37}$$

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[11] It is to be noted that, as E. A. Guggenheim (J. Phys. Chem. **33**, 842 (1929); **34**, 1540 (1930)) has shown, the quantities μ_i and φ are in general thermodynamically indeterminate. According to Guggenheim, the difference, $\varphi^\alpha - \varphi^\beta$, in electrical potential between two phases is thermodynamically defined only if (i) the two phase interiors are of identical chemical composition, (ii) the two phase interiors consist of ideal solutions in the same solvent, (iii) one or both phase interiors are non-ideal solutions in the same solvent, but the deviations from ideality depend only upon the valence type of the electrolyte components (as in the theory of Debye and Hückel) and are otherwise not specific. *Changes* in $\varphi^\alpha - \varphi^\beta$ are furthermore thermodynamically defined for two phases of *any* composition if the surfaces of the phases are altered without affecting the interiors; this is possible in the perfectly polarizable system (cf. pp. 119 and 120) and also in systems where the two phases can be separated by insoluble films of various sorts (cf. A. Frumkin: Z. physik. Chem. **116**, 485 (1925)).

which is essentially the general equation (30), specialized for the physical dividing surface, $x = x'$, characteristic of the perfectly polarizable system.

(2) *Introduction of the applied potential* $\mathfrak{E}$. Imagine the phase α to be electrically connected with a piece of some arbitrary metal, Me: whether the connection is established by direct contact of α and Me, or alternatively a series of other conducting phases in contact is interposed between α and Me, is immaterial, as long as the absolute potential difference $\Delta\varphi$ across each phase boundary between the interior of α and the interior of Me depends only on the temperature, pressure, and composition of the two phases adjacent to it, i.e., as long as chemical effects and polarization effects are absent. Imagine the phase β to be similarly connected to another piece of the same metal Me. Let φ^{I} denote the absolute electric potential of the Me connected with α, φ^{II} that of the Me connected with β. Then the electromotive force $\mathfrak{E}$ between the two pieces of Me, is given by

$$\mathfrak{E} = \varphi^{\mathrm{II}} - \varphi^{\mathrm{I}} \tag{38}$$

$\mathfrak{E}$ may evidently be varied at will by connecting the two pieces of Me to the poles of a potentiometer. If, as will always be the case from now on, α is taken to be the metallic phase, β the nonmetallic phase, then the quantities defined by equation 38 are the abscissas of the electrocapillary curves of the system. $\mathfrak{E}$ may be introduced into equation 37 by writing

$$(\varphi^{\alpha} - \varphi^{\beta}) = (\varphi^{\alpha} - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^{\beta}) - \mathfrak{E} \tag{39}$$

the substitution of which into equation 37 gives

$$\begin{aligned} d\sigma = -s^{\omega}dT - \sum_{i=1}^{p^{\alpha}} \Gamma_i^{\alpha} d\mu_i^{\alpha} - \sum_{i=1}^{p^{\beta}} \Gamma_i^{\beta} d\mu_i^{\beta} - \sum_{k=1}^{r} \Gamma_k d\mu_k - e^{\alpha} d\,\{(\varphi^{\alpha} - \varphi^{\mathrm{I}}) \\ + (\varphi^{\mathrm{II}} - \varphi^{\beta}) - \mathfrak{E}\} \end{aligned} \tag{40}$$

This equation is immediately applicable to the problems arising in practice and is to be regarded as the general equation of the electrocapillary curve.

(3) *The Lippmann-Helmholtz equation.* At constant T, P^{α}, P^{β} and composition the quantities μ_i^{α}, μ_i^{β}, μ_k, $\varphi^{\alpha} - \varphi^{\mathrm{I}}$, $\varphi^{\mathrm{II}} - \varphi^{\beta}$ are constant; consequently the differentials of these quantities vanish from equation 40 along with that of T, leaving

$$\left(\frac{\partial\sigma}{\partial\mathfrak{E}}\right)_{T, P^{\alpha}, P^{\beta}, \text{composition}} = e^{\alpha} \tag{41}$$

This equation, the so-called Lippmann-Helmholtz equation, is thus shown to depend upon no assumptions save that of perfect polarizability as defined in this paper; it is, therefore, true for any perfectly polarizable system irrespective of composition.

In the determination of an electrocapillary curve by the Lippmann electrometer, the (variable) surface tension σ is measured by observing the (variable) height of a column of mercury (1) necessary to bring the boundary layer between the mercury (or amalgam) and the solution to a fixed position in the capillary of the instrument, the pressure P^β of the solution remaining constant (cf. equation 16). Actually, therefore, P^α is somewhat variable along the electrocapillary curves determined by the Lippmann electrometer, so that equation 41 does not apply rigorously to such curves. The limits of the variation of P^α are, however, small, being always such that (at constant P^β),

$$0 < P^\alpha - P^\beta < 1 \text{ atmosphere} \tag{42}$$

and within these limits the variation of μ_i^α with P^α may without appreciable error be neglected. If the μ_i^α are assumed to be constant, then $\varphi^\alpha - \varphi^{\mathrm{I}}$ is also constant, and since the electrically neutral components are in practice always confined to the solution β, whose pressure P^β remains constant, μ_k, μ_i^β and $\varphi^{\mathrm{II}} - \varphi^\beta$ are constant as before. On the assumption that the variation of the μ_i^α with P^α is negligible, equation 40 therefore gives for the slope of the electrocapillary curves determined by the Lippmann electrometer

$$\left(\frac{\partial \sigma}{\partial \mathfrak{E}}\right)_{T,\, P^\beta,\, \text{composition}} = \epsilon^\alpha \tag{43}$$

Equation 43 is the best known equation concerning electrocapillary curves and has been verified by experiment in various ways (5).

In concluding it may be mentioned that the equation 40 leads directly to the exact equations for the variation of the electrocapillary curve with the composition of the two phases; these equations will be deduced in a subsequent communication.

III. SUMMARY

1. Attention is called to a number of inconsistencies in the existing theory of the electrocapillary curve.

2. These inconsistencies are removed by developing the theory afresh, starting from only one assumption, that of perfect polarizability, which is defined in this paper as meaning impermeability of the boundary layer between two conducting phases to electrically charged particles. This definition is known to correspond closely to the actual physical conditions in the Lippmann electrometer.

3. The general equations resulting from the initial assumption of perfect polarizability are the Gibbsian equations for any boundary layer in equilibrium, with electroneutrality conditions attached.

4. The Lippmann-Helmholtz equation is found to depend upon no

assumptions whatever save the initial one of perfect polarizability; it thus holds for all perfectly polarizable systems regardless of their composition.

The author is indebted to Professor E. Lange, formerly of Munich, now of Erlangen, for calling his attention to some of the difficulties which his paper is an attempt to solve; and to Mr. E. A. Guggenheim, formerly of Copenhagen, at present Visiting Professor in Stanford University, for much valuable aid and advice.

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NEW BOOKS

Flotation. By A. M. Gaudin. 552 pp.; 145 illustrations; 20 chapters. New York and London: McGraw-Hill Book Co. Inc., 1932. Price: $6.00.

An introduction, written for this book by Dean Theodore J. Hoover, of Stanford University, who wrote the first book on flotation almost twenty-five years ago, states that, "One of the outstanding merits of this book is that it much more fully than any previous attempt gives a practically complete exposition of the scientific principles underlying a process which is treating millions of tons of ore every year."

The author also drew assistance from the other writers of books on flotation, including the present reviewer, who, with the distinguished T. A. Rickard, prepared the second book on flotation about seventeen years ago; the book is dedicated to the author's former teacher, Professor A. F. Taggart, of Columbia University, who prepared the third major treatise in English on flotation at a much more recent date. The result of many suggestions and much criticism before printing has justified Hoover's estimate of the book.

Theory, description, practice, economic effects, are all included. While readers of This Journal are not greatly interested in "Pointers on Mill Design," "Elements of Costs," or "Machinery," there are many chapters on the theory of the process and the technical problems in its application which carry a message.

With rare exceptions the researchers on flotation as a method of ore concentration have not been physical chemists and were inadequately prepared to study a phenomenon which is essentially a problem in physical chemistry. The author himself is not a physical chemist, but has striven faithfully to remedy that defect and has called in the help of many physical chemists, so that his theories might have the background least liable to criticism. The trouble with the periodical literature has been that the physical chemists did not know much about flotation, and the flotation engineers did not know enough physical chemistry. The result has been a flood of near-worthless papers on the theory of the subject.

Gaudin's book goes far toward remedying this defect and starts off with chapters on the following subject: "The Physicochemical Foundations of Flotation," "The Phases in Flotation Systems," "Colloid Systems," "Flotation Reagents," and "The Mechanical Aspects of Froth Production." The physicochemical problem in flotation is first of all to produce a suspension of finely ground ore in water to which is added reagents that will produce froths of the desired consistence and life. Secondly, other reagents must be added which will cause the desired minerals to cling to the bubble interfaces so that they will concentrate in a froth layer or the upper surface of the ore pulp. From a colloid standpoint it is a problem more or less of differential flocculation, attachment of certain classes of mineral particles to bubble surfaces being a function of the degree of flocculation of desired minerals and of gangue minerals. To alter the surface films on particles that normally are not easily floated until they are susceptible of flotation concentration is another problem in physical chemistry.

This book is a good start in the direction of discarding misapprehensions and misapplications of science to a process whose application in industry long ago outdistanced its scientific explanation.

Oliver C. Ralston.

Les Sciences Geologiques et la Notion d'État Colloidal. By Pierre Urbain. "Actualités Scientifiques et Industrielles, No. 69. Exposés Geochemie. Paris, 1933.

The origin and definition of the term "colloid" are given. The first part of the paper consists of a general discussion of the colloidal state. Colloids are heterogeneous and represent transitions between true solutions and suspensions, and it is impossible to define rigidly the concentration of a colloidal solution. Such a solution is preferably designated as a "pseudo solution." Mixed systems are frequently found, the same substances furnishing crystalline particles, colloidal particles, and dissolved molecules. Silica is cited as an example.

The second part of the paper is concerned with the principal natural colloids. Colloidal phenomena are common in the alteration of minerals near the surface of the earth, but the colloidal form is always transitory and crystalline material is eventually formed. The principal natural colloids are silica, aluminum hydroxide, and iron hydroxide.

Kaolinization is the most universal process in which colloidal minerals are developed. This process attacks the great number of aluminosilicates found in igneous and metamorphic rocks and it frees the alkalies and alkaline earths which then form bicarbonates in superficial waters. Hydrated aluminum silicates are formed and excess silica freed. In laterization the aluminosilicates are destroyed with the elimination of silica and the formation of aluminum and ferric hydroxide. It is suggested that laterization may be due to the decrease in the solubility of carbonic acid with the increase in temperature, since laterites are found mainly in tropical regions. The pH content is important in this connection.

Sodium chloride is an important coagulant of silica in weak solutions; also of clay and limonite where rivers empty into the sea.

The ability of colloids to adsorb plays an important rôle in the elimination of alkalies liberated by the process of kaolinization. Potassium and sodium are present in nearly the same amount in the average rock, but in river and ocean waters sodium is several times as abundant as potassium. This is said to be be due to adsorption of the potassium in preference to sodium. Potassium is favored in the formation of aluminates. Thus potassium is much more abundant than sodium in clays and even in average sedimentary rock. It is concluded that in nature potassium is sixteen times more adsorbable than sodium.

The origin of chalk in the Paris basin is reviewed and the rôle of colloids discussed. Silica and its relation to colloidal processes is briefly discussed. Varieties of silica originally colloidal are opal, chalcedony, and quartz.

Only two varieties of hydrous ferric oxide are recognized, goethite and lepidocrocite, both with the formula $Fe_2O_3 \cdot H_2O$.

The use of the term "metacolloid," suggested by Wherry for microcrystalline minerals originally colloidal, is approved. Lindgren's list of the principal natural amorphous gels and metacolloids is given. Criticisms are given of some of the minerals included and some of those left out and the general significance of the group is discussed. Finally several good microphotographs of rocks of colloidal origin are included in the plates at the end of the paper.

G. M. Schwartz.

Jahrbuch des Forschungs-Instituts der allgemeinen Elektricitätsgesellschaft. Dritter Band, 1931–32. 29.5 x 21.5 cm.; 205 pp. Berlin: Julius Springer, 1933.

The third volume of this important yearbook covers so wide a field that it is impossible to analyze its contents briefly in any connected manner. The simplest way of giving to the readers of This Journal some knowledge of the topics treated is to append a list of the titles of the papers which make up the volume: (1) Die Entwicklung des Tonfilmverfahrens der AEG; (2) Verbesserungen des Zeitdehners und Anwendung in der Aufnahmepraxis; (3) Zur Elektrotechnik der Entladungsgefässe; (4) Zur Physik der Entladungsgefässe; (5) Gaskonzentrierte Elektronenstrahlen und ihre Anwendung; (6) Geometrische Elektronenoptik; (7) Mitarbeit der AEG an der Nordlichtforschung; (8) Untersuchungen uber das Wesen des Elektrons; (9) Wirkung neutrales Gasmoleküle gegenüber langsamen Elektronen und langsamen Protonen; (10) Über die physikalischen Grundlagen der Ionentherapie; (11) Neuartige Werkstoffe für Pupinspulen; (12) Einzelarbeiten des metallurgisch-magnetischen Laboratoriums; (13) Neue magnetische Messmethoden; (14) Beiträge zur Physik der Nitrobenzol Kerrzelle; (15) Über lichtelektrische Alkalizellen.

This table of contents will serve to give some notion of the very varied fare presented, and those interested in any special subject can judge whether any topic of importance to them is discussed in this volume. It is hardly necessary to say that the subjects are handled in a very thorough and interesting fashion, and the volume, both in content and in the matter of mechanical production, is a worthy record of very important work.

ALLAN FERGUSON.

Molecular Rays. By RONALD G. FRASER. xii + 204 pp.; 78 figs. Cambridge University Press. New York: The MacMillan Company.

This book is one of the Cambridge series of physical chemistry under the editorship of E. K. Rideal. The book is of the sort that the English seem to do unusually well, being an account of the technical methods and state of progress in research involving the molecular ray technique. The author spent some time in Stern's laboratory at Hamburg and is qualified by training and experience to write such a manual. He naturally gives a great deal of prominence to the Hamburg laboratory and very properly so, since the molecular ray technique was originated by Professor Stern and its most important applications have been made by him. The consideration given to work along this line in American laboratories is all that could be expected from a book written on the other side of the water. The trend of recent events indicates that molecular ray research may become peculiarly an American institution. The only defect to be noted in the book is the lack of a bibliography.

W. H. RODEBUSH.

Some Physical Properties of the Covalent Link in Chemistry. By NEVIL VINCENT SIDGWICK. 23 x 15 cm.; 249 pp. Ithaca, New York: Cornell University Press, 1933. Price: $2.00.

The volume under consideration is based upon a series of lectures given at Cornell University by the author while he held the George Fisher Baker Non-resident Lectureship during the second semester of 1930–1931.

Owing to the high degree of specialization in chemistry, it is rare to find a chemist who has succeeded in achieving a comprehensive grasp of the science as a whole. Professor Sidgwick is one of the most distinguished of these few. In the present work he has brought together bits of information gathered from the most diverse sources and has interpreted them with reference to their bearing on our conception of the nature of the covalent bond. The result constitutes a classic treatise—the purpose of which is expressed by the author in the following characteristically modest fashion. "The book is an attempt to set out the methods of measurement of some of the more important properties of non-ionized links, and to discuss the results so far obtained." "I have tried to include the more important researches bearing on these questions which have appeared up to the summer of 1932, and a few later ones of special interest."

Following an admirable introductory lecture on the relation of physics to chemistry, the following topics are treated: atomic cohesion; electrovalence and covalence; dimensions of covalent links; heats of formation of covalent links; electrical dipole moments; stereochemistry.

The material presented is of the greatest interest to chemists of every persuasion, and it has been treated in a manner which renders it readily understandable even by those who are not familiar with the original sources from which the work is drawn. The book is highly recommended to all serious students of chemistry.

Reynold C. Fuson.

Die Bedeckungstheorie der Passivität der Metalle und ihre experimentelle Begründung. By W. J. Müller. 23 x 16 cm.; 102 pp. Berlin: Verlag Chemie, 1933. Price: paper, 6 marks; bound, 7 marks.

The study of anodic behavior, which has been made by W. J. Müller and his pupils at Vienna over a period of several years, is well-known to all who are interested in the corrosion and passivity of metals. No adequate description of this work exists, other than the large number of experimental papers which have emanated from Müller's laboratory, so that the present book, which describes all the essential matter in a compact form, will be welcomed.

It should be pointed out, however, that the scope of the book is precisely as indicated by the title; that is to say, it is essentially a monograph devoted to the author's own contributions to the subject, and scant mention is made of other views. The book is in no sense a balanced dissertation on passivity, and much work on anodic phenomena which has been carried out by other investigators, and which definitely has a bearing on Müller's work, is passed over with a mere reference.

After demonstrating Müller's most striking contribution to the subject—that anodic passivity is a time phenomenon—the author formulates equations which represent the laws of sideways-growth and thickening of the film, relates these to specific anodic systems, and incidentally uses the results to explain the rectifying action of the aluminum electrode.

The book is well illustrated with photomicrographs and diagrams and can be commended as a valuable addition to the literature on passivity.

E. S. Hedges.

Infra-red Photography. By S. O. Rawling. 13 x 19 cm.; x + 57 pp. London: Blackie and Son, Limited, 1933. Price: 3s. 6d.

The recent introduction of easily handled infra-red plates by the leading manufacturers of photographic materials has rendered possible the application of infra-red photography to long distance and aerial photography, chemical record work, detection of forgery, photomicrography, and spectroscopy. The author has written an admirably clear account of the handling and applications of the new commercial plates. The chapters which deal with the choice of suitable safelights, light filters, lenses, and photographic apparatus should be carefully read by all who use, or intend to use, infra-red photography for any purpose whatever. In particular it will surprise most photographers to learn that leather camera bellows and the various woods used in the construction of dark-slides may transmit sufficient infra-red radiation to cause fogging of the sensitive material.

The value of the book is enhanced by the inclusion of a number of excellently reproduced photographs.

Edwin E. Jelley.

THE ELECTROKINETIC (ZETA) POTENTIAL OF THIN METAL FILMS[1]

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One of the problems in the study of the electrokinetic potential has been the proof that the potentials as measured are different from the thermodynamic potentials of Nernst. The development of the glass electrode by Haber and Klemensiewicz enabled investigators to compare the potentials of this electrode in various solutions of electrolytes with the potentials obtained by streaming the same solutions through glass capillaries made from the same glass as the glass electrode. Measurements of this kind have shown a real difference in the values of the potential as measured by the two methods. The glass electrode behaved essentially as a hydrogen electrode, while the measurements of potentials by streaming solutions through glass capillaries showed that these potentials were sensitive to small changes in ion concentrations, especially if the ions were polyvalent. In addition it has been shown that the glass electrode is far from a simple system. As a result it is doubtful whether a real comparison can be made between the two potentials by the use of glass. The desirability and importance of finding a simple metal-solution system for streaming potential study becomes clearly evident.

Previous work in this laboratory has shown that silica gel could be metallized so that the extensive surface of the gel was well covered by a metal deposit. The evidence further showed that metal layers could be made thick enough to show the crystal structure of the metal in x-ray studies. Accordingly it was felt that such metallized gels might be used in streaming potential measurements and that a direct comparison with the thermodynamic potential thus could be obtained. The gel itself would act as an insulator having the metal film on it. In the following investigation, streaming potential measurements are reported for nickel and silver surfaces in solutions containing the ions of the metals used. These metals were chosen so as to have one metal above and the other below hydrogen in the electromotive force series. The results on two such metals would

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[1] The material here presented formed a part of a thesis submitted to the graduate faculty of the University of Minnesota by Grant W. Smith in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1932.

more nearly answer the question of the similarity or dissimilarity of the two potentials.

EXPERIMENTAL PROCEDURE

The metallized silica gels were prepared by allowing a purified silica gel to adsorb the complex ammonia ions of silver, $Ag(NH_3)_2^+$, or of nickel, $Ni(NH_3)_4^{++}$, from an aqueous solution. Silica gel adsorbs these cations very strongly, 1 g. of silica gel adsorbing as much as 0.32 g. (1.692 millimoles) of the silver complex and 0.31 g. (1.10 millimoles) of the nickel complex.[3] After adsorption had reached equilibrium the liquid was drained from the gel, the gel was dried, and finally heated in a current of hydrogen until the complex salt in the gel was reduced and the metal left in a free state on the surface of the gel. The product was a deep black, and microscopic examination of the granule showed no uncovered silica surfaces.

In order to make sure that the metallized gels were sufficiently coated, they were analyzed by means of x-rays. Using copper radiation, definite patterns of the metals deposited on the gel were obtained. Silver wire and nickel wire produced patterns which were identical with those of the corresponding powdered gels. The lines of the nickel gel were faint but definite. Both gels gave broader lines than the metal wire, indicating that the metallic film was very thin and of approximately colloidal dimensions.

The apparatus used in this investigation consisted of three essential parts: a diaphragm of finely divided material packed between two perforated electrodes, with a system for forcing the liquid through the diaphragm under known hydrostatic pressures; a potentiometric device for measuring the E.M.F. developed between the two electrodes; and a conductivity bridge.

The streaming potential cell was of the same general type as that used by Briggs, except that some of the dimensions were altered to suit the particular case at hand. The ring in which the diaphragm material was packed was made of clear Bakelite, furnished by the Bakelite Corporation. Its outside diameter was 4.5 cm.; its inside diameter, 3.5 cm. It was 2.5 cm. in width. The two electrodes were made to fit on either side of the ring. They were of 14 K gold, 4.5 cm. in diameter and 1 mm. thick. The electrodes were perforated with 0.5 mm. holes to within 0.5 cm. of the circumference, the holes lying as closely together as they could be drilled without weakening the electrodes too much. A platinum wire was soldered with gold solder to the edge of each electrode to form a connection with the electrical measuring instruments. The two flared tubes which formed the rest of the cell were made of Pyrex glass. The cell was assembled with thin rubber gaskets to insure against leaks, and the whole was clamped tightly together with a specially constructed clamp.

[3] Unpublished results of a series of similar experiments in this laboratory confirm the strong adsorption of complex ammonia ions in ammoniacal solution.

Figure 1 shows the complete cell and pressure system. Z is the zeta potential cell which has just been described. M is a mercury manometer by which pressures up to about 80 cm. can be read. N is a cylinder of nitrogen which was used to supply the pressure on the streaming liquid; V is a reducing valve for controlling the pressure. S_1, S_2, S_3, and S_4 are stopcocks, and A_1 is a "valve" controlled by a screw clamp. F_1 is a 5-liter Pyrex flask in which the liquid which is to be streamed through the cell is placed. It is fitted with a three-hole stopper through which go the inlet tube from the pressure line, the outlet tube to the cell, and a closed-end glass tube holding a piece of ruled paper for measuring the water level. E is a clamp. F_2 is another 5-liter flask which is used to catch the waste liquid from the cell. C is a piece of flexible metal tubing which is grounded, and is used to carry off the waste liquid after it has streamed through the cell. This was found to be necessary, for the flow of liquid down a glass tube caused very disturbing electrical effects. D is a sulfur block holding two mercury cups in which dip the leads from the cell and from the measuring instruments. A and B are "rocker" switches, consisting of mercury cups set in sulfur blocks. B is a reversing switch which reverses the direction of the E.M.F. of the cell with reference to the potentiometer in the circuit. When A is to the left, the cell is in the circuit of the conductivity bridge; when it is to the right, the cell is in the potentiometer circuit. H_1 shows the leads to the bridge, while H_2 shows those to the potentiometer. GS is

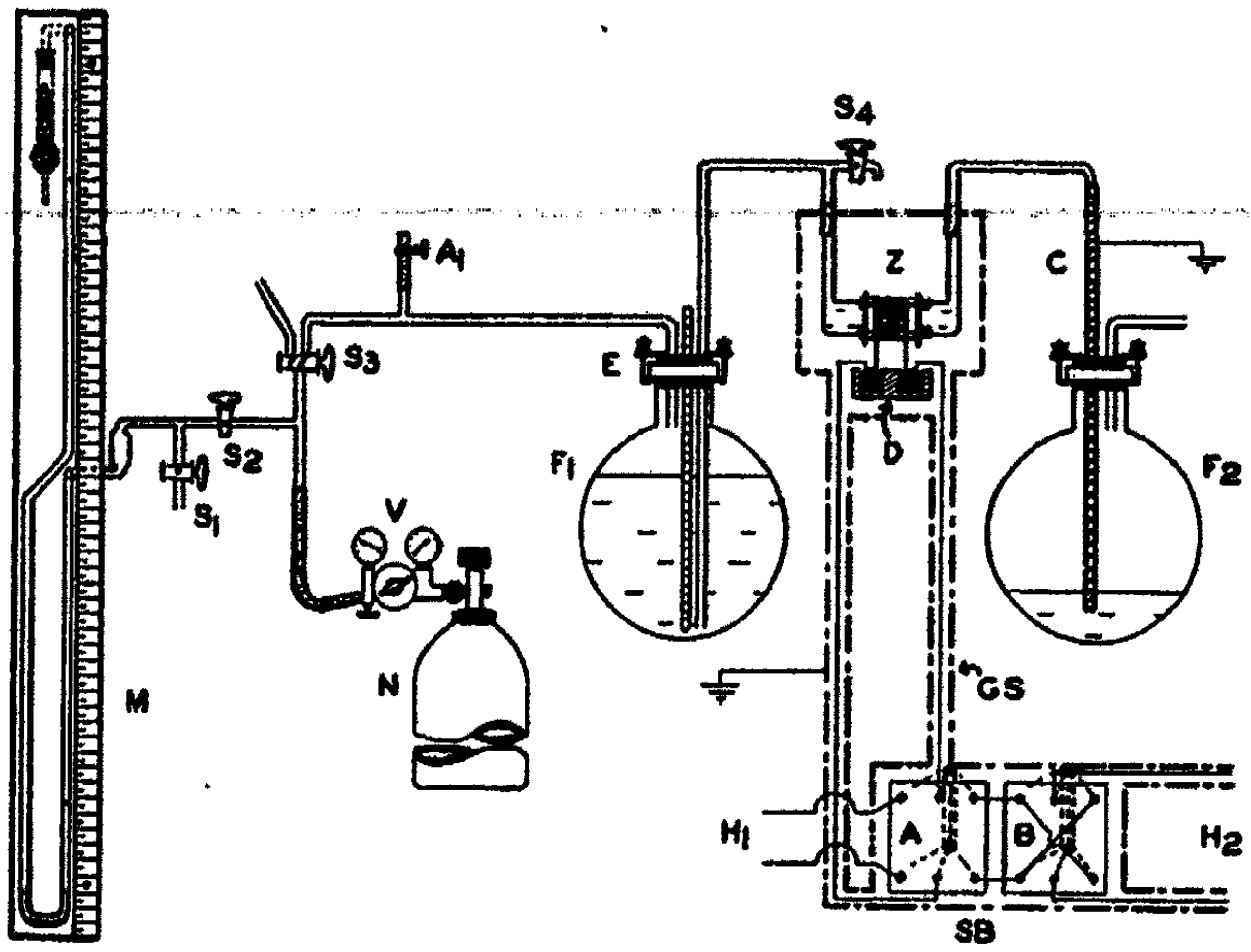

FIG. 1. THE COMPLETE CELL AND PRESSURE SYSTEM

grounded shielding about the leads from the cell, the cell itself, and the switches, A and B. The shielding about the lead wires consists of 1½ inch brass tubing. The cell is shielded with copper gauze. The switches are in a copper switch box, SB, made of copper sheeting.

It was originally intended to use a quadrant electrometer as the null instrument in the measurement of the E.M.F. of the cell, but vibrations in the room used for this investigation made it impossible. Several cushion and suspension mountings were tried without avail. A vacuum tube potentiometer was then built for the purpose. The circuit used was much the same as described by Fosbinder (4) (see also Nottingham (6)). The set-up as constructed employs a potentiometer as a null instrument, and a screen grid vacuum tube as amplifier. It draws only a negligible amount of current from the cell during adjustment and no current at all at the balance point. Furthermore it is not affected by ordinary mechanical vibrations.

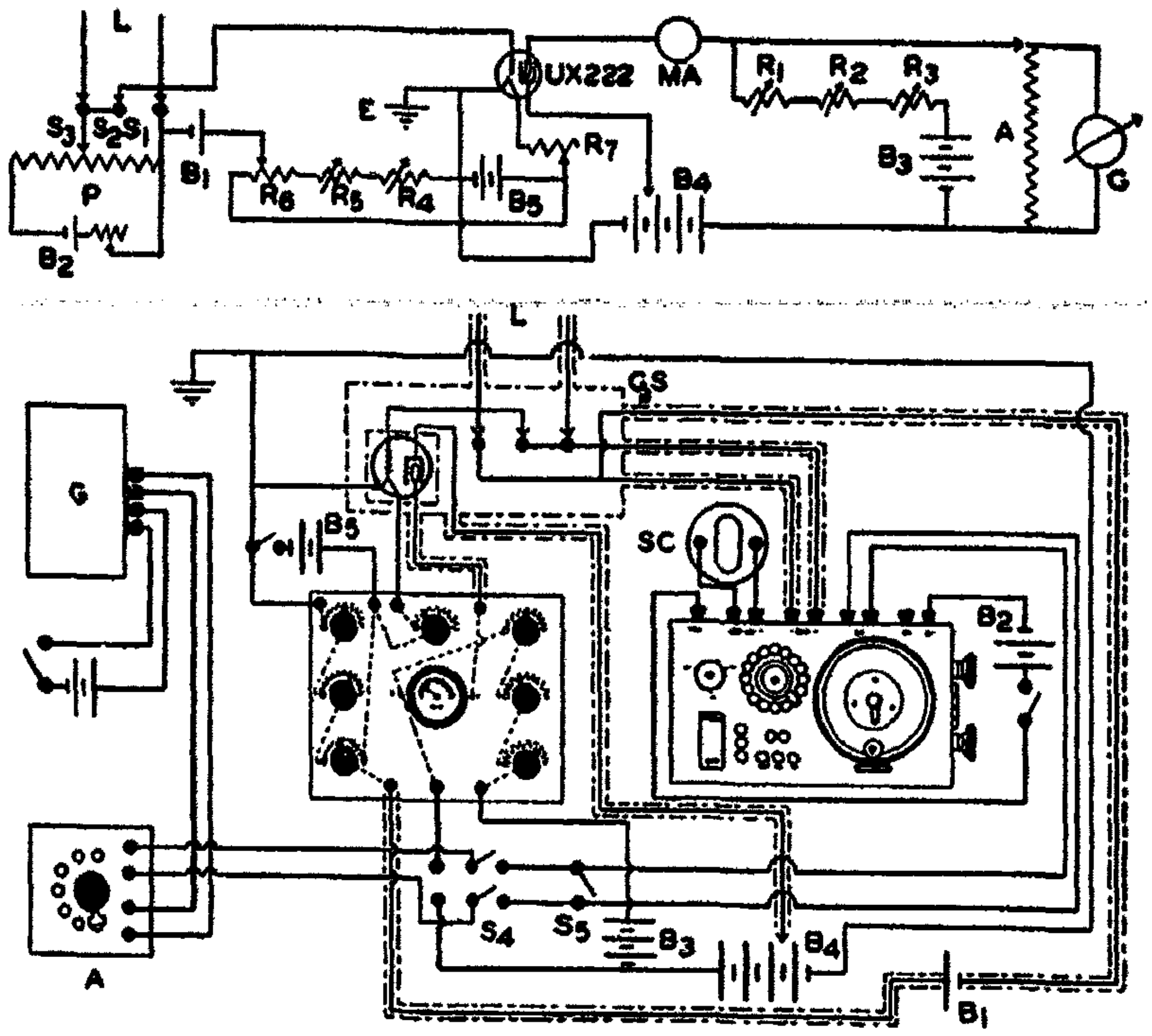

FIG. 2. THE ELECTRICAL CIRCUIT AND THE WIRING DIAGRAM

Figure 2 gives both the electrical circuit and the wiring diagram. The principle of operation is as follows: With the grid circuit open, the plate current through a sensitive galvanometer (G) is adjusted by means of a shunt resistance and battery (R_1, R_2, R_3, and B_3) until there is no galvanometer deflection. Now the grid circuit is closed by means of a switch (S_1), and adjusted by a shunted resistance and battery (R_4, R_5, R_6, and B_5) until there is again no deflection on the galvanometer in the plate circuit. This adjustment has brought the grid to the same potential it was at when the grid was open, i.e., at "floating potential," as it is sometimes called. The switch (S_1) is now opened, and another switch (S_3) is closed, which brings the cell and the potentiometer into the grid circuit. The potentiometer is now balanced against the cell in the usual manner, until there is again no galvanometer deflection, and the reading on the potentiometer is the potential difference across the cell. No current is drawn from the cell at the balance point, for the grid is always at "floating potential" just as though it were an open circuit, i.e., as though the resistance of the grid circuit were "infinite" as it was when the first adjustment was made.

The vacuum tube is of the screen grid type, UX 222. MA is a milliammeter with a full scale deflection of 1.5 milliamperes; during use this reads about 0.5 milliampere. R_1, R_2, and R_3 are radio rheostats with resistances of 10,000 ohms, 5,000 ohms, and 100 ohms, respectively. R_4 and R_5 are 6-ohm and 100-ohm rheostats, and R_7 is a 30-ohm rheostat. R_6 is a radio potentiometer of 2000 ohms resistance. B_1 is an ordinary dry cell. B_2 is the potentiometer battery, two dry cells in series. B_3 is a 4.5-volt battery composed of nine dry cells in series-parallel. B_4 is the plate battery, two heavy duty 45-volt "B" batteries. B_5 is a lead storage battery of 6 volts. A is a Leeds and Northrup 40,000 ohm Ayrton shunt. G is a Leeds and Northrup #2420c galvanometer. L indicates the leads to the zeta potential cell (see H_2, figure 1). P is a Leeds and Northrup Type K potentiometer. S_1, S_2, and S_3 are specially constructed switches of small electrical capacities. SC is a Leeds and Northrup Weston standard cell, #7307. S_4 is a double throw double pole switch by means of which the galvanometer may be brought into the Type K potentiometer circuit so that the latter may be checked with the standard cell, or into the vacuum tube plate circuit. When S_4 is in the latter position, S_5 must be closed to short the galvanometer connections on the Type K potentiometer. GS is grounded shielding, indicated throughout the wiring diagram by broken lines. The wire leads are shielded with metal tubing. The switches, S_1, S_2, and S_3 are enclosed with the vacuum tube in a large copper box, and are controlled from outside conveniently by means of threads which run over pulleys to some little distance from the box. The vacuum tube is mounted on a cast sulfur base, inside a small copper box which is suspended by rubber bands in the larger copper box which also encloses the switches mentioned above. It was found necessary to shield all vital parts carefully, as shown in the diagram. The whole apparatus was shielded as completely as was practical by building a large "cage" of copper gauze about it. The potentiometer was found to be very satisfactory in this work, being unaffected by vibration in the building. It proved to be very sensitive also, for a change of 0.0001 volt on the potentiometer from the balance point was easily detected on the galvanometer.

Figure 3 shows the conductivity bridge. The arrangement is adapted from the Wheatstone bridge circuit used by Jones and Josephs (5). The apparatus was modified in several particulars, but the working principle is the same. The oscillator is shown at O; it is a vacuum tube oscillator, and although it was constructed so that it created little external field, it was placed at a distance of about ten feet from the rest of the apparatus. T_1 is a "power tube," UX 171 A. B_1 is the filament battery, a 6-volt storage or Edison battery. B_2 is a "B" battery of 67.5 volts. L_1, L_2, and L_3 are the grid, plate, and output coils, respectively. They are wound about an iron core, with #30 B & S gauge enameled wire, and mounted in a copper box to shield them from the rest of the apparatus. The plate coil, L_2, is tapped in four places, and by means of the multiple switch shown in the diagram the pitch of the sound may be varied readily. C_3 is a fixed condenser of 0.11 microfarad capacity, found suitable by trial.

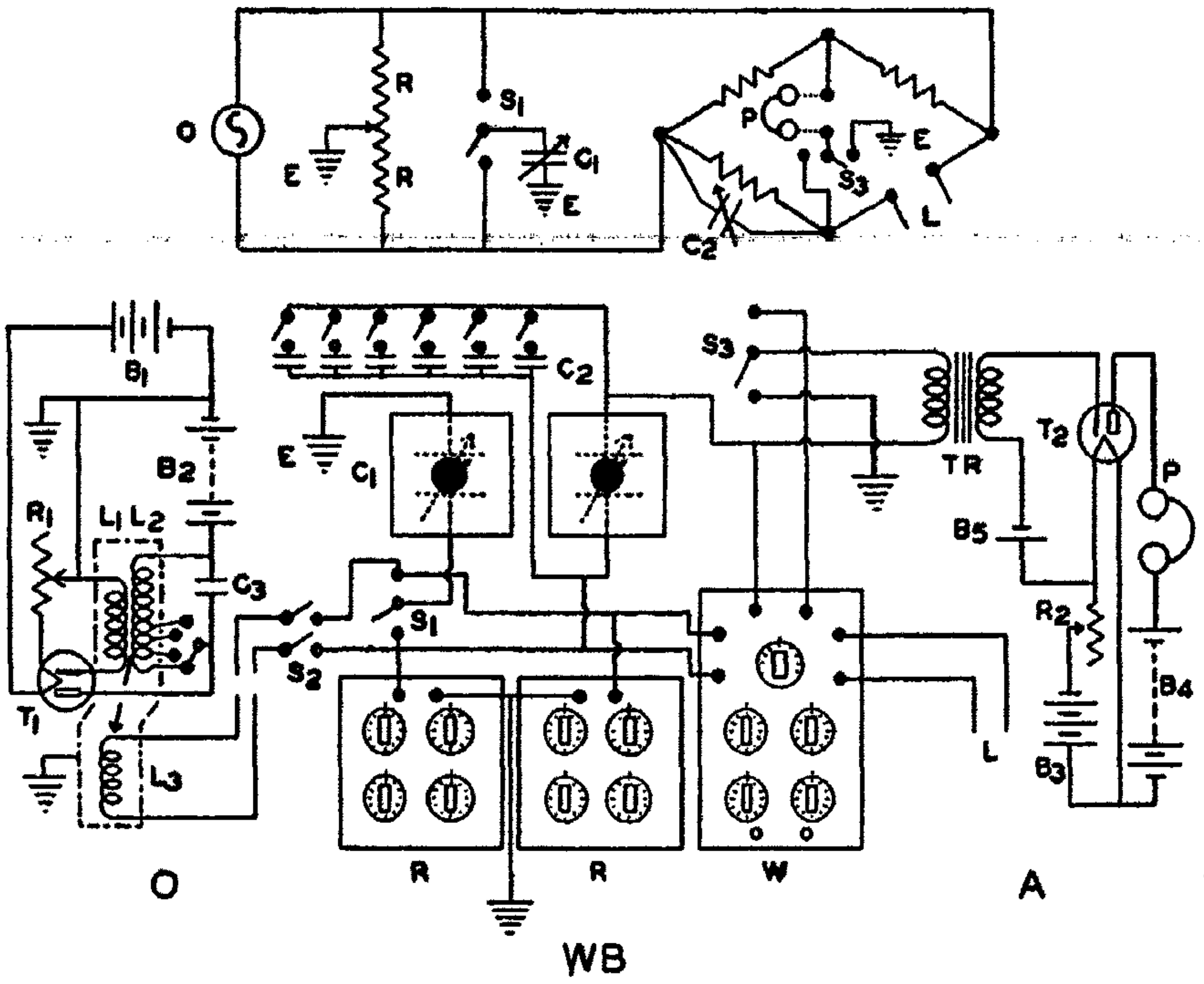

FIG. 3. THE CONDUCTIVITY BRIDGE

A vacuum tube amplifier is shown at A. T_3 is a UX 201 A tube. B_3 is a 6-volt storage battery; B_4 is a "B" battery of 90 volts. P is a set of phones. TR is an audio transformer of four to one ratio.

The Wheatstone bridge itself is at WB. W is a Wheatstone bridge of the dial type, equipped with a multiplier. R and R are variable resistances of 10,000 ohms each. C_1 is a variable condenser of 0.0005 microfarad capacity. C_2 is a variable capacity consisting of seven condensers in parallel: a variable capacity of 0.0005 microfarad, and six fixed condensers of respective capacities, 0.0005, 0.001, 0.002, 0.002, 0.004, and 0.1 microfarad, so that any desirable values from 0.0 to 0.02 microfarad may be obtained by manipulating the switches properly. S_3 is a switch used to connect the phones either to earth or to the bridge, as shown. L indicates the leads to the cell (see H_1, figure 1). The operation of the bridge is as follows: With S_3 in position so that the phones are in the bridge circuit, the bridge, W, and the capacity, C_2, are adjusted so that the sound is as near a minimum as possible; S_3 is then thrown to the other position, grounding the phones, and the resistances, R, R, and the condenser, C_1, are adjusted until the sound is again a minimum. This adjustment brings the phones to earth potential. Now S_3 is put back in its original position, and W and C_2 further adjusted until a minimum is reached. If the position of W is much different from its former setting, the process should be repeated. In this manner, a very distinct minimum point is obtained. The two points on the bridge (see upper diagram) which are joined to the phones are now both at earth potential, and noises which are due to the difference in potential between the phones and the earth are eliminated. In fact, in the operation of this conductivity bridge, a point of dead silence was practically always obtained at a very sharply defined dial position on W. The resistance can be determined accurately to four figures, and the multipliers on W can be used for very large or very small resistances.

The water which was used for streaming through the cell and for making all solutions was conductivity water which was reboiled just before use. Its specific conductivity at room temperature ranged between 0.9×10^{-6} and 1.6×10^{-6} mhos, and was generally about 1.1×10^{-6} mhos. Mallinckrodt's "Reagent Quality" nickel nitrate and silver nitrate were used without further purification for making up the streaming solutions. Since from three to five liters of solution were prepared for each streaming potential run, they could be made up with considerable accuracy even though the concentrations were only fractions of millimoles per liter. The volumetric apparatus and the weights used to weigh the salts were calibrated. The greatest care was exercised at all times to prevent contamination of the water and solutions while handling, and the air over the liquids was displaced by nitrogen from the pressure tank (N, figure 1) as soon as they were placed in the apparatus in preparation for a run.

The diaphragm was prepared in the following manner. The diaphragm material, i.e., the silica gel, was ground in an agate mortar and separated by screening into four groups according to size, (1) larger than 28 mesh, (2) between 28 and 65 mesh, (3) between 65 and 200 mesh, and (4) smaller than 200 mesh. The diaphragm was made up almost entirely of the finest material (4). The coarser gels were used only to fill in the holes in the electrodes so that the finely powdered material would not be washed away when the liquid was forced through the cell. That is, right next to the electrodes on either side, was, first, a thin layer of the coarsest gel, followed by a thin layer of the next size, and then a layer of the next finest gel. With the holes well stopped in this manner, the rest of the diaphragm was made up with the gel of finest particle size. This was kept moist with pure water and packed very tightly.

METHOD OF MAKING A RUN

The cell was now assembled in place as shown in figure 1. The water or aqueous solution was put into the reservoir flask (figure 1, F_1) and the air above it displaced by nitrogen. By applying pressure, the liquid was then streamed through the cell at a very slow rate for at least twenty-four hours before any readings were taken. It was found that about this length of time was required for the diaphragm and liquid to reach equilibrium. If too short a time were allowed for this operation, reproducible stream potentials could not be obtained. It is to be noted that, owing to the porous nature of the diaphragm materials, a considerably longer time was required for equilibrium conditions to be set up than would be the case with such materials as glass, quartz, cellulose, and other substances which have been used hitherto in streaming potential work.

About twenty minutes were required for the potentiometer to reach a steady state so that readings could be made. The liquid was streamed through at a given pressure until at least three consecutive readings in good agreement were obtained over a period of several minutes. Immediately after measurement of the E.M.F. the mercury manometer was read, the difference in level between the liquid in the reservoir and the liquid leaving the cell was taken (pressure correction), the temperature read, and the conductivity was measured by switching the cell over to the bridge circuit. The pressure was then changed and the process repeated. The potentiometer was frequently checked with the Weston standard cell. Since the laboratory in which this work was done was an inner room, the temperature was quite constant, and was always near 25°C.

After all of the desired runs were made upon any one diaphragm, the cell constant was determined by streaming a standard $N/50$ potassium chloride solution through it until a constant resistance was reached. The specific conductivity of the liquid in the diaphragm could then be calculated for each run.

RESULTS

The values of the electrokinetic (zeta) potential are calculated according to the expression used by Briggs (1),

$$\zeta = \frac{4\pi\eta H\kappa_s}{P\epsilon} \qquad (1)$$

where H is the electromotive force set up across the diaphragm, κ_s is the specific conductivity of the liquid in the diaphragm, η the viscosity of the solutions, P the hydrostatic pressure, and ϵ the dielectric constant. Using the proper constants at 25°C.,

$$\zeta(\text{volts}) = 97.165 \times \frac{H\kappa_s}{P} \qquad (2)$$

where H is measured in millivolts, κ_s in reciprocal ohms, and P in centimeters of mercury. Bull and Gortner (2) suggest, in view of the existing doubt as to the correct value of the dielectric constant which should be used in the formula, that the value of the electric moment of the double layer be used to express the capillary electric conditions at the interface instead of the electrokinetic potential. The electric moment of the double layer is equal to the charge per unit area multiplied by the distance between the layers. This expression was met in the derivation of the formula for the streaming potential. It is

$$qd = \frac{\zeta\epsilon}{4\pi} \qquad (3)$$

If the value of ζ from equation 1 be substituted in equation 3 we obtain the following expression for the electric moment

$$qd = \mu = \frac{\eta\kappa_s H}{P} \qquad (4)$$

Thus the value of the dielectric constant has been eliminated from the calculation. In the tables given in the following sections the values of ζ are negative unless otherwise indicated. The value of the electric moment μ was also calculated and included in the results. The negative value of ζ means that the fixed wall bears a negative charge with reference to the movable liquid layer.

In the preliminary measurements purified silica gel was used for the diaphragms. The H/P ratio was found to be constant at pressures above about 25 cm., but the values fell at lower pressures. Bull and Gortner (3) ascribe a similar result on their quartz diaphragms to a difference in the size of the particles composing the diaphragm. In the present case the fall in H/P values in the low pressure range may be attributed logically to the porous character of the material, rather than to variations in particle size. It was found that gels prepared under different conditions gave different potential values, so that samples of the same gel were used throughout the entire investigation. Table 1 gives a typical set of determinations on pure silica gel.

TABLE 1

ζ-Potential of water–silica gel

$t = 24.9°C$. Average $\kappa_s = 2.04 \times 10^{-5}$

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
72.6	153.8	2.12	4.2
53.4	115.2	2.16	4.3
52.0	112.0	2.15	4.3
58.9	125.5	2.13	4.2
48.5	103.8	2.14	4.2
37.3	78.5	2.11	4.2
22.0	48.5	1.97	3.9
11.6	17.7	1.53	(3.0)
12.3	18.9	1.54	(3.0)

TABLE 2

ζ-Potential of water–nickel

$t = 24.8°C$. Average $\kappa_s = 2.6 \times 10^{-5}$

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
47.2	110.0	2.33	6.0
69.6	172.8	2.48	6.3
69.3	172.7	2.49	6.3
55.5	134.0	2.41	6.2
54.9	132.0	2.40	6.1
30.4	67.7	2.22	5.7
29.7	65.9	2.22	5.7
18.1	37.6	2.08	(5.3)
38.6	88.9	2.30	5.9
Average..................			6.0

TABLE 3

ζ-Potential of N/10,000 nickel nitrate–nickel

$t = 25.4°C$. $\kappa_s = 4.47 \times 10^{-5}$

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
48.7	74.8	1.54	6.6
47.9	72.8	1.52	6.6
65.8	95.6	1.45	6.3
65.6	95.2	1.45	6.3
75.5	113.0	1.50	6.5
Average..................			6.5

TABLE 4

ζ-Potential of N/5000 nickel nitrate–nickel

$t = 25.4°C$. Average $\kappa_s = 5.09 \times 10^{-6}$

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
49.3	58.4	1.19	5.9
73.5	86.4	1.18	5.8
72.9	85.0	1.17	5.8
52.0	61.4	1.18	5.8
63.9	74.2	1.16	5.7
34.5	41.6	1.20	5.9
25.8	31.4	1.21	6.0 (over)
Average.............			5.9

Following the preliminary determinations of the electrokinetic potentials of water–silica gel, it was decided to limit the present investigation to the study of gels metallized with nickel and with silver. This gives one metal above and one below hydrogen in the E.M.F. series.

Tables 2, 3, 4, 5, and 6 give the results of electrokinetic potential measurements on nickel-coated silica gel in pure water, $N/10{,}000$ nickel nitrate, $N/5000$ nickel nitrate, $N/2000$ nickel nitrate, and $N/1000$ nickel nitrate solutions, respectively.

Figure 4 shows these results graphically and compares the electrokinetic potential with the Nernst potentials for the same concentrations of Ni^{++}. The full curve gives the character of the change of the ζ-potential with concentration, while the broken line shows the ϵ-potential values through a like change in concentration. In order to get both curves on the same figure, it was necessary to use a different scale for plotting the two potentials. This is indicated on the margin in figure 4.

TABLE 5

ζ-Potential of $N/2000$ nickel nitrate–nickel

t = 24.4°C. Average κ_s = 1.14×10^{-4}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
59.7	0.0	0.0	0.0
73.8	0.0	0.0	0.0
73.5	0.0	0.0	0.0
41.5	0.0	0.0	0.0
40.7	0.0	0.0	0.0
Average..................			0.0

TABLE 6

ζ-Potential of $N/1000$ nickel nitrate–nickel

t = 25.0°C. Average κ_s = 1.71×10^{-4}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
36.6	0.0	0.0	0.0
75.7	0.0	0.0	0.0
74.7	0.0	0.0	0.0
46.7	0.0	0.0	0.0
32.0	0.0	0.0	0.0
Average..................			0.0

TABLE 7

ζ-Potential of $N/10{,}000$ silver nitrate–silver

t = 26.2°C. Average κ_s = 2.32×10^{-4}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
68.2	8.6	0.148	3.3
73.6	14.9	0.202	4.5
73.4	14.5	0.197	4.3
63.6	10.5	0.165	3.6
46.4	3.7	0.079	1.7

TABLE 8

ζ-Potential of water–silver

t = 25.2°C. Average κ_s = 4.88×10^{-5}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
75.4	112.9	1.50	7.3
66.0	101.3	1.53	7.2
57.4	95.6	1.66	7.8
41.0	70.1	1.71	8.0
53.9	86.4	1.60	7.5
Average..................			7.6

Following the work on the nickel-coated gels, a series of measurements were carried out on the silver-coated gel. Table 7 gives a typical set of results. It was apparent that the silver gels were not giving uniform results. Figure 5 shows the dependence of H on the pressure for three solutions of silver nitrate as well as for pure water. The values given in table 7 are shown as No. II in figure 5. Theoretically the curves in the pressure-potential diagram should be straight lines passing through the origin.

The curve No. I for water is the only one that passes through the origin. It appears as though some positive potential were being superimposed on the negative streaming potentials. This is approximately given by the intercept of the extended curves on the ordinate. If this is corrected for by moving the curves parallel to themselves until they pass through the origin, then the values seem reasonable as shown in figure 6. Here the curves of figure 5 have been moved parallel to themselves until they passed through the origin. An additional set of values for $N/1000$ silver nitrate has been added.

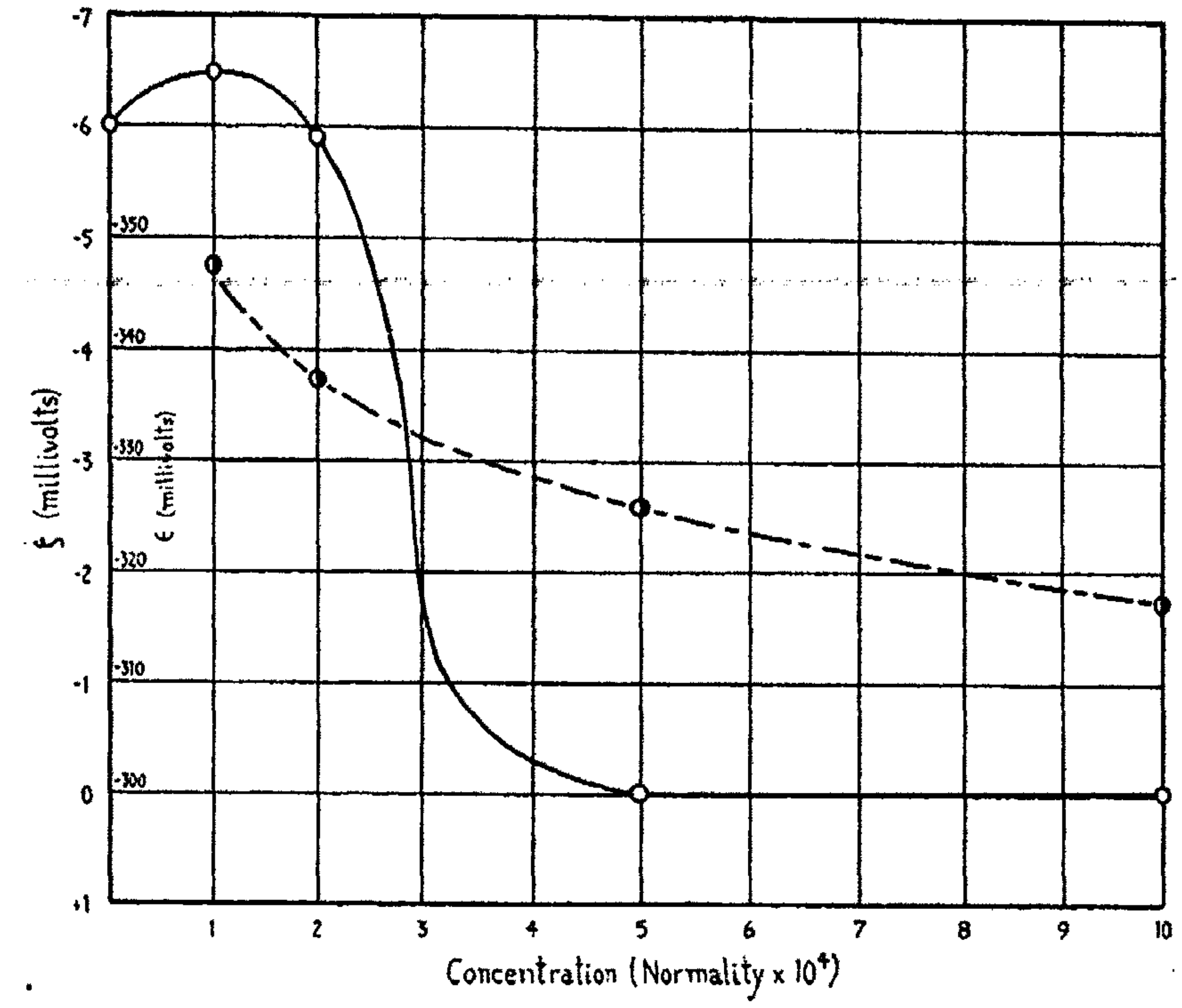

FIG. 4. NICKEL-NICKEL NITRATE

The anomalous behavior of the silver gels was early shown to be due to other factors than the silver ions. Measurements of the streaming potentials for dilute silver nitrate solutions on pure silica gel gave uniform results. It was then suspected that the silver gels might be acting as an

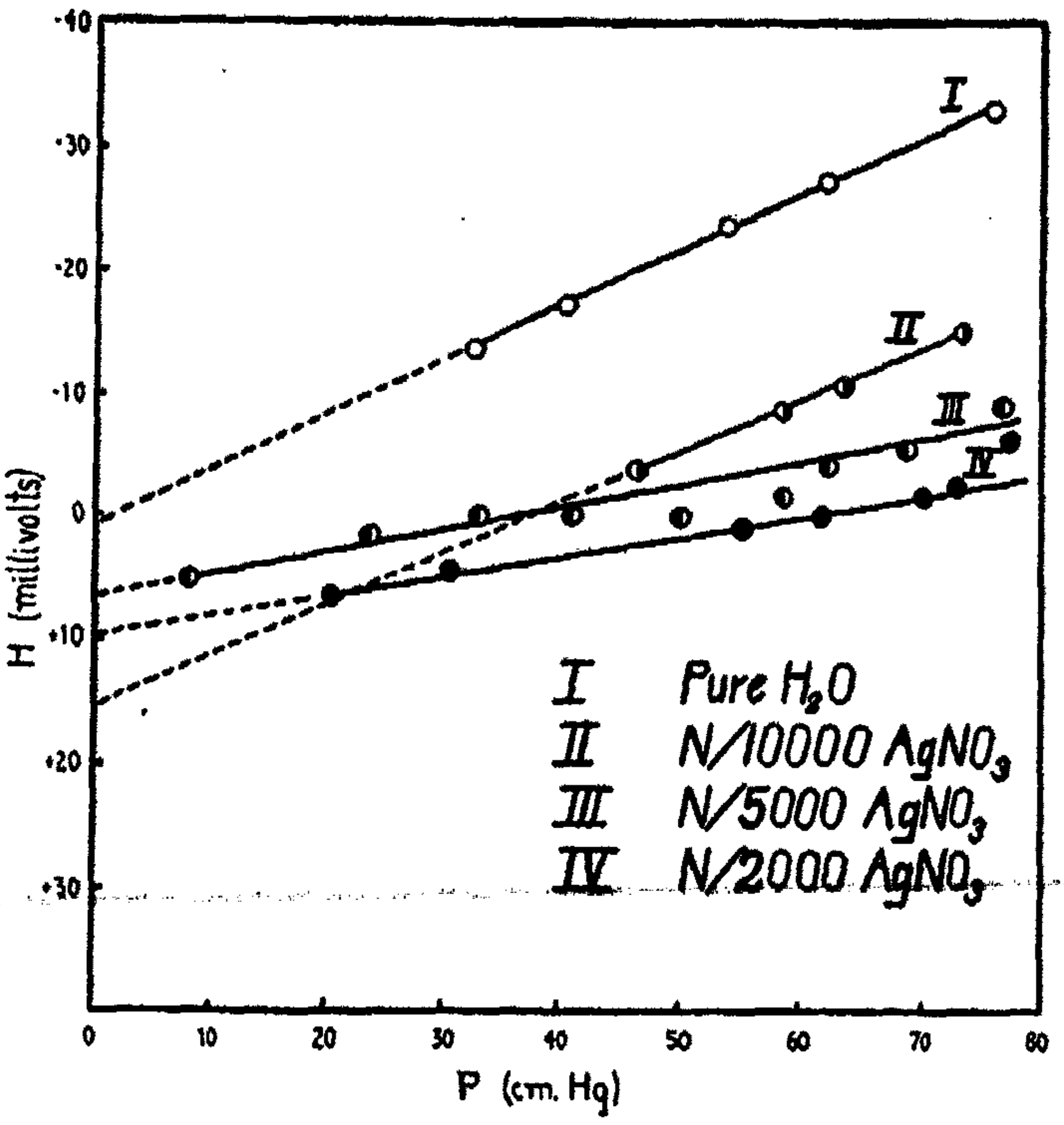

FIG. 5. ABNORMAL SILVER-SILVER NITRATE CURVES

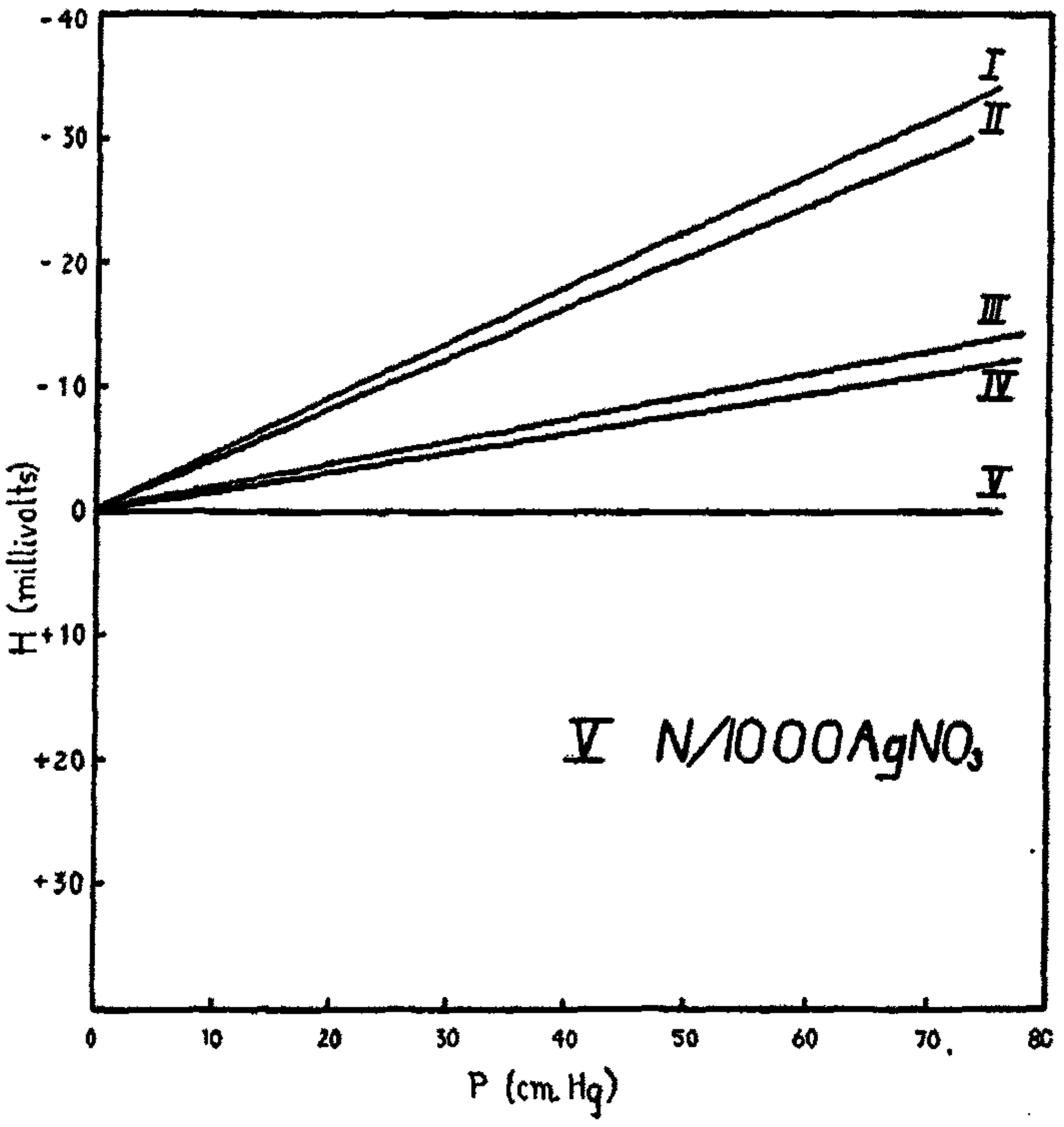

FIG. 6. CURVES FROM FIG. 5 MOVED TO A COMMON ORIGIN

oxygen electrode. A sample of the silvered gel was ground and resilvered. Every precaution was taken to keep oxygen from the gel or the solutions used. The solutions were prepared and stored under nitrogen. The silvered gel was kept in a hydrogen atmosphere until used. The streaming potential results on these gels gave the same anomalous results. In fact at the end of a run using $N/2000$ silver nitrate, a positive potential was registered after the pressure on the flowing liquid was brought to zero. This potential persisted for more than an hour after the liquid had ceased to flow.

TABLE 9

ζ-Potential of N/10,000 silver nitrate-silver

$t = 25.5°C$. Average $\kappa_s = 8.98 \times 10^{-5}$

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
70.6	42.4	0.600	5.2
77.1	44.4	0.575	5.0
63.7	35.6	0.560	4.8
46.3	24.0	0.519	4.5
59.0	32.4	0.549	4.8
Average..................			4.9

TABLE 10

ζ-Potential of N/5000 silver nitrate-silver

$t = 25.8°C$. Average $\kappa_s = 1.17 \times 10^{-4}$

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
74.5	39.3	0.528	5.9
70.1	36.6	0.522	5.9
43.1	21.3	0.495	5.5
56.4	27.9	0.494	5.5
Average..................			5.7

TABLE 11

ζ-Potential of N/2000 silver nitrate-silver

$t = 25.9°C$. Average $\kappa_s = 1.67 \times 10^{-4}$

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
77.8	22.6	0.290	4.6
66.4	18.1	0.272	4.3
43.3	12.0	0.277	4.4
63.2	16.5	0.261	4.2
51.9	14.5	0.279	4.4
70.3	18.2	0.259	4.2
(00.0)	(00.0)	(0.000)	(0.0)
52.9	15.2	0.287	4.6
Average..................			4.4

TABLE 12

ζ-Potential of N/1000 silver nitrate-silver

$t = 25.3°C$. Average $\kappa_s = 2.27 \times 10^{-4}$

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
64.1	8.0	0.124	2.7
76.1	9.6	0.126	2.8
49.9	7.2	0.143	3.1
36.5	4.7	0.129	2.8
60.2	7.8	0.130	2.9
Average..................			2.9

Since the metallized gels were reduced and stored in an atmosphere of hydrogen it was felt that there might be some hydrogen electrode effect,

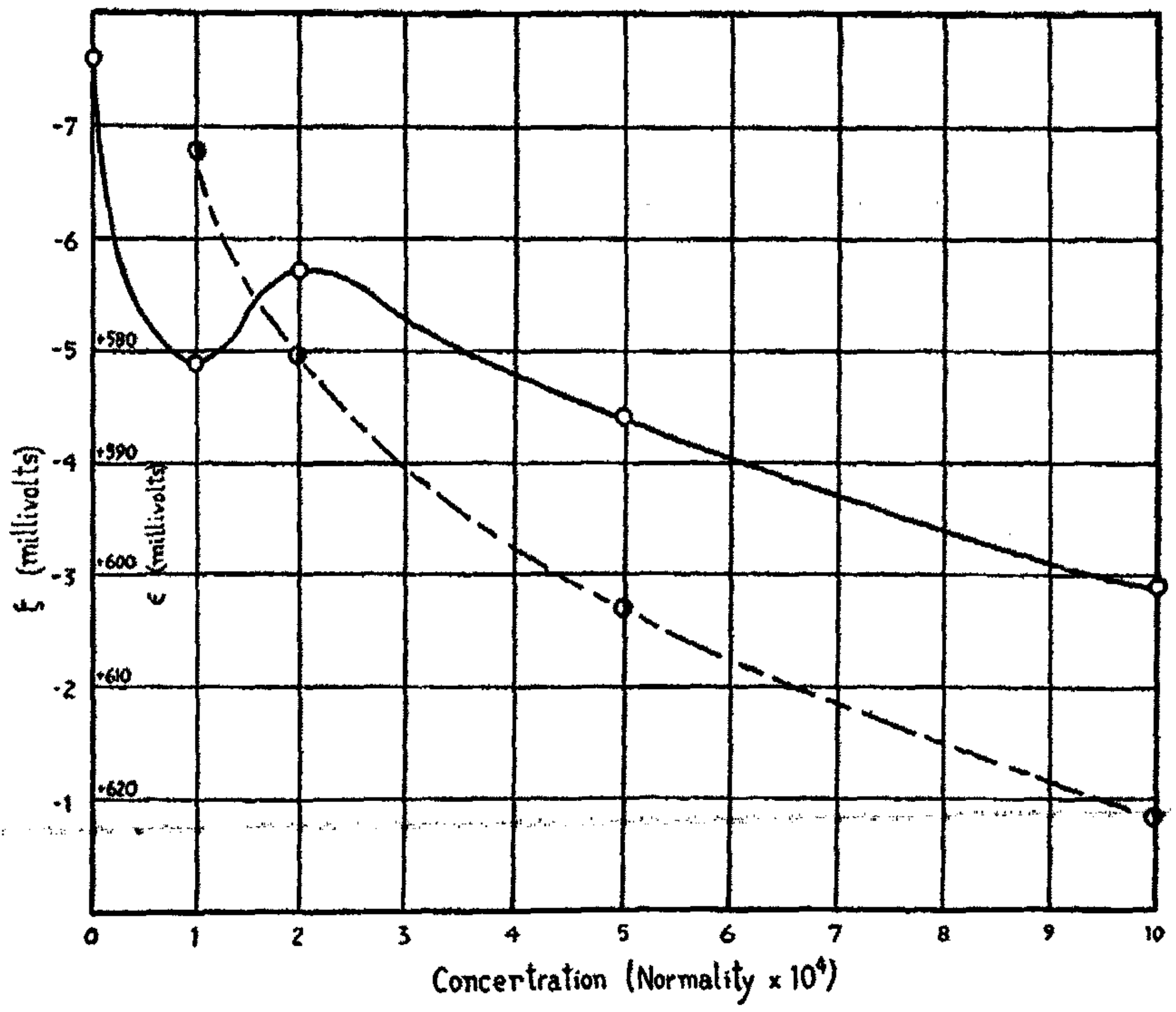

Fig. 7. Silver–Silver Nitrate

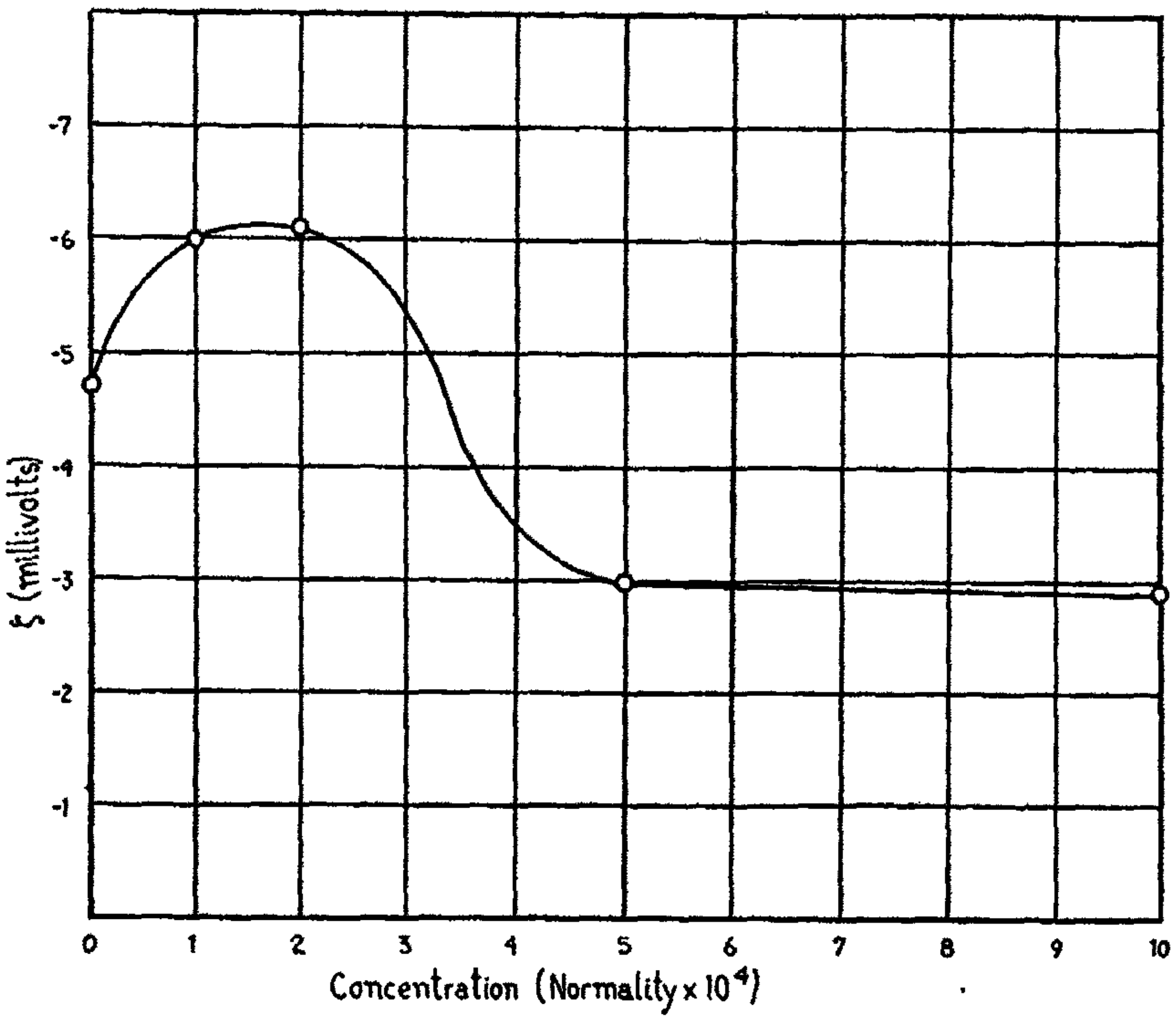

Fig. 8. Silica Gel–Silver Nitrate

since oxygen had been eliminated from the system. Accordingly a fresh sample of silvered gel was prepared as previously described. This was placed in bulbs and sealed to a vacuum line. The bulbs were heated for two hours at a temperature above 350°C. while the vacuum pump was running. The bulbs were sealed off under vacuum and later opened under freshly boiled water. As a result a diaphragm of silverized gel was prepared under conditions which practically eliminated both oxygen and hydrogen from the system. A series of measurements were made on this gel and the results are given in tables 8, 9, 10, 11, and 12. These results show that the disturbing influence was eliminated by the above treatment. Figure 7 graphically shows the effect of the concentration of silver nitrate on the zeta potential. As in figure 4 the broken curve shows the change of the Nernst potential with concentration. The values of the Nernst potential in both cases are those referred to the standard hydrogen electrode.

TABLE 13

Summary of results for the systems nickel–nickel nitrate

CONCENTRATION	ζ	μ
normality	*mv.*	*e.s.u.* $\times 10^5$
0×10^{-4}	6.0	11.2
1×10^{-4}	6.5	12.1
2×10^{-4}	5.9	11.0
5×10^{-4}	0.0	0.0
10×10^{-4}	0.0	0.0

TABLE 14

Summary of results for the system silver–silver nitrate

CONCENTRATION	ζ	μ
normality	*mv.*	*e.s.u.* $\times 10^5$
0×10^{-4}	7.6	14.1
1×10^{-4}	4.9	9.1
2×10^{-4}	5.7	10.6
5×10^{-4}	4.4	8.2
10×10^{-4}	2.9	5.4

TABLE 15

Summary of results for the system silica gel–silver nitrate

CONCENTRATION	ζ	μ
normality	*mv.*	*e.s.u.* $\times 10^5$
0×10^{-4}	4.7	8.7
1×10^{-4}	6.0	11.1
2×10^{-4}	6.1	11.3
5×10^{-4}	3.0	5.6
10×10^{-4}	2.9	5.4

The results of a similar series of determinations on pure silica gel, using silver nitrate solutions, are shown graphically in figure 8.

A summary of the results obtained on nickel-surfaced gel, silver-surfaced gel, and pure silica gel is given in tables 13, 14, and 15. The last column gives the values of the electric moment of the double layer.

DISCUSSION

The streaming potential measurements in this investigation plainly indicate the difference in character between the ϵ and ζ potentials. The electrokinetic potential is negative for both the nickel and silver systems, while the silver-silver ion system would normally be expected to be positive. The actual change in the electrokinetic potential is usually small as compared to the ϵ-potential changes in the same concentration range, but the relative change in the zeta potential is much larger. The zeta potential in the nickel-nickel nitrate system reached a zero value at a concentration of $N/2000$. This is characteristic of the effect of divalent ions in streaming potential studies. No such results are found in ϵ-potentials. The curve obtained for silver nitrate-silver is different from any hitherto reported for monovalent ions. In the case of monovalent cations of K^+ and Na^+, an initial rise in the zeta potential is observed and then a gradual decrease. In the silver nitrate-silver case there is the initial sharp decrease, then a rise which is followed by the usual gradual decrease. This was at first attributed to experimental error, but check runs gave the same results.

In order to explain this unusual result it is necessary to consider the factors affecting the potential at the interface. If the diffuse double layer is considered as a plane condenser with the planes representing the average positions of the two layers, i.e., the electrogravitational planes, then the potential across these planes depends upon the distance between them and upon the charge density.

If the charge density is constant, then the difference in potential is directly proportional to the distance across the double layer, whereas, if the distance is kept constant, the potential is proportional to the charge density of the layers. This assumes that the dielectric constant does not change. However it may be considered as a constant factor, and as such will not affect the conclusions.

The distance across the double layer varies with the concentration of ions in the solution, the thickness being greatest in pure water and dilute solution. The first addition of electrolyte causes the greatest decrease in the distance, with successive additions causing less and less change. The potential should thus decrease sharply at first with a further fall occurring on addition of electrolyte. On the other hand, the addition of electrolyte will affect the charge on the double layer. If adsorption into the interface tends to increase the net charge of the double layer, i.e., by preferential adsorption of negative ions on a negatively charged fixed layer, then the potential will increase. If positive ions are adsorbed into the negative layer then the potential must decrease, for the charge is lowered.

The resultant change in potential must therefore depend on the relative magnitude of these three factors: (1) change in thickness of the double layer, (2) adsorption of anions, and (3) adsorption of cations. Changes in these three factors have been used to account successfully for the changes which occur when solutions of such salts as potassium chloride, sodium chloride, etc., are streamed through glass capillaries. In the case of the silver–silver ion system, changes in the relative magnitude of the three factors give rise to a different type of potential curve. It is probable that the heavy metal ion is adsorbed to a much greater degree than was the case with the alkali cations. This effect, together with any drop in potential due to the shrinkage in the double layer, probably more than balances the effect of anion adsorption. On increased concentration the effect of shrinkage in the double layer becomes less significant, and we have the usual rise in potential due to preferential anion adsorption. As the double layer becomes more nearly saturated with ions, we obtain the final gradual fall in potential due to the decrease in double layer thickness.

The electrokinetic potentials of the silver–silver ion system differ from those of the nickel–nickel ion system. However they both exhibit changes in the ζ-potential which are unpredictable on the basis of consideration of the ϵ-potential theory. The Nernst potentials over this same concentration range vary in a perfectly regular manner. The variations in the electrokinetic potential depend upon the nature of the substances concerned and the concentration of the electrolyte. The Nernst potential, ϵ, depends upon one variable factor, the osmotic pressure of those ions which the metal supplies and a factor which is constant for each metal, the electrolytic solution pressure.

SUMMARY

A streaming potential method for the determination of the electrokinetic potentials of metals in contact with their ions has been developed, and measurements were made on the systems silver–silver ion and nickel–nickel ion, as well as on pure silica gel.

Metallized silica gels were used in the investigation. They were prepared by the new process of adsorbing complex ions of ammonia on the silica gel and later reducing to the metallic state.

A vacuum tube potentiometer and a vacuum tube conductivity bridge have been adapted to this type of work with excellent results.

Fundamental differences between the electrokinetic potentials and the Nernst potentials were found for the systems studied.

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THE AUTOXIDATION OF STANNOUS CHLORIDE. IV

THE EFFECT OF SOME NON-AQUEOUS SOLVENTS[1]

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Previous work by the authors (4) has shown that the autoxidation of stannous chloride is a thermal and photochemical chain reaction, showing peroxide formation, induced oxidation of other molecular species present in the solution, and great sensitivity to positive and negative catalysts. The complex $HSnCl_3$ or H_2SnCl_4 was described as playing an important rôle in the oxidation of the stannous chloride.

Because of the interference of hydrolysis in the study of the reaction in aqueous solution, it was desired to determine the effect of acid concentration in some organic solvent. After many preliminary experiments, some of which are reported in paper II of this series (4), benzyl alcohol was finally selected as a suitable solvent.

AUTOXIDATION OF STANNOUS CHLORIDE IN BENZYL ALCOHOL

Benzyl alcohol was purified by vacuum distillation. The product boiled at 98–99°C. (uncorrected) at 17 mm. pressure, a value consistent with those recorded in the literature. Five different batches were prepared and found to give reproducible results. Dry hydrogen chloride was passed into the alcohol, and the solution was used immediately in order to prevent any invalidation of the results by the formation of benzyl chloride through esterification.

The autoxidation in benzyl alcohol was characterized by a short period of rapid absorption of oxygen, followed by a period of slow oxygen consumption, progressing toward complete oxidation. The initial period lasted from 5 to 8 minutes, and in order to express all data on a comparable basis, an arbitrary period of 10 minutes was taken, and the data expressed as the number of milliatoms of oxygen consumed in that time. This value, plotted against the normality of the hydrochloric acid, gives a straight line nearly to the point where the hydrochloric acid is equivalent to the stannous chloride, and then approaches a constant value. This effect was

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studied at two concentrations of stannous chloride, and the data are given in table 1 and figure 1. The effect of varying the concentration of the stannous chloride at a constant hydrochloric acid concentration was also studied at one acid concentration. These data are presented in table 2 and figure 2.

In both studies it will be noticed that the amount of oxygen consumed in the 10-minute period approaches a constant value as the variable concentration increases. The data for the variable stannous chloride concentration show this in the more pronounced way, since complete oxidation was not approached in the 10-minute absorption period in these runs.

TABLE 1

Effect of concentration of hydrochloric acid on the autoxidation of stannous chloride in benzyl alcohol

(A) STANNOUS CHLORIDE CONCENTRATION = 1.019 MILLIMOLES IN 25 CC		(B) STANNOUS CHLORIDE CONCENTRATION = 2.038 MILLIMOLES IN 25 CC.	
Concentration of hydrochloric acid	Oxygen used in 10 minutes	Concentration of hydrochloric acid	Oxygen used in 10 minutes
N	*milliatoms*	*N*	*milliatoms*
None	0.063	0.037	0.596
0.016	0.235	0.074	1.11
0.020	0.296	0.114	1.64
0.034	0.463	0.127	1.86
0.041	0.590	0.159	2.09
0.049	0.700	0.189	2.21
0.059	0.713	0.236	2.32
0.063	0.787	0.263	2.37
0.071	0.924	0.329	2.40
0.082	1.02		
0.095	1.13		
0.101	1.20		
0.221	1.18		
0.226	1.20		
0.233	1.23		
0.368	1.17		

It was found that induced oxidation of the benzyl alcohol occurs. At a stannous chloride concentration of 1.019 millimoles in 25 cc. of benzyl alcohol, and hydrochloric acid concentration varying from 0.10 *N* to 0.35 *N*, 1.21 milliatoms of oxygen were used, on the average. Since one milliatom of oxygen is equivalent to one millimole of stannous chloride, this was an excess of 18.6 per cent. Two runs with twice the amount of stannous chloride and an acid concentration of 0.25 *N* to 0.35 *N* gave practically the same value, 20.9 per cent.

The fact that the curves of figures 1 and 2 approach constant values,

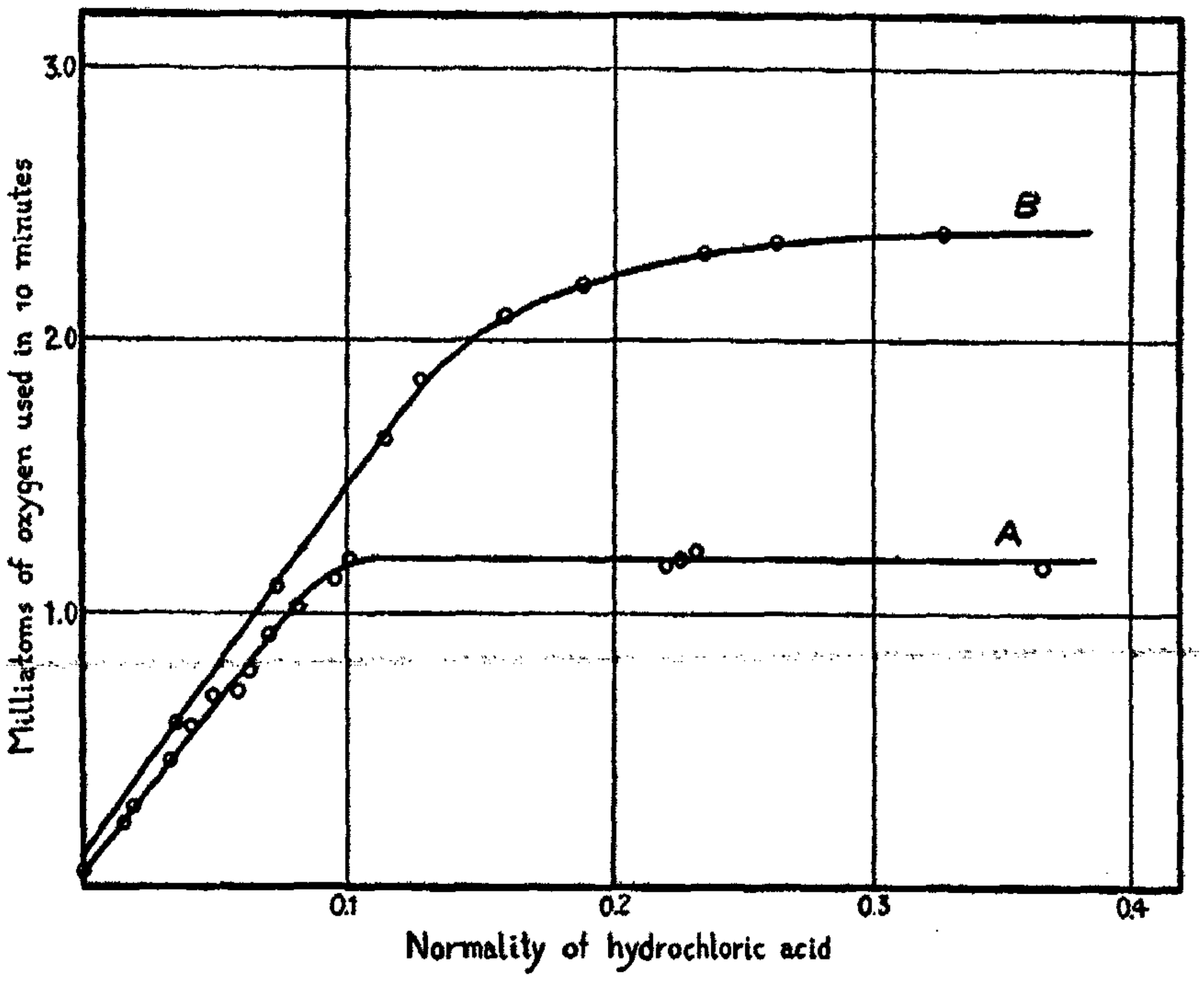

FIG. 1. THE EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID ON THE AUTOXIDATION OF STANNOUS CHLORIDE IN BENZYL ALCOHOL

A, stannous chloride concentration = 1.019 millimoles in 25 cc.; B, stannous chloride concentration = 2.038 millimoles in 25 cc.

TABLE 2

Effect of concentration of the stannous chloride on its autoxidation in benzyl alcohol
Hydrochloric acid concentration = 0.078 *N*

STANNOUS CHLORIDE CONCENTRATION	OXYGEN USED IN 10 MINUTES
millimoles in 25 cc.	*Milliatoms*
0	0
0.509	0.589
1.019	0.960*
1.528	1.18
2.038	1.18*
3.057	1.28
4.076	1.28

* Interpolated from figure 1.

shows again the presence of the equilibrium between stannous chloride and hydrochloric acid, and shows that these complexes are the principal forms in which the stannous chloride is oxidized in benzyl alcohol. As the concentration of *either* of the constituents of the complex is increased, holding the other constant, the concentration of the complex, and thus the rate of oxidation, increases toward a constant value.

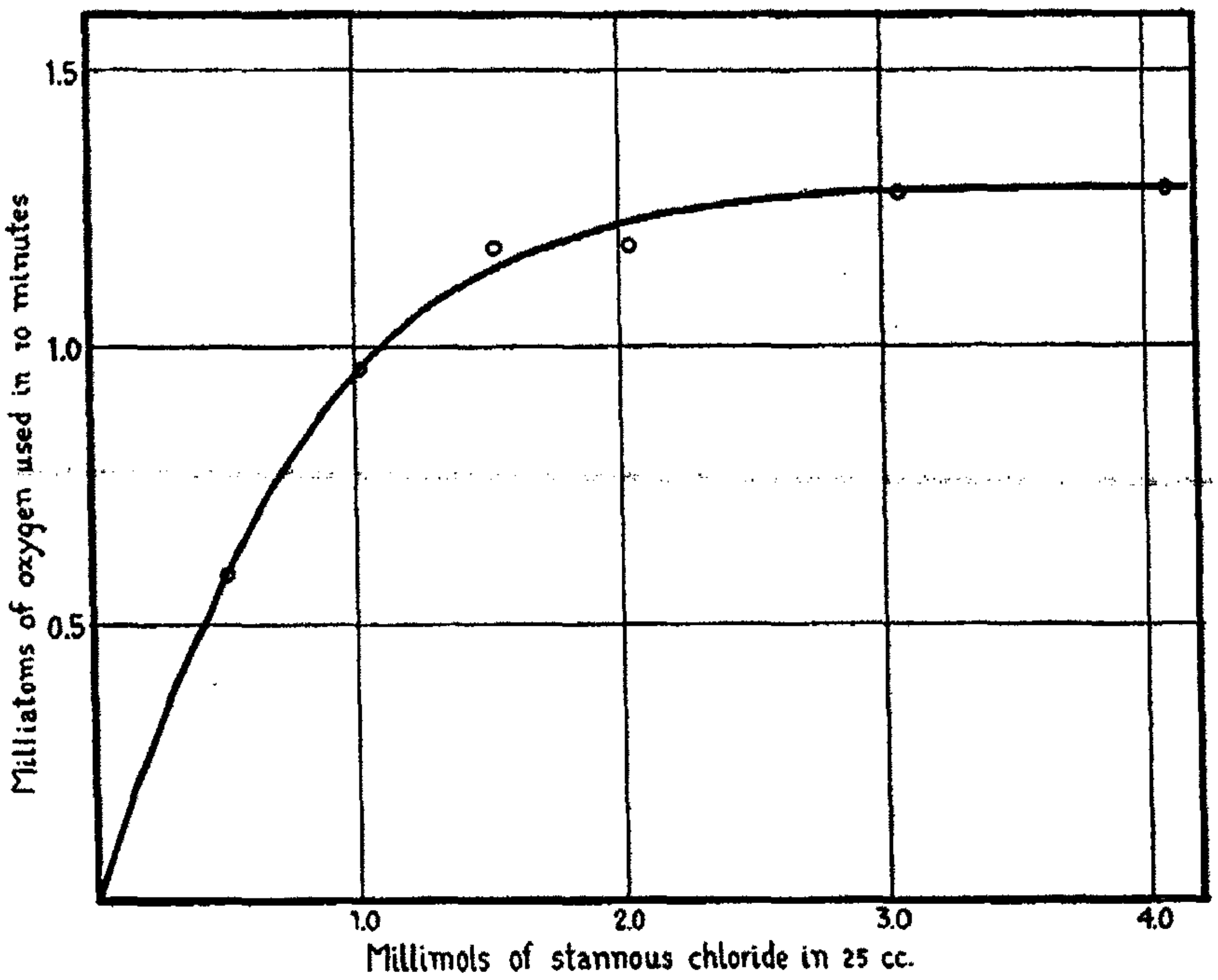

FIG. 2. THE EFFECT OF CONCENTRATION OF STANNOUS CHLORIDE ON ITS AUTOXIDATION IN BENZYL ALCOHOL
Hydrochloric acid concentration = 0.078 *N*

AUTOXIDATION OF STANNOUS CHLORIDE IN DIOXAN

A large amount of time was spent on the autoxidation of stannous chloride in dioxan (1,4-dioxane), since this solvent was expected to be very resistant to oxidation or reduction.

The dioxan was purified by refluxing for 7 to 12 hours with one-tenth its volume of 1 *N* hydrochloric acid to hydrolyze the acetal of ethylene glycol, which is always found as an impurity. Oxygen was passed through the ether during the hydrolysis to oxidize the aldehyde produced. The product was dried with solid potassium hydroxide, fractionated to remove low boiling material and the ethylene glycol, and finally was refluxed over molten sodium until no further reaction occurred, and the globules of sodium appeared bright (12 to 36 hours). The pure dioxan was then distilled from the sodium (boiling point, 99.7–99.9°C., uncorrected, at 740 mm.; freezing point, 11.80° ± 0.01°C.). This product is apparently of a higher degree of purity than that previously reported in the literature (1, 6).

Stannous chloride was found to form a molecular compound with dioxan in the ratio 1:1. The salt was recrystallized from dioxan of high purity, and the product analyzed. The percentages of chlorine and tin were found to be 25.40 and 43.12, as compared with 25.54 and 42.75 calculated for a 1:1 ratio of stannous chloride to dioxan.

This recrystallized molecular compound was used to determine the extent of complex formation between stannous chloride and hydrochloric acid in dioxan solution. This was determined by the method of freezing point lowering, for which the constant in dioxan is 5.0 (5). The freezing point lowering of solutions of stannous chloride and of hydrochloric acid in dioxan were determined, equal volumes of the two solutions mixed, and the freezing point lowering again determined.

TABLE 3

Complex formation between stannous chloride and hydrochloric acid in dioxan

STANNOUS CHLORIDE CONCENTRATION	HYDROCHLORIC ACID CONCENTRATION	FREEZING POINT LOWERING			
(Before mixing)		Obsd.	Calcd. (No complex)	Calcd. ($HSnCl_3$)	Calcd. (H_2SnCl_4)
M	*M*				
0.0315	0.1828	0.491°	0.536°	0.457°	0.378°
0.0315	0.3656	0.901	0.993	0.914	0.835

Complex formation is definitely shown in the data of table 3, which gives the experimental lowering compared with the theoretical lowering calculated (a) with no complex formation, (b) with all the stannous chloride present as $HSnCl_3$, and (c) with all the stannous chloride present as H_2SnCl_4.

High accuracy is not claimed for these results because of the extreme difficulty of preventing oxidation of the stannous chloride in acid concentrations as high as these. These determinations were made under nitrogen, and the solutions kept under nitrogen during as much of the handling as was possible, but a filtration was necessary, and a small amount of oxidation is very probable.

The autoxidation of stannous chloride in dioxan was found to resemble the oxidation in benzyl alcohol. There is a period of rapid absorption followed by a slow period in some runs. The oxidation is faster than in benzyl alcohol however, the initial rapid period being complete in 1½ minutes. In the purest samples, freshly distilled, the subsequent slow absorption was not present, but these samples of dioxan developed the slow absorption period after standing for several days, even under pure nitrogen. This effect is not due to water, since known amounts of water added to runs in freshly distilled dioxan do not produce the slow absorption period. Water does, however, increase the amount taken up in 1½ minutes of rapid absorption.

If oxygen is bubbled through an old sample of dioxan which shows the subsequent absorption period, just before its use in an autoxidation run, the subsequent absorption period is destroyed, and the amount of oxygen consumed in the initial period greatly reduced.

The results of the autoxidation could not be reproduced very well from one preparation of dioxan to the next, so that the results concerning the effect of hydrochloric acid concentration have no quantitative value, but about twenty-five runs in freshly distilled dioxan, out of more than a hundred, show a qualitative trend similar to that found with benzyl alcohol, that is, some oxygen is taken up even with no hydrochloric acid present; the amount of oxygen used up increases with the acid concentration, and approaches a constant value at high acid concentrations. Induced oxidation was also found, 1.01 millimoles of stannous chloride consuming 1.52 (average of ten runs) milliatoms of oxygen, an excess of 50.0 per cent.

Water added to the stannous chloride–hydrochloric acid–dioxan system was found to increase the amount of oxygen absorbed during the first 1½ minutes of the run. The amount of this increase was variable but ranged from 25 to 75 per cent for an addition of 0.10–0.30 g. of water.

Some preliminary experiments were also made in the following solvents: diamyl ether, dibenzyl ether, β,β′-dichlorodiethyl ether, nitrobenzene, diphenyl ether, and diethyl malonic ester. These all proved to be unsatisfactory from the standpoint of solubility, or reaction.

THE ACTION OF POSITIVE AND NEGATIVE CATALYSTS IN NON-AQUEOUS SOLVENTS

In order to correlate the reaction in organic solvents with the reaction in water, a few experiments were made with some positive and negative catalysts. Picric acid has been found to be a good inhibitor in aqueous solution, and it proved to be one in non-aqueous solvents as well. It was used, qualitatively, to inhibit the reaction in the following solvents: benzyl alcohol, β, β′-dichlorodiethyl ether, and glacial acetic acid. Its inhibitory power can best be shown by the acetic acid experiments. In this solvent one millimole of stannous chloride is oxidized in 2 minutes, whereas with 0.02 g. of picric acid added, less than 0.005 milliatom of oxygen is taken up in 20 minutes. *m*-Dinitrobenzene, *p*-aminophenol, and *p*-nitrotoluene were also found to be good inhibitors in acetic acid solution. All these inhibitors seem to be more effective in acetic acid than they were in aqueous solution.

Thiourea, which is a strong accelerator in aqueous solution, also catalyzes in benzyl alcohol, and in β, β'-dichlorodiethyl ether, but 0.01 *M* accelerates the reaction only about 150 per cent as compared with about 2000 per cent in water. However, this may in part be due to the low solubility of thiourea in these solvents. Tetraethyllead was found to accelerate the reaction in benzyl alcohol as it did in water, but willow charcoal had the anomalous effect of showing no catalytic effect in benzyl alcohol.

DISCUSSION

In this paper further evidence has been presented to show that the chloro acid complexes are important in the mechanism of the autoxidation of stannous chloride. The approaching of a constant value for the rate of ~~autoxidation with increasing concentration of *either* of the constituents of~~ the complex indicates this, and it is further proven by the determination of complex formation in dioxan solution. The close analogy between the effect of hydrochloric acid on the reaction in water and organic solvents, and the identical action of inhibitors and accelerators show that the mechanism of the reaction is not affected appreciably by the solvents.

The summation of the work presented in this series of papers leads the authors to believe that the autoxidation of stannous chloride may be represented by the series of reactions designating the typical autoxidation, viz., if A and $\underline{A}$ represent autoxidant molecules (in this case $HSnCl_3$ or H_2SnCl_4) and * represents energy of vibrational activation (from thermal or photochemical sources), then

$$A + {*} \rightarrow A^{*} \qquad (1)$$

$$A^{*} + O_2 \rightarrow AO_2^{*} \qquad (2)$$

$$AO_2^{*} + \underline{A} \rightarrow A^{*} + \underline{A}O_2 \qquad (3)$$

$$AO_2^{*} + I \rightarrow AO + IO^{*} \qquad (4)$$

$$\underline{A}O_2 + A \rightarrow 2AO \qquad (5)$$

The symbol $\underline{A}$ is used to show the transfer of two atoms of oxygen instead of an energy transfer. This mechanism was proposed by Bodenstein (3), and amplified by Bäckström and Beatty (2). I represents the inhibitor molecule, and the IO* molecule has a lower specific reaction rate with $\underline{A}$ than has the activated peroxide AO_2^{*}. Thus the widely differing powers of various inhibitors in a reaction are due to their differing abilities to react with $\underline{A}$ and perpetuate the reaction chain. This also accounts for the ability of one substance to be an inhibitor for one reaction and an accelerator for another, since the effect the substance has will depend on the reactive ability of its oxide (or peroxide) *relative* to that of the autoxidant. In this general scheme, the reaction chain is reaction 1 followed by an alternation between reactions 2 and 3, while reaction 4 is the chain-breaking mechanism. Reaction 5 occurs subsequent to the chain, and may, under the proper conditions, be slowed sufficiently to permit the detection, and even the isolation, of the peroxide, as has been reported by many investigators in widely differing reactions.

SUMMARY

1. Very pure dioxan (f.p. = 11.80 ±0.01°C.) has been prepared, and complex formation shown between stannous chloride and hydrochloric acid by means of freezing point lowering in this solvent.
2. A molecular compound of one mole of stannous chloride with one mole of dioxan has been identified by analysis.
3. The rate of autoxidation of stannous chloride in dioxan and in benzyl alcohol has been studied. It was found to increase nearly linearly with the acid concentration up to a point where the acid concentration is close to that of the stannous chloride, and then to approach a constant value.
4. The postulation of the chloro acid complex as the form in which the stannous chloride is oxidized was confirmed by the above experiments, and by those in which the rate also approached a constant value with increasing stannous chloride concentration, at a constant acid concentration.
5. Induced oxidation of dioxan and benzyl alcohol was demonstrated during the autoxidation of stannous chloride in those solvents.
6. Several positive and negative catalysts were shown to have qualitatively the same effect in non-aqueous solvents as they have in aqueous solution.

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A STUDY OF THE INFLUENCE OF AN ELECTRIC FIELD ON THE POTENTIAL AT A METAL-SOLUTION INTERFACE

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Numerous studies have been made on the electrical potential difference between a metal and an aqueous solution which does not contain a salt of the metal but contains other electrolytes and dissolved gases. The so-called oxygen electrode in particular has received much attention (5, 6, 9, 10, 16, 21, 23, 25). The influence of the movement of the electrolyte on such a potential difference has also been investigated (1, 11, 19, 20, 22, 26).

These electrical potentials are of considerable significance. Many are the systems that present the contact of a metal with an aqueous solution containing few if any of the metal ions. Colloidal metals such as platinum, silver, and gold reveal systems which owe their stability and cataphoretic behavior to the potential between the colloidal metallic particle and the dispersion medium. It is well-known, too, that the electrolyte present markedly influences the potential of such a metal-liquid interface.

In treating the electrical potential across this type of metal-liquid interface, investigators have considered two potentials. The first is the Nernst potential obtained by the usual potentiometric determination of the potential difference by the use of a standard half-cell. The second is the electrokinetic or "zeta" potential between the liquid adhering to the solid wall and the bulk of the mobile liquid. This is always estimated by a hypothetical consideration of the data from experiments on cataphoresis, electroösmosis, or streaming potentials.

If the accepted theory of electrokinetic phenomena is correct there should be some relation between changes in the zeta potential and the Nernst potential. All experimental evidence points to the interface as the region in which these changes which affect the electrokinetic potential occur, and certainly the Nernst potential extends across this interface.

The effect of mechanical and electrical forces acting on the potential at the metal-electrolyte interface should afford information that can be used in determining the nature of this potential. The results might also be applicable in the development of a satisfactory theory of electrokinetic phenomena and the zeta potential. The very imperfect status of our knowledge of this topic has been adequately summarized by McBain (12, 13).

The work presented in this paper is an attempt to determine the effect of an electric field on the potential at the interface metal–electrolyte. The way in which this was accomplished is indicated by the following considerations.

The potential of a cell under ordinary circumstances may be considered as made up of two parts: first, of the potential of metal, electrolyte (dissolved gas) (E_m); and second, of the potential of electrolyte (dissolved gas), half-cell (= constant). The potential of the cell is

$$E = E_m + \text{Constant} \tag{1}$$

If there exists in the electrolyte an impressed potential gradient, the potential of the cell will contain an additional term Fx, where F is the field strength in volts per centimeter, and x is the distance in centimeters between the electrode and the tip of the half-cell bridge, measured parallel to the direction of the field. The potential of this cell is

$$E' = E'_m + Fx + \text{Constant} \tag{2}$$

Then

$$E - E' = E_m - E'_m - Fx \tag{3}$$

By adjusting the position of the electrode and bridge it is possible to make $x = 0$, whence

$$E - E' = E_m - E'_m$$

EXPERIMENTAL

The experimental set-up consisted of a small rectangular electrolysis vessel fitted at each end with electrodes, which, when differently charged, produced a potential gradient through the solution. The experimental electrode and half-cell bridge were placed in this field in a position such that $x = 0$ (equation 3). The set-up is shown in figure 1.

The electrolysis vessel (M) was a rectangular glass trough, 7.5 × 2.5 × 2.5 cm., which was fitted at each end with a sheet of platinum (F) which served as a field electrode. The glass–glass and glass–platinum contacts were sealed with picein wax in some experiments and with de Khotinsky cement in others. The electrolysis vessel was fixed with appropriate insulation in a small wooden box which was lined with metal foil electrically grounded.

The experimental electrodes (E) were very small, which reduced conduction through the metal. It was thought that the factors involved might better be differentiated by the use of differently shaped electrodes. Since a flat surface might give different results than a curved surface, two types of electrodes were used. Type A electrodes were made by covering the tip of the wire with a glass bead and then sealing the wire into a small thin glass tube, leaving a 1-mm. length of wire uncovered. Type B electrodes were made by sealing the wire in a small thin glass rod and then, by grinding and polishing, the metal and glass were smoothed. This gave a very small electrode surface which was exactly flush with the glass surrounding it.

Electrodes were made of platinum and of gold wire, each as pure as was possible to obtain. These metals were used because there are experimental data in the literature on the cataphoresis of gold and platinum sols. The gold wire was 0.0193 cm. in diameter. Two sizes of platinum wire were used,—0.0315 cm. in diameter and 0.0193 cm. in diameter.

The other half of the cell measured was a normal calomel electrode (C), connected through a bridge (L) which contained 0.1 M potassium chloride in an agar gel. The end of the bridge (T) in the electrolysis vessel was drawn out to a very fine tip which turned at right angles to the bridge tube. The size of the opening of the bridge tip was found to make no difference when it was of the same order of magnitude as that of the electrode. This was carefully checked by the use of different bridge tips of widely varying diameter.

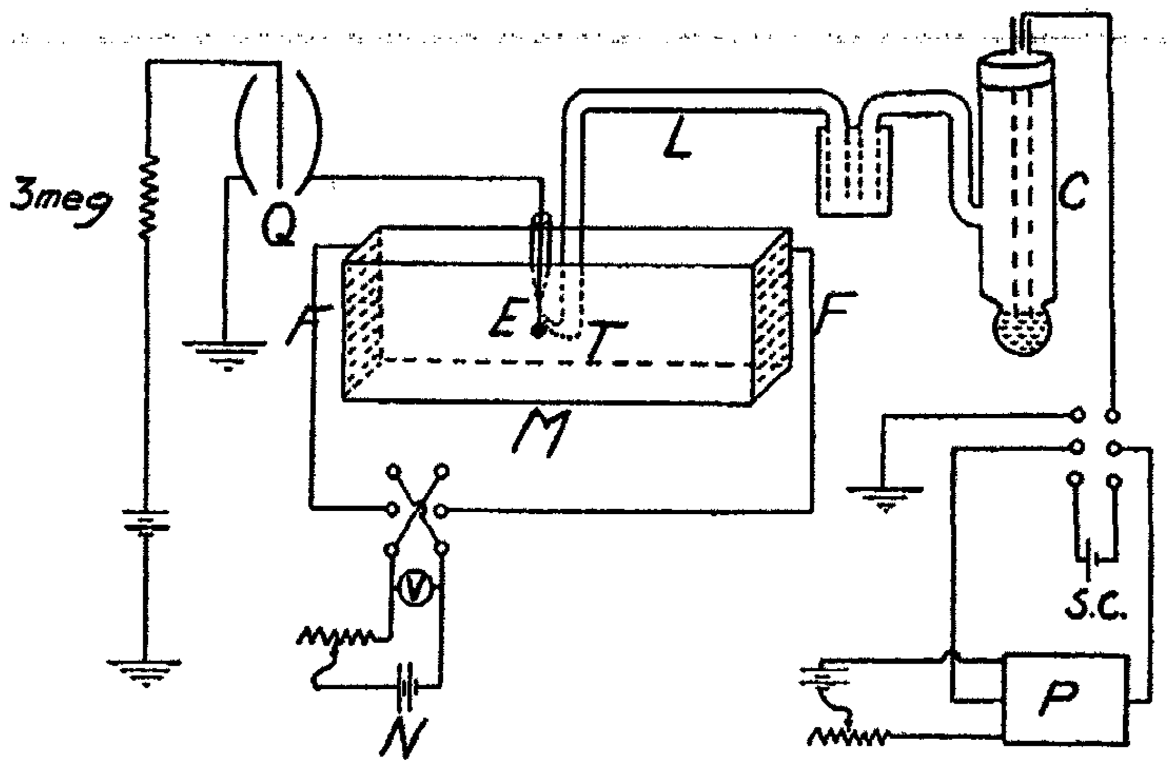

FIG. 1. ELECTRICAL CIRCUITS (diagrammatic)

The bridge was held in place by a clamp which was attached to a long lever arm. One end of the lever arm was fastened to a rigid upright rod about which the lever could turn; the other end was moved by means of a screw which could be set to 0.003 mm. The screw had a mechanical advantage of 4 over the tip of the bridge, which facilitated accurate setting of the bridge tip with respect to the experimental electrode.

The potential for the applied field was obtained from a large size "B" battery (N), which was connected to the field electrodes at the ends of the electrolysis vessel through a commutator which reversed the field every 1.8 seconds. The potential of the experimental electrode was affected in the same way by a field which was reversed every 50 seconds, but the shorter period proved most convenient. The field could not be reversed too rapidly, because the electrometer needle would not follow accurately the changes in the measured potential when $x \neq 0$. This change in the direction of the field reduced polarization at the field electrodes, which increased the agreement between the calculated and actual values of the field strength. Both "B" battery and commutator were supported by sulfur blocks.

The potential of the cell:

metal, electrolyte (dissolved gas), 0.1 M KCl, 1 M KCl, HgCl, Hg

was measured by means of a Leeds and Northrup potentiometer and a quadrant electrometer of the Compton type (Q) as shown in figure 1. It is necessary that the experimental electrode be connected to the electrometer, because otherwise circuit leakage may cause a current through the electrode.

The sensitivity of the electrometer varied from day to day, but was always in the neighborhood of 700 cm. per volt on a scale 1 meter distant, but the scale actually used was placed at a distance of 3.4 m. and was illuminated.

The first step in setting up the apparatus was to clamp the electrolytic vessel firmly in place. Then the leads from the commutator were connected to the field electrodes, and the glass rod holding the electrode was fixed in such a manner that the experimental electrode was held in the center of the electrolysis vessel.

The electrodes were placed so that the smooth metal surface of the type B electrodes was parallel to the direction of the field and the axis of the cylinder of the type A electrodes was perpendicular to the direction of the field. Great care was necessary in the adjustment of the cylindrical electrodes, because if the angle was much less than 90° the electrode potential became very erratic. The flat electrodes were not so sensitive, but gave best results when carefully adjusted.

When the experimental electrode was in place, the bridge was set so that the tip was within 2 mm. of the electrode. The smaller the distance between them, the easier it was to adjust the bridge to the correct position.

After filling the electrolysis vessel with the solution, the potential of the electrode was read at intervals until it had become fairly constant. In some cases this took a long time and in others only an hour or two. When the potential had become nearly steady the key to the electrometer was clamped down so that the potential could be followed continuously. Next the commutator was started and the field turned on. The measured potential changed as the field was reversed, owing to the factor Fx (see equation 2). This could readily be observed as the electrometer needle swung back and forth, but when the bridge had been set carefully this factor was only about 20 millivolts. Next the position of the bridge was adjusted so that the electrometer needle became stationary, and the potential of the cell was measured. When the needle was stationary, ($x = 0$, $\therefore Fx = 0$) $E_0' = E_m' +$ Constant. The field was turned off and the potential of the electrode measured. The difference between these two potentials is the value $E_m - E_m'$.

TABLE 1

Change in millivolts of the potential of gold electrodes caused by fields of value F volts per centimeter ($E_m - E_m'$)

ELECTROLYTE	MOLARITY	ELECTRODE DIAMETER 0.0193 CM.		
		Type A		Type B
		$F = 2.2$	$F = 3.1$	$F = 3.1$
H_3BO_3	10^{-6}	1		0
	10^{-5}	0		0
	10^{-4}	0		0
	10^{-3}	0		0
	10^{-2}	0		0
KH_2PO_4	10^{-6}		0	0
	10^{-5}		0	0
	10^{-4}		0	0
	10^{-3}		0	0
	10^{-2}		−1	0
Na_2HPO_4	10^{-6}		0	0
	10^{-5}		0	0
	10^{-4}		0	0
	10^{-3}		0	0
	10^{-2}		−1	1
$Al_2(SO_4)_3$*	10^{-6}		0	0
	10^{-5}		0	0
	10^{-4}		0	0
	10^{-3}		−1	0
	10^{-2}		−1	0

* Contained hydrochloric acid at a concentration one-tenth that of the aluminum sulfate.

It was found that the length of time the field was on in one direction did not necessarily need to be the same as the length of time in the other direction. Various ratios of these two periods were tried and the results were the same in all except the extremes, where the ratio was 1:5.

It was thought that perhaps the position of the electrometer needle with respect to the quadrants might have an influence on the measurement of the potential. To check this the measurement was carried out in three different ways. First, the potentiometer was set so that when the needle was brought to rest by adjusting the position of the bridge, it was turned to the left of the zero point. This was repeated with the potentiometer set first so that the needle was at the zero point and then to the right of the zero point. The potential calculated from the deflection, the sensitivity, and the potentiometer reading was the same in each case, which showed that the position of the needle with respect to the quadrants was not a source of

TABLE 2

Change in millivolts of the potential of platinum electrodes caused by fields of value F volts per centimeter ($E_m - E_m'$)

ELECTROLYTE	MOLARITY	ELECTRODE DIAMETER 0.0315 CM.				ELECTRODE DIAMETER 0.0193 CM.	
		Type A		Type B		Type A	Type B
		$F = 2.5$	$F = 2.1$	$F = 3.1$	$F = 6.2$	$F = 3.1$	$F = 3.1$
H_3BO_3	10^{-6}	1		0	0	0	0
	10^{-5}	0		0	1	0	1
	10^{-4}	2		0	3 1	0	0
	10^{-3}	1		0	2	2	0
	10^{-2}	0		0	1	2	0
KH_2PO_4	10^{-6}		0	0	3	0	0
	10^{-5}		0	0	1	0	0
	10^{-4}		0	0	2	0	0
	10^{-3}		0	0	0	0	0
	10^{-2}		0	0	1 0 −1	0	0
Na_2HPO_4	10^{-6}		0	0	2	1.5	0
	10^{-5}		0	2	3	−1	0
	10^{-4}		0	1	3	0	0
	10^{-3}		0	1	3	2	0
	10^{-2}		0	1	1.5	0	0
$Al_2(SO_4)_3$*	10^{-6}		0	1	2	0	0
	10^{-5}		0	1	3	0	0
	10^{-4}		2	0	1	0	0
	10^{-3}		0	2	2	0	0
	10^{-2}		0	†	†	0	0

* Contained hydrochloric acid at a concentration one-tenth that of the aluminum sulfate.

† Potential too unstable to give results.

error in the measurements. The quickest method of measurement was to bring the needle to the zero position by changing the potentiometer setting.

No attempt was made to have pure gases over the solution since it is our experience (24) that air or oxygen gives a very sensitive potential with electrodes of this type.

The materials used were well purified and the solutions were made up with a good grade of conductivity water which contained dissolved air. The experiments were carried out in a room which was held at 20 ± 1°C.

The procedure described above was carried out for solutions of several compounds. The range of concentrations employed was from 10^{-6} to 10^{-2} molar. The compounds used were those which previous work (24) had indicated would be most likely to produce the most favorable conditions for a change in potential of the electrode. The concentrations studied were chosen after a consideration of the effects of electrolytes on cataphoresis and streaming potentials. More concentrated solutions could not be used because of the increased conductance of the electrolysis cell.

Tables 1 and 2 give the values of $E_m - E_m'$ for the several electrodes in the different solutions.

For field strengths greater than those reported above, the change in potential was entirely different in character. The potential became so unsteady and unreproducible that it was evident that some new factor had been brought in. Furthermore, recovery by the electrode of its original potential was very slow. A second difficulty of the stronger fields was the fact that the bridge could not be set accurately enough to eliminate completely the oscillations of the electrometer needle.

DISCUSSION

The data presented above show that the potential of gold or platinum against a solution is only slightly affected by an electric field of moderate strength. The changes in potential which do occur may be due to any one of several factors.

a. Conduction through the electrode

If an appreciable current flowed through the metal there might be some hydrogen or oxygen liberated which would change the potential. This explanation of the change does not seem probable when we consider that the changes occur as frequently in the two most dilute solutions as in the two most concentrated solutions.

The instability and change of the potential of electrodes of type A in strong fields was attributed to conduction, because any change in conditions which would increase conduction through the electrode always increased the instability of the potential. The rate at which the electrode recovered the original potential was very slow, which was probably due to the slow change in amount of gas at the surface of the electrode.

These results throw some doubt on the deductions of Coehn and Schafmeister (2) and of Theissen and Heumann (27). These workers used a small metal wire suspended in electrolytes through which the field drop was 110 and 46 volts per centimeter, respectively. They measured the deflection of the wire caused by the field, then determined the potential of the metal in the same solution when there was no potential gradient through it. Our results indicate that the potentials measured by these workers were quite different from the potentials of the wires when the field was on. It is impossible to estimate what error appeared in their work, because the fields they used were from fourteen to thirty-five times as strong as those used in our experiments.

b. Surface conduction

McBain and his coworkers (14, 15) have shown that the electrical conductivity at a glass-solution interface is greater than in the bulk of the solution, and this same phenomenon may occur at a metal-solution interface. The movement of ions longitudinally through the diffuse double layer would somewhat change the distribution in the double layer and would, if the distribution were sufficiently disturbed, cause a change in the potential.

It was found that the addition of a small amount of a substance which is known to be highly absorbed at the metal-liquid interface, such as tannic acid or gelatin, would reduce the change in potential of the small cylindrical platinum electrodes. A thin coating of collodion would accomplish the same result. This indicates that the change occurs at the interface.

Whatever may be the true cause of the observed changes of potential brought about by the electric field, the results have a very significant value to the theory of electrokinetic phenomena.

The experimental results reported show that the potentials of the smallest electrodes are affected least by the electric field. Going further one may say that the potential of an electrode the size of a colloidal particle would not be affected at all. That small platinum or gold wires in an electric field behave similarly to a platinum or gold sol has been shown by Kleeman and Fredricksen (7).

The results further show that a greater change is observed when the field strength is increased. The field strengths used in the ordinary measurement of cataphoretic velocities of gold and of platinum sols (8, 18) are less than those used in these experiments. Therefore we can conclude that in cataphoresis experiments of gold and platinum sols, the Nernst potential of the gold or platinum against the solution is unchanged by the field.

If we consider one side of the "double layer" as diffuse, after Gouy (4), and develop the idea of the relation between the Nernst potential and the zeta potential as was done by Smoluchowski (3), we find that the Nernst potential contains the zeta potential. It is evident that since the Nernst potential of gold or platinum colloidal particles is unaffected by the applied electrical field, we are certain that the zeta potential also is unchanged by the same conditions.

The potential across the double layer depends upon the charge per unit area and also upon the charge distribution in the outer or diffuse layer. One would not expect an applied field to affect the charge per unit area. Furthermore, it is almost beyond the bounds of possibility that, if the charge per unit area were affected, the outer or diffuse layer would be affected an exactly equal amount in the opposite direction, which would be necessary in order for the potential to remain the same. Therefore, since the zeta potential of a colloidal particle remains constant, we must conclude that the charge distribution, or its physical symmetry, in the diffuse layer is unaffected by an electric field of the strength used in cataphoresis experiments.

This assumption is common to both the Helmholtz-Lamb and Debye-Hückel theories of cataphoresis (17). Actual experimental tests of the other assumptions will be of great value in testing these theories, and in the ultimate explanation of the mechanism of cataphoresis. A more extensive knowledge of the interface is also necessary for a more complete explanation of the potential of the oxygen electrode.

SUMMARY

The effect of an electric field of moderate strength on the potentials of gold and platinum against several solutions has been determined.

The results prove the validity of one fundamental assumption in the treatment of cataphoresis, namely, that the charge distribution in the double layer is unaffected by an applied field of the strength used in cataphoresis experiments.

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HALIDE-IODINE EQUILIBRIA IN NEUTRAL SALT SOLVENTS[1]

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I. INTRODUCTION

Interest in the triiodide equilibrium

$$I_3^- \rightleftharpoons I_2 + I^- \qquad (1a)$$

was renewed with the appearance of a paper by Brönsted and Pedersen (1922) (1). These authors determined the solubility of iodine in an aqueous solution of 1.65 molar potassium chloride with sufficient hydrochloric acid to produce an acidity of pH 5, thereby preventing hydrolysis[2] (2). By measuring the increase in the solubility of iodine produced by the addition of relatively small amounts of potassium iodide at 15° and 18.5°C., they gave an extrapolated value for the mass action function,

$$L = \frac{c_{I_2} \times c_{I^-}}{c_{I_3^-}}$$

namely, 0.00611 for 25°C. In calculating L they considered this increase in the solubility of iodine as triiodide and the concentration of free iodine equal to the solubility of iodine in the potassium chloride solvent.

Their purpose in employing 1.65 molar potassium chloride as solvent was to minimize the changes in ionic environment (3) produced by varying the concentration of added potassium iodide.

Carter and Hoskins (1928) (4) pointed out that Brönsted and Pedersen failed to recognize the possibility of a salting-out effect of the chloride ion on the neutral molecule, iodine, and the formation of a chloride-iodine complex:

$$ClI_2^- \rightleftharpoons I_2 + Cl^- \qquad (1b)$$

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[1] This paper was constructed from a dissertation submitted by M. Helene Lewinsohn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1933.

[2] The reactions are:

$$I_2 + H_2O \rightleftharpoons H^+ + I^- + HIO$$
$$3I_2 + 3H_2O \rightleftharpoons 6H^+ + 5I^- + IO_3^-$$

Iodine on dissolving in water may be interpreted as undergoing internal oxidation and reduction.

Carter and Hoskins also asserted that "when suitable corrections are made for the disturbing effect of polyhalide formation, it is found that the resulting value of K is approximately the same as when the solvent is water." However, they submitted no experimental proof for this statement. This important conclusion was also tacitly assumed by Kiss and Urmanczy (1931) (5). It may be interpreted as a reiteration of part of the well-established principle enunciated by Brönsted (6); namely, "that the simple gas laws hold good for ions or salts when other salt solutions are employed as solvents, the concentration being large in comparison with the dissolved ion or ions," i.e., in a constant ionic environment. This principle involves two fundamental ideas; namely, that the concentration of the salt serving as solvent is large in comparison with the dissolved ion and that the solvent salt gives no evidence of interacting chemically with the dissolved molecule or ion.

These two conflicting opinions and the fact that the triiodide constant frequently enters into the interpretation of the equilibria involving iodine occasioned this investigation, the purpose being to determine this constant, $K_{cI_3^-}$, in solvents of constant thermodynamic environment in a manner which would be free from the objections raised by Carter and Hoskins.

In order to test the applicability of Brönsted's principle to the aforementioned equilibria it was necessary to establish the following:

(1) The solubility of iodine in water at pH 5 with a greater precision than had been heretofore obtained.

(2) The values for the mass action functions for the three equilibria

$$ClI_2^- \rightleftharpoons I_2 + Cl^- \qquad (1b)$$

$$BrI_2^- \rightleftharpoons I_2 + Br^- \qquad (1c)$$

$$I_3^- \rightleftharpoons I_2 + I^- \qquad (1a)$$

in high concentration (2 molar) of a salt, such as potassium nitrate, which gives no evidence of interacting chemically with iodine.

(3) The constancy of the mass action function for the triiodide equilibrium,

$$I_3^- \rightleftharpoons I_2 + I^- \qquad (1a)$$

in a high concentration of potassium chloride, which salt, however, gives evidence of combining chemically with iodine.

In each of the above equilibria, the excess iodine dissolved in a halide salt solvent shall be designated as halide–iodine complex, and by measuring this increase in solubility the values for the mass action function will be calculated.

II. EXPERIMENTAL

The following are the source, preparation, and purification of chemicals required in the course of solubility measurements.

Potassium nitrate and potassium chloride were recrystallized twice from distilled water, dried in an oven at 120°C., ground in an agate mortar, and dried again at 120°C. for twenty-four hours. The salts were kept in a desiccator over calcium chloride until cool, then the samples were weighed.

Potassium bromide, Kahlbaum's "Zur Analyse," was dried in an oven at 120°C. and was kept in a desiccator over calcium chloride.

Potassium iodide, Mallinckrodt "Reagent Quality," was kept in a desiccator over phosphorus pentoxide. Samples gave no color with starch in neutral solution after twenty-four hours in the dark and no color with starch after acidification.

Iodine was resublimed once from a mixture of potassium iodide and iodine and twice without potassium iodide. The iodine was kept over calcium chloride in a desiccator, the cover of which had not been greased (7). Solutions of iodine containing 4 per cent potassium iodide (8) were used as primary standards.

Solutions of arsenious oxide, standardized against iodine solutions, were used as secondary standards. All titrations were made in bicarbonate buffers according to the directions of Washburn (8), using weight-burets (9).

The concentration of iodine necessary to produce a detectable color with the sterilized starch paste was of the order of 5×10^{-6} normal, and appropriate corrections were made.

Nitrogen, commercial, was purified by passing it through a solution of potassium pyrogallate (10), over heated copper gauze in a quartz tube, through dilute sulfuric acid, thence through a tube filled with soda lime. Finally, nitrogen was bubbled through the solvent solution so as to insure the same aqueous tension.

All salt solutions in which the solubility of iodine was to be determined were maintained at a pH of 5 to prevent hydrolysis of the iodine (see footnote 2) (2). This pH was adjusted by indicators.

All solubility measurements are reported as moles per liter of solution and were performed at 25 ±0.005°C.

Procedure in determining solubilities

The apparatus used is shown in figure 1, and is similar in principle to that used by Brönsted and Pedersen (1).

The solubility tube B was filled with a mixture of iodine and glass beads, and was plugged at the lower end with silica fiber and at the upper end with glass wool[3], since silica fiber proved to be too brittle to serve as a plug.

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[3] This experimental work was considerably delayed by the inability to obtain reproducible values for the solubility of iodine. This difficulty was traced to the

Flasks D, E, and F contained iodine crystals to maintain a constant vapor pressure of iodine. Flasks E and F contained in addition to the iodine crystals about 50 cc. of the solvent to serve as an extra precaution to saturate the nitrogen entering at 5 and 7 with respect to iodine and water vapor. Nitrogen was passed through stopcocks 4, 5, and 6 for 3 hours and through the solution in flask A in the ratio of one hour for each 50 cc. of solution to displace oxygen.

To flush the contents of the solubility tube B and to insure complete removal of the previous solution of different concentration, one portion of 25 cc. and two portions of 50 cc. each of solution were placed in flask A. The solution passed at the rate of 50 cc. of solution in 25 minutes, over the iodine into flask D, and remained there for 20 minutes. Pressure of nitrogen then forced the solution into flask F, gentle suction being applied at K. However, some of the solution remained in tube B, and was removed to

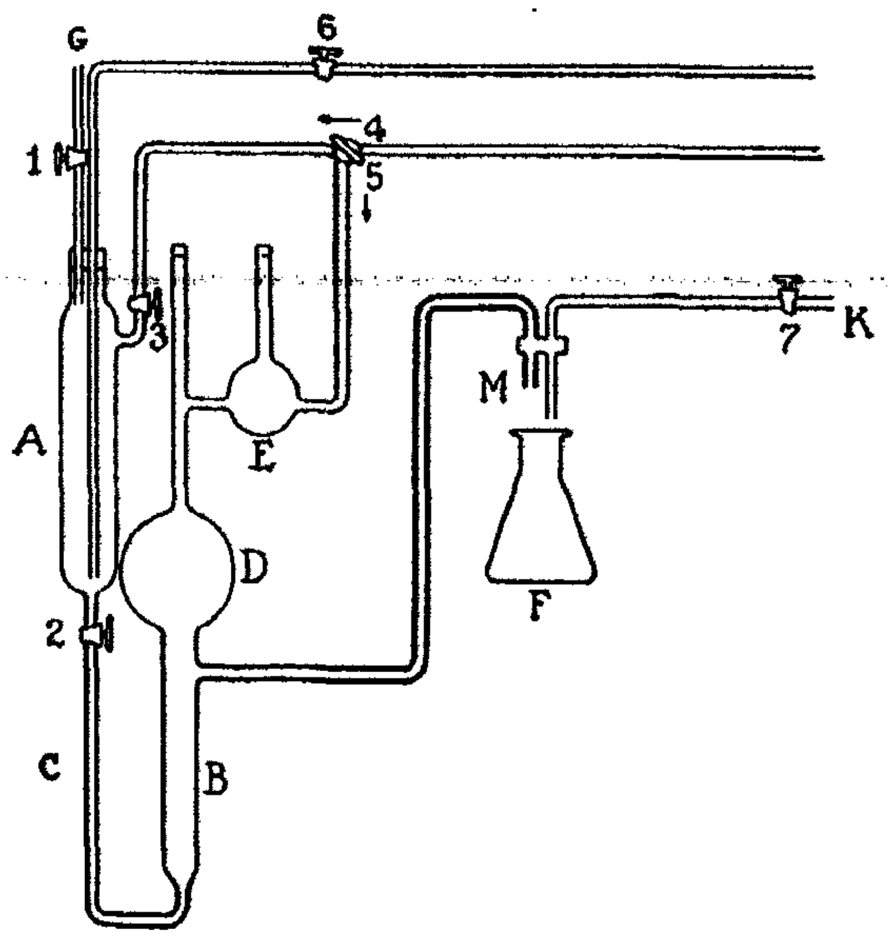

FIG. 1

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alkaline reaction produced by the dissolving of the glass wool used as filter. Ten different samples of glass wool were tested as follows: 10 g. of glass wool were left in contact with 250 cc. of distilled water. After 4 hours these samples of glass wool yielded pH values ranging from 7.8 to 10.6, which did not change on standing. Alkali-free glass wool was essential to obtain concordant values for the solubility of iodine, for any other glass wool rendered the solutions basic and formed hypoiodites by the hydrolysis of iodine. The firm of Friedrich and Dimmock of Millville, New Jersey, spun especially some alkali-free glass wool which yielded an equilibrium pH of 6.8.

flask A by suction applied at G. This procedure was repeated four times to assure complete removal of the previous solution.

One hundred and fifty cubic centimeters of the solvent were placed in flask A, and the air was replaced by nitrogen. The solvent was passed through the iodine crystals into flask D, and thence back to flask A. A 150-cc. sample was taken so that each run could be separated into two parts, the second half passing through the solute at least four times. In each case there were at least two samples of 150 cc. each, thereby giving four weight-buretfuls and a minimum of ten titrations for the iodine concentration for each solubility measurement.

The sample in which the concentration of iodine was to be determined was transferred as follows: Flask F was removed. The saturated iodine solution flowed from the solubility tube B directly into a weight-buret, suspended under M, containing 5 cc. of a concentrated potassium iodide solution to prevent loss of iodine during transfer and subsequent titrations.

TABLE 1

Solubility of iodine

2 *M* KNO_3 + 0.0025 *M* KI		1.65 *M* KCl + 0.1 *M* KI	
TIMES SOLUTION OVER IODINE	SOLUBILITY VALUE $\times 10^6$	TIME SOLUTION IN CONTACT WITH IODINE	SOLUBILITY VALUE $\times 10^6$
4	2137 ±2	Overnight	4421 ±1.4
6	2138 ±2	2.5 days	4418 ±2.5
2	2139 ±1.6	Overnight	4420 ±2.2
5	2140 ±1.4	7.5 days	4425
	2138.5 (average)		4421.0 (average)

Kolthoff (11) states that in a solution less concentrated than 0.01 molar, the color appears somewhat too late in titrations of sodium thiosulfate with iodine, using starch as an indicator. This was found not to be true when arsenious oxide was used as the reductant. Solutions faintly colored blue with starch iodine were left for about seventeen hours and there was no perceptible color change. This indicates that there was no retardation in the appearance of the end point, and that the resultant solution had the correct pH according to Washburn (8). All titrations were made by daylight.

After six different determinations had been made, it was found necessary to refill the solubility tube B. This probably was due to the contamination of the iodine in tube B with traces of stopcock grease (7).

The proofs that solubility equilibrium was obtained are as follows: (1) A solution saturated with iodine at 30°C. was passed over the iodine at 25°C.; a solution saturated with iodine at 25°C. was passed over the iodine at 25°C. The solubility values in the two cases were within limits of experimental error. By the former method the solubility of iodine in a 1.65 molar potassium chloride solvent was found to be 0.003534 ± 4×10^{-6}; by the latter, 0.0035336 ± 5×10^{-7}. (2) Less than 0.15 per cent change in the solubility value was found by passing the solution over the solid phase as many as six times, or by allowing the solution to remain in contact with iodine for a maximum time of seven days (see table 1).

III. PRESENTATION AND DISCUSSION OF EXPERIMENTAL DATA

Solubility of iodine in water

As a mean of six experiments the solubility of iodine in water at pH 5 was found to have been 0.001321 moles per liter of solution, thus substantiating the value of Carter (12) and of Bray (2), the latter to within 0.1 per cent. Table 2 cites the values for this solubility appearing in the literature.

TABLE 2

Solubility of iodine in water

SOLUBILITY OF IODINE	pH VALUE	DATE	INVESTIGATOR
0.001337		1894	Jakowkin (13)
0.001341 ±4×10^{-6}		1898	Noyes and Seidensticker (14)
0.001333		1908	Campbell and Hartley (15)
0.001320 calculated	Acid solution	1910	Bray (2)
0.001310		1920	Oliveri, Mandala, and Angencia (16)
0.001329	Conductivity water	1924	Pearce and Eversole (17)
0.001321 ±2×10^{-6}	5	1925	Carter (12)
0.001321 ±2×10^{-6}	5	1930	Present investigation
0.001332 ±3×10^{-6}		1931	Kiss and Urmanczy (5)

Theoretical

It is a well-known fact that the addition of a neutral salt to a system in equilibrium with the solid phase changes the solubility of the non-electrolyte, i.e., salting out the neutral molecule. The amount salted out depends upon the specific properties of the non-electrolyte, or neutral molecule, and the added salt,—the dielectric constant of the medium, the radius of the ion, and the distance of closest approach of ion to non-electrolyte. The total decrease in the concentration of the non-electrolyte or that salted out by a single ion has been recently calculated by Butler (18) and is equivalent to that calculated by Debye and McAulay (19), except for the fact that the latter equation requires the dielectric constant of the pure solvent and the former that of the solution. Experimental data have been examined from the point of view of the Debye-McAulay equation by Randall and Failey (20) who conclude that, "there seems to be a qualitative agreement with the demands (of the equation) in most cases, but not a quantitative one." Unfortunately, at the present time, there is not sufficient independent data to make the equations of Butler or of Debye and McAulay feasible for this problem. Consequently, in this report the values for the salting-out constants are those given by Kiss and Urmanczy (5).

These authors[4] calculate the salting-out constant in the Setschenow equation (21),

$$\log s = \log s_0 - kC \qquad (2)$$

where s_0 is the measured solubility of iodine in water at pH 5,
s is the calculated concentration of the iodine molecule,
C is the measured concentration of the solvent salt, and
k is the salting-out constant.

The average of these values for k is used as the salting-out constant and the concentration of free iodine is determined by means of the same equation. This direct method is used for salts like potassium nitrate, sodium sulfate, etc., which salts give no evidence of combining with iodine. Values for k for these salts using either acetylene or nitrous oxide or both as solutes are calculated. From these values the following average ratios are observed:

$$\frac{k_{C_2H_2}}{k_{I_2}} = 1.15 \quad \text{and} \quad \frac{k_{N_2O}}{k_{I_2}} = 1.25$$

Therefore, for salts like potassium chloride, magnesium chloride, potassium bromide, etc., which give evidence of combining chemically with iodine, the k for iodine has to be determined indirectly and the preceding approximations are used. At best, the values for k and s so calculated are subject to error.

The concentration of iodine, of chloride, bromide, and iodide, and of chloride-iodine, bromide-iodine, and triiodide ions and the mass action functions are calculated as follows. s_0, s, and C have the same significance as previously stated, and S is the measured (total) solubility of iodine as I_2, ClI_2^-, etc. Then for the assumed equilibria, namely,

$$ClI_2^- \rightleftharpoons I_2 + Cl^- \qquad (1b)$$

$$BrI_2^- \rightleftharpoons I_2 + Br^- \qquad (1c)$$

$$I_3^- \rightleftharpoons I_2 + I^- \qquad (1a)$$

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[4] Whenever Kiss and Urmanczy transposed from natural logarithms to common logarithms, they multiplied the natural logarithm by the factor 2.303 instead of dividing as they should have done. Inasmuch as they were consistent in the use of this factor, their values for s and K agreed to within 0.1 per cent with those values found by us when the factor 2.303 was used correctly in transposing from the natural to the common system of logarithms.

the concentrations at equilibrium are:

$$c_{ClI_2^-},\ c_{BrI_2^-} \text{ or } c_{I_3^-} = S - s$$

$$c_{Cl^-},\ c_{Br^-}, \text{ or } c_{I^-} = C - (S - s)$$

$$c_{I_2} = s$$

Then in terms of the mass action law, we have:

$$K_{c_{ClI_2^-}} = \frac{c_{I_2} \times c_{Cl^-}}{c_{ClI_2^-}} = \frac{(s)\ (C - S + s)}{(S - s)} \tag{3b}$$

and, similarly, for the two equilibria, BrI_2^- (3c) and I_3^- (3a).

The value for the activity coefficient, f, of a solute in a saturated solution is determined by the relationship (22):

$$\log \frac{s}{s_0} = \log \frac{f_0}{f} \tag{4}$$

where s and s_0 have the same significance as previously stated, and the characters with the subscript 0 refer to water at a pH of 5 as solvent, and those without the subscript refer to a solvent prepared by adding neutral salts to water and adjusting the pH to 5. There are two possible standard states of reference, namely, water and the solvent salt (23). In the first case, f_0, the activity coefficient of the saturating solute, iodine, in water is set equal to unity. In the second case, f, the activity coefficient of the saturating solute, iodine, in the salt solvent is set equal to unity.

Defining

$$K_c \times K_f = K_a \tag{5}$$

where K_c, K_f, and K_a represent the constants for the mass law expression in terms of concentrations, activity coefficients, and activities, respectively. In each case K_a is determined graphically by plotting the values of $K_{c_{ClI_2^-}}$ or of $K_{c_{BrI_2^-}}$ or of $K_{c_{I_3^-}}$ against the concentration of added halide, and extrapolating to zero concentration of added salt. K_a is a constant for any given temperature and pressure which is independent of the changes in concentration. K_a for any given equilibrium changes only as the solvent changes. Since in a solution saturated with iodine,

$$c_{I_2} \times f_{I_2} = a_{I_2} \tag{6}$$

a_{I_2} is a constant, the change in the values for K_c with the total salt concentrations is due largely to the variations in the ratios of $f_{\text{halide-iodine ion}}$ to

$f_{\text{halide ion}}$. This ratio of the activity coefficients of ClI_2^- to Cl^-, of BrI_2^- to Br^-, and of I_3^- to I^- may be calculated from

$$\frac{f_{ClI_2^-}}{f_{Cl^-}} = \frac{K_{e_{ClI_2^-}} \times f_{I_2}}{K_{e_{ClI_2^-}}} \tag{7b}$$

similarly, for the ratio of $f_{BrI_2^-}$ to f_{Br^-} (7c), and for the ratio of $f_{I_3^-}$ to f_{I^-} (7a). If these solubility measurements are made in concentrated salt solutions and if the ratio of the activity coefficients is determined solely by the electrical charge type, this ratio should be unity (24). Any deviations from unity must be due to specific individual properties of the halide ion as contrasted with the halide-iodine ion. That is, in solutions of high salt concentration, whereby the environment is held constant, a constant value for the mass action function, K_e, independent of the halide-iodine formation is a sufficient explanation for the increased solubility of iodine.

Discussion of the halide-iodine equilibria

The solubility of iodine was determined in a 1.65 molar and in a 2.0 molar potassium chloride solution. It is evident from column 5 of table 3 and from curve 3 of figure 2 that the value for $K_{e_{ClI_2^-}}$ increases slightly with increasing concentration of added halide ion. Kiss and Urmanczy's data substantiate this statement (figure 2, curve 1), but are not in quantitative agreement with these values.

This increasing value for the mass action function, K_e, signifies that as the chloride ion concentration increases, relatively less of the chloride ion combines with the iodine to form the chloride-iodine complex. This drift indicates either (a) that a different method of calculating the concentration of free iodine should be derived, (b) that the formation of a complex other than ClI_2^- ion should be considered, or (c) that the environment is not strictly constant, i.e., the simple gas laws are not obeyed.

This non-attainment of constant values for the $K_{e_{ClI_2^-}}$ expression is apparently in contradiction to data obtained experimentally by Carter and coworkers (25). The latter determined the solubility of iodine in different chlorides (potassium chloride, sodium chloride, barium chloride, etc.) of varying concentration and calculated the values for the $K_{e_{ClI_2^-}}$ function. Curve 4 of figure 2 records these values for sodium chloride as given by Dawson and Carter (25) and shows that practically constant values for $K_{e_{ClI_2^-}}$ are obtained. However, their method of calculating the salting-out constant for the chloride ion on iodine is such that the concentrations of iodine, chloride ion, and chloride-iodine ion complex are idealized, i.e., these values used are really activities and not concentrations.

This may be shown as follows: Carter and his associates did not consider

TABLE 3

Solubility of iodine in water to which two concentrations of potassium chloride were added

$k = 0.162$; $K_{a_{\mathrm{ClI_2^-}}} = 0.629$; all solubilities are multiplied by 10^3

KCl ADDED	S	s	$c_{\mathrm{ClI_2^-}}$	$K_{c_{\mathrm{ClI_2^-}}}$	REFERENCE STATE	
					$f_{\mathrm{I_2}}$	$\frac{f_{\mathrm{ClI_2^-}}}{f_{\mathrm{Cl^-}}}$
molar						
	1.321					
1.65	3.533	1.012	2.521	0.658	1.31	1.37
2.0	3.829	0.956	2.870	0.664	1.38	1.46

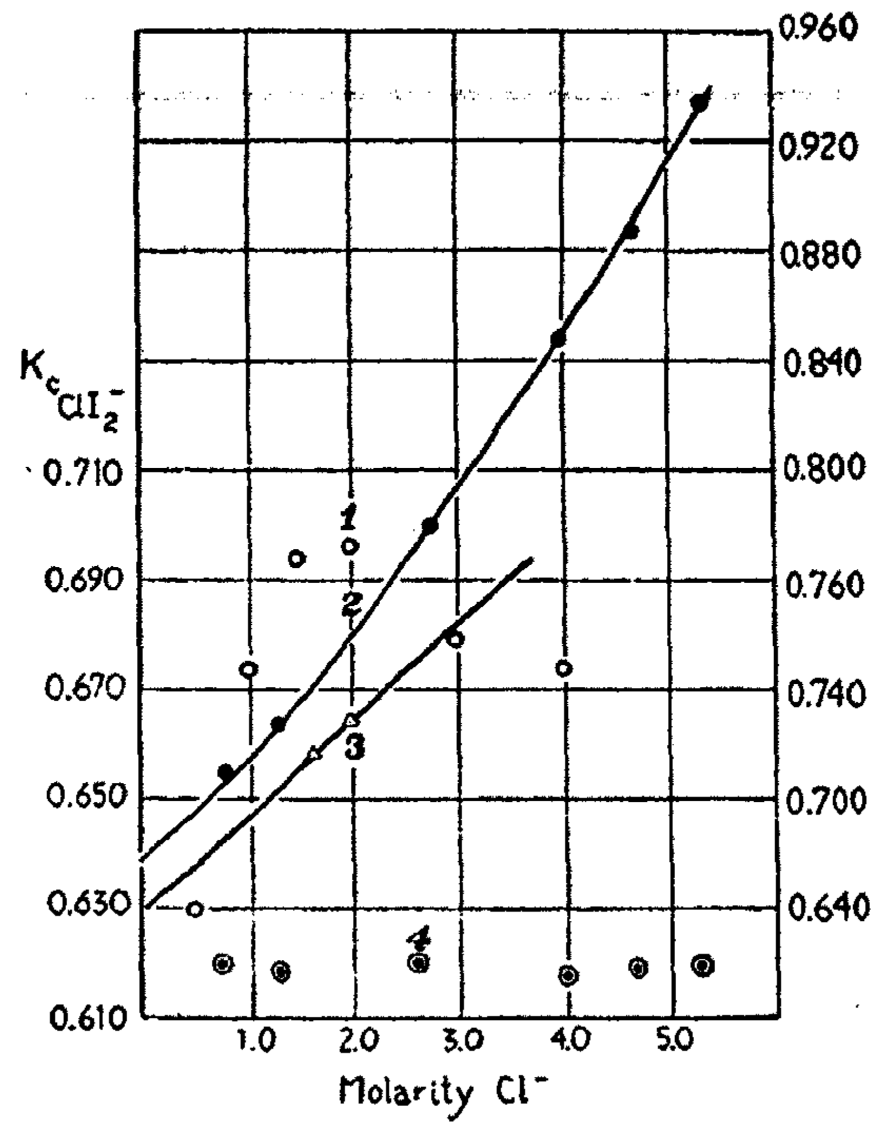

FIG. 2

○ Potassium chloride (Kiss and Urmanczy); ordinates on the left.
● Sodium chloride (Dawson and Carter, recalculated); ordinates on the right.
△ Potassium chloride (present investigation); ordinates on the left.
⊙ Sodium chloride (Dawson and Carter, original); ordinates on the left.

the salting-out effect,—they therefore assumed that the concentration of free iodine was equal to its concentration in water, and that the increase in the solubility of iodine on the addition of potassium chloride was due entirely to the formation of ClI_2^- ion and they calculated the values for the mass action expression according to equation 3b. These values were then plotted against the concentration of added chloride ion and were extrapolated to $C = 0$ to obtain $K_{a\mathrm{ClI}_2^-}$ value, termed by these workers $K_{0\mathrm{ClI}_2^-}$. Mathematically this may be expressed as

$$\lim_{c_{\mathrm{Cl}^-} \to 0} K_c = \lim_{c_{\mathrm{Cl}^-} \to 0} \frac{c_{\mathrm{I}_2} \times c_{\mathrm{Cl}^-}}{c_{\mathrm{ClI}_2^-}}$$

which has a definite value corresponding to an extrapolation of the constant to infinite dilution. This limit, which Carter calls $K_{0\mathrm{ClI}_2^-}$ is designated in the present notation as $K_{a\mathrm{ClI}_2^-}$. Carter and coworkers (25) combined the two subjoined equations to eliminate s,

$$K = \frac{(s)\ (C - S + s)}{(S - s)}$$

and

$$s = s_0 e^{-kC} \tag{2}$$

and assuming that $(S - s)$ is small as compared with C, and $K_{c\mathrm{ClI}_2^-}$ equal to $K_{a\mathrm{ClI}_2^-}$, they obtained the following approximation:

$$k = 1/C \log_e s_0 \ (1 + C/K)/S$$

Thus they obtained the value for k (salting-out constant), and the value for s (concentration of free iodine) could then be calculated by the Setschenow equation (2).

Inasmuch as they set $K_0 = K_c$ in calculating the value for k (equation 2), and as this value was used to determine s, the concentration of free iodine—the most important factor, for at equilibrium the concentration of each substance is determined in part by this value—the values for k, I_2, ClI_2^- ion and Cl^- ion approximate ideally perfect ones, and the values reported for the mass law expression lose the significance intended for them.

The justification of the present reasoning and criticism is now presented and is independent of a statement made by Kiss and Urmanczy (5). Setting

$$x = c_{\mathrm{I}_2} = s' \neq s_0$$

s' is used rather than s to avoid confusion, but it will be seen subsequently that $s' = s$ (Carter) $\neq s$ (Kiss and Urmanczy). Carter and his associates stated that

$$\frac{(x)\ (C - S + x)}{(S - x)} = K_c$$

whereas it is really K_o. For this value for K_c was found by plotting the concentration of added halide against the values obtained for the mass action expression, assuming $k = 0$ and extrapolating to $C = 0$ (previously described). Since x is the only unknown, the equation takes the quadratic form yielding,

$$x^2 + x\,(C - S + K_c) - K_cS = 0;\ x = \phi(CS).$$

For each concentration of added halide the value of x, the concentration of free iodine, is calculated and substituted in the Setschenow equation (2) to find the value for k. The value for k so derived is identical with that of Carter and coworkers as was expected. Thus the values for I_2, ClI_2^- ion, and Cl^- ion approximate activities rather than the desired concentration values.

TABLE 4

Solubility of iodine in 2.0 molar potassium nitrate to which three different concentrations of potassium chloride were added

$k = 0.162$; all solubilities are multiplied by 10^3

KCl ADDED	S	x	$c_{ClI_2^-}$	$K_{c_{ClI_2^-}}$	STATES OF REFERENCE		
					H_2O $K_o = 0.029$	2 M KNO_3 $K_o = 0.028$	
					f_{I_2}	f_{I_2}	$f_{ClI_2^-}/f_{Cl^-}$
molar							
	1.039				1.27	0.787	
0.05	1.112	1.031	0.0815	0.631	1.28	0.780	0.784
0.5	1.725	0.9583	0.7667	0.624	1.38	0.725	0.720
1.0	2.285	0.8839	1.4011	0.630	1.49	0.669	0.671

Curve 4 of figure 2 gives the values for $K_{c_{ClI_2^-}}$ function for sodium chloride as calculated by Dawson and Carter (25). The values for this function have been recalculated (using the salting-out constant as given by Kiss and Urmanczy) and have been plotted in figure 2, curve 2.

Since it is probable that changes in ionic environment are responsible for the deviations in these values for the mass law expression, the values for the $K_{c_{ClI_2^-}}$ function have been determined in the neutral salt solvent, 2 molar potassium nitrate. Table 4, column 5, shows that these values are practically invariant. Consequently, the assumptions that the only complex which need be considered is the ClI_2^- ion and that if the environment is stabilized then constant values for the $K_{c_{ClI_2^-}}$ function are obtained, are valid.

It will be noted (table 5, column 5, and figure 3), that in replacing a solution of potassium chloride by one of potassium bromide the values for the mass action function,

$$K_{c_{BrI_2^-}} = \frac{c_{I_2} \times c_{Br^-}}{c_{BrI_2^-}} \tag{3c}$$

decrease with increasing concentration of added halide, though in each case the environment has been stabilized with 2 *M* potassium nitrate. However, this drift in the value for the $K_{c_{BrI_2^-}}$ could have been predicted, for

TABLE 5

Solubility of iodine in 2.0 molar potassium nitrate to which six different concentrations of potassium bromide were added

k = 0.151; K_a = 0.0820 (water as standard state); K_a = 0.0759 (2.0 molar potassium nitrate as standard state); all solubility values are multiplied by 10^3

KBr ADDED	S	s	$c_{BrI_2^-}$	$K_{c_{BrI_2^-}}$	STATES OF REFERENCE: H₂O: f_{I_2}	H₂O: $\frac{f_{BrI_2^-}}{f_{Br^-}}$	2.0 *M* KNO₃: f_{I_2}	2.0 *M* KNO₃: $\frac{f_{BrI_2^-}}{f_{Br^-}}$
molar								
	1.039							
0.025	1.375	1.035	0.340	0.0752	1.27	1.17	0.783	0.776
0.05	1.717	1.031	0.696	0.0741	1.28	1.16	0.780	0.762
0.1079	2.508	1.022	1.486	0.0732	1.29	1.15	0.774	0.746
0.2	3.760	1.008	2.752	0.0722	1.31	1.16	0.763	0.726
0.5	7.741	0.9636	6.777	0.0701	1.37	1.17	0.729	0.673
1.0	14.06	0.8938	13.162	0.0670	1.48	1.20	0.677	0.598

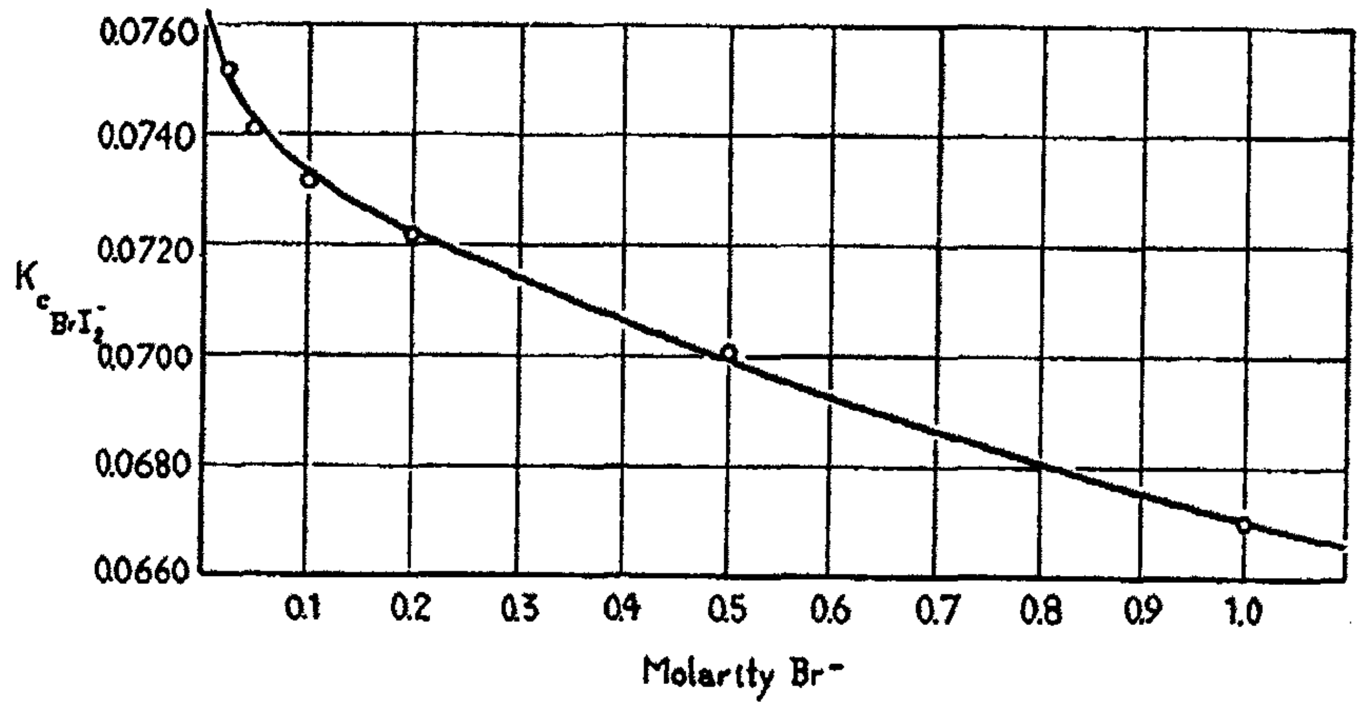

FIG. 3

the solubility of iodine is approximately 8.5 times as great in a potassium bromide solution as it is in a potassium chloride of the same molar concentration (table 11, columns 2 and 3). That this variation in the mass law expression is due to the formation of a complex other than BrI_2^- ion and is not in contradiction to the Brönsted principle may be concluded from the following statements: In both potassium chloride and potassium bromide solutions the solubility of iodine increases almost linearly with the increasing concentration of added halide ion. Up to 0.5 molar, for the molarity of the potassium bromide solution there is a decrease in the mass action function of approximately 1.5 per cent, while as the concentration of potassium bromide is doubled (0.5 *M* to 1.0 *M*) the decrease in the $K_{c_{BrI_2^-}}$ value is 4.5 per cent. This indicates that as the concentration of added halide increases, the excess solubility of iodine in potassium bromide is due more and more to the formation of a complex other than BrI_2^-, probably BrI_4^-. Table 5, columns 7 and 9, shows how far variations in the activity coefficient ratio, $f_{BrI_2^-}/f_{Br^-}$, are responsible for this decrease in the mass action function.

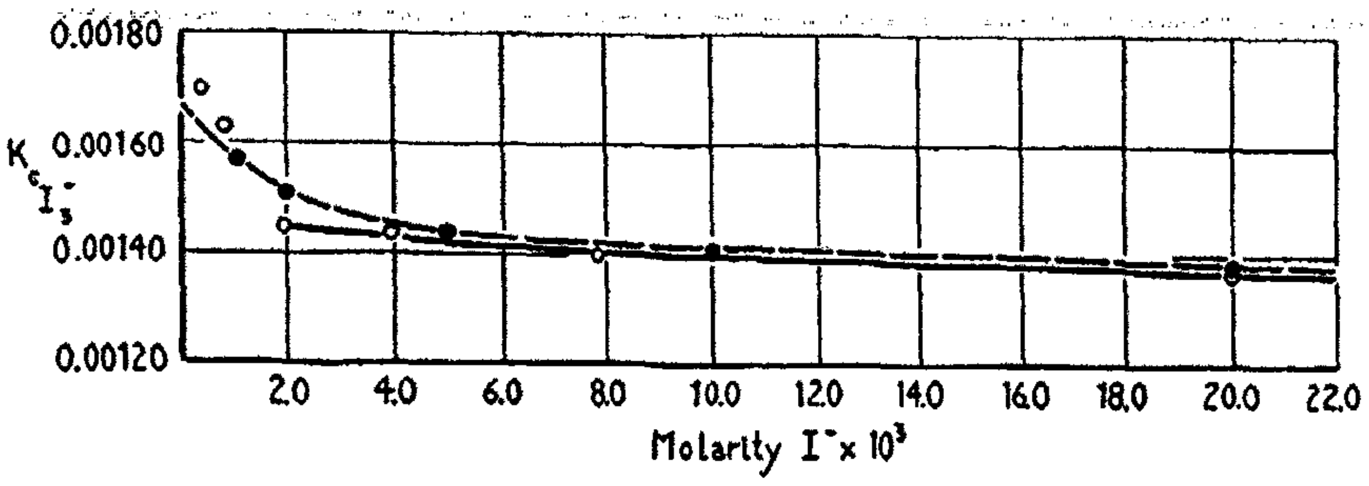

FIG. 4

○ Sodium iodide (Carter (12)).

● Potassium iodide (Bray and MacKay (27)), $K_{a_{I_3^-}}$ is 0.00153; (Lewis and Randall (28)), $K_{a_{I_3^-}}$ is 0.00143 from these measurements.

The study of addition complexes, i.e., BrI_2^- and ClI_2^- ions, resulted in part from that of the triiodide ion complex, which, without doubt, was the first halide–iodine equilibrium to be studied. From an exhaustive study of all pertinent literature, Grinnell Jones (26) has concluded that iodine does dissolve in a solution of an iodide ion to form the triiodide ion, and the value for the mass action function for this equilibrium decreases with increasing concentration of added halide ion.

To substantiate this statement there has been included the data of Bray and MacKay (27) and of Carter (12) (figure 4, curves 1 and 2). Bray and MacKay gave a value of 0.00153 for the K_a representing the triiodide equilibrium. Jakowkin (13) from distribution measurements and Grinnell Jones (29) from solubility measurements gave 0.00140 as the value for this equilibrium. This value has been used throughout the present calculations as K_a to evaluate the ratio of the activity coefficients of the triiodide to the iodide ion when water is chosen as the reference state, according to equation 7.

Although the triiodide equilibrium has been investigated in considerable detail, it has received little attention in neutral salt solvents. Values for the equilibrium function are often needed for such solvents, and should be in closer agreement, for the environment is constant, than they are in water as solvent, though perhaps decreasing slightly with increasing concentration of the halide ion, as postulated by Brönsted.

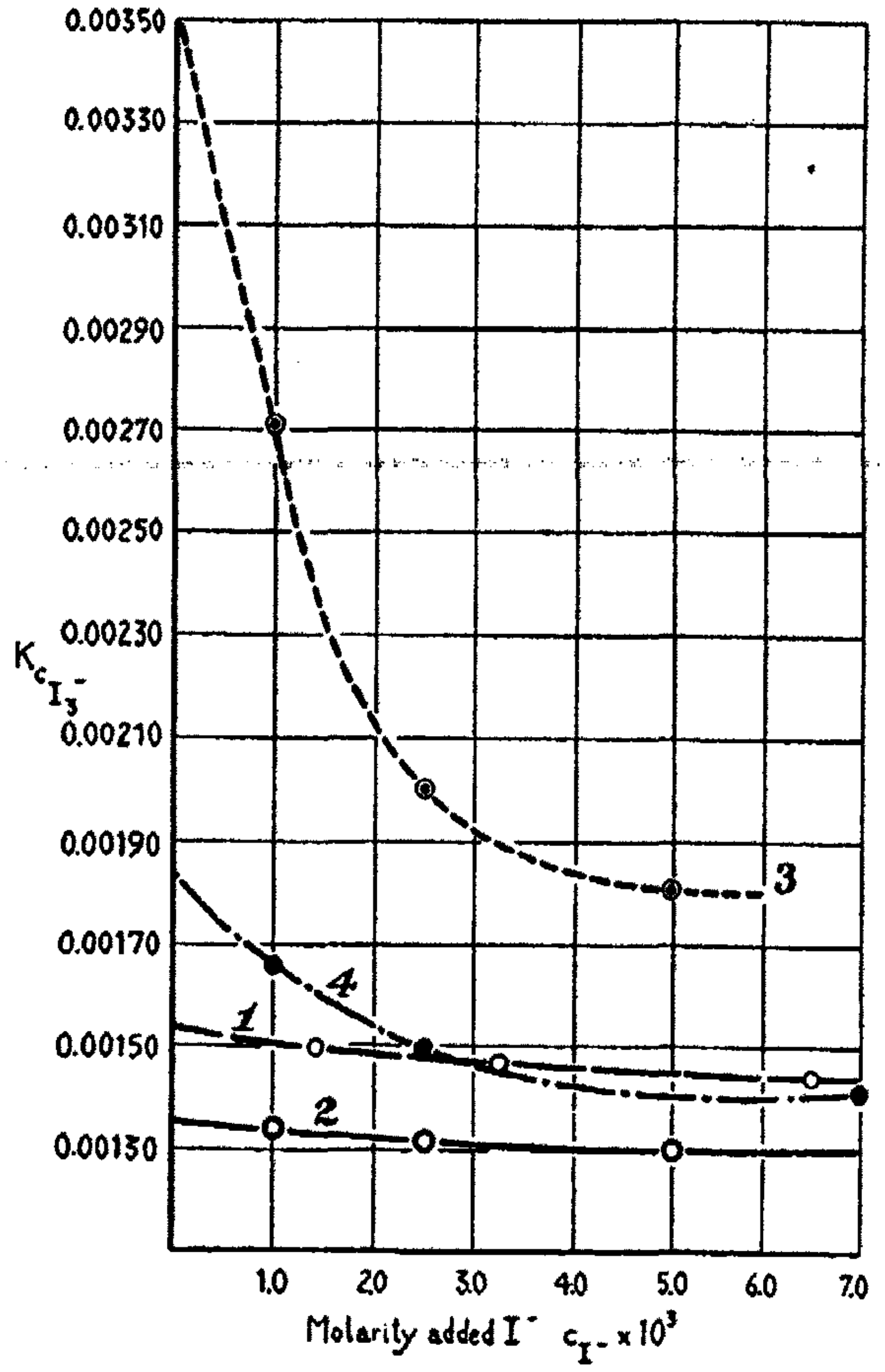

FIG. 5

○ 1.698 *M* sodium sulfate as solvent (Carter).
○ 2.0 *M* potassium nitrate as solvent.
⊙ 2.0 *M* potassium chloride as solvent.
● 2.0 *M* potassium nitrate plus 1.0 *M* potassium chloride as solvent.

Carter (12) used 1.698 molar sodium sulfate as the neutral salt solvent to which sixteen different concentrations of sodium iodide were added, and then through solubility measurements calculated the values for $K_{e_{I_3^-}}$ expression. From this data there have been computed the values for the ratio of $f_{I_3^-}/f_{I^-}$. These values (figures 5 and 5a, curve 1) show a decided downward drift with increasing concentration of added iodide ion.

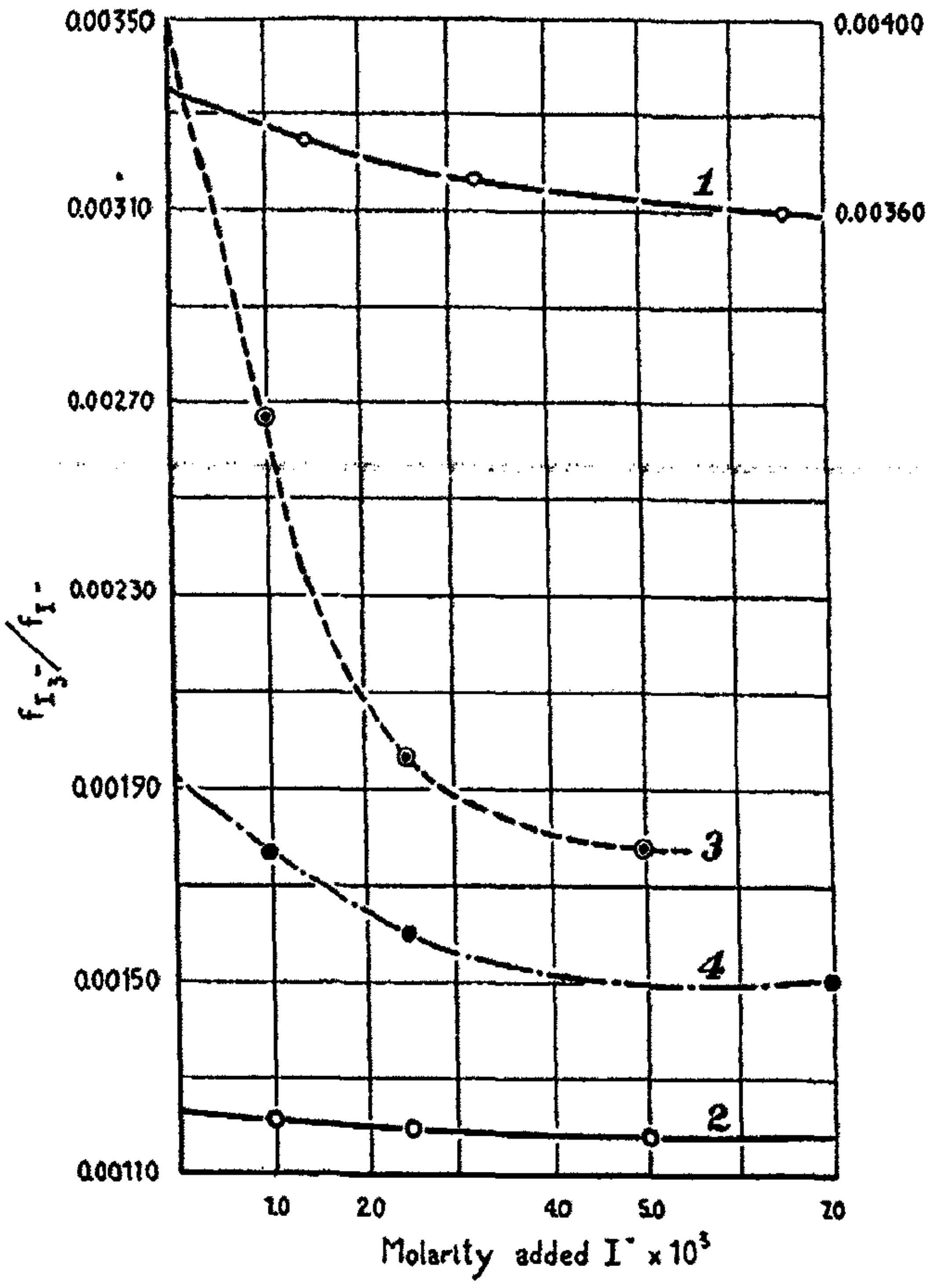

FIG. 5a

◦ 1.698 *M* sodium sulfate as solvent (Carter).
○ 2.0 *M* potassium nitrate as solvent.
⊙ 2.0 *M* potassium chloride as solvent.
● 2.0 *M* potassium nitrate plus 1.0 *M* potassium chloride as solvent.
Ordinates on the left are for curves 2, 3, and 4; ordinates on the right for curve 1.

A solution of 2.0 molar potassium nitrate was preferred to one of sodium sulfate, as the solvent maintaining constant ionic environment for the nitrate ion is known to have a salting-out effect 2.2 times smaller than the sulfate ion has. In neither case was it necessary to calculate the concentration of free iodine considering the salting-out effect of the sulfate ion or of the nitrate ion on iodine, for here the concentration of free iodine would not change the numerical value of the more important ratio of c_{I^-} to $c_{I_3^-}$. Therefore, the per cent drift in the value for $K_{c_{I_3^-}}$ should be the same, although the numerical value would be altered slightly. The salting-out effect of the iodide ion on iodine was ignored.

It is evident from table 6 (columns 5, 7, and 9) and curve 2 of figures 5 and 5a that the values for the $K_{c_{I_3^-}}$ function and those for the ratio $f_{I_3^-}/f_{I^-}$ decrease very slightly with increasing concentration of added iodide ion. However, it must be pointed out that the values for the equilibrium expression, when 2.0 molar potassium nitrate is used as solvent, are more nearly constant on varying the concentration of added iodide ion, than are the values when either water or 1.698 molar sodium sulfate is used as solvent.

TABLE 6

Solubility of iodine in 2.0 molar potassium nitrate to which four different concentrations of potassium iodide were added

K_c = 0.00135 (2.0 molar potassium nitrate as standard state); K_a = 0.00140 (water as reference state); all solubility values are multiplied by 10^3

KI ADDED	S	s	$c_{I_3^-}$	$K_{c_{I_3^-}}$	STATES OF REFERENCE			
					H_2O		2.0 *M* KNO_3	
					f_{I_2}	$f_{I_3^-}/f_{I^-}$	f_{I_2}	$f_{I_3^-}/f_{I^-}$
molar								
	1.039				1.27		0.787	
0.001	1.475	1.039	0.436	0.00134	1.27	1.215	0.787	0.799
0.0025	2.139	1.039	1.1	0.00132	1.27	1.20	0.787	0.771
0.005	3.256	1.039	2.217	0.00130	1.27	1.18	0.787	0.763
0.02	9.945	1.039	11.09	0.00129	1.27	1.17	0.787	0.756

In their recent publication Kiss and Urmanczy (5) made the tacit assumption that the triiodide equilibrium is the only one involved to account for the increase in the solubility of iodine on the addition of dilute solutions of iodide ion to neutral salts used as solvents, whereby the environment is stabilized. These authors used only one concentration of potassium iodide (0.025 *M*) added to the solvent salt, and consequently ignored the possibility that there might be a drift in the values for the $K_{c_{I_3^-}}$ function. Their value for the $K_{c_{I_3^-}}$ function is 0.00130 in 2.0 molar potassium nitrate as solvent. However, it is evident from the values obtained in the course of this investigation for the mass law expression, which decrease from 0.00134 to 0.00129 as the concentration of added iodide ion increases from

0.001 to 0.01 molar, that their unproven assumptions, i.e., that the triiodide is the only important polyiodide and that the salting-out effect of the iodide ion on the iodine molecule may be discounted, are valid for solvents, like potassium nitrate, sodium sulfate, etc., which salts give no evidence of combining chemically with the iodine.

Several authors (30) have assumed that regardless of the salt used as solvent to stabilize the environment, the value for the mass action function $K_{c_{I_3^-}}$ shall be invariant. Therefore, two different concentrations of potassium chloride were used as solvent, namely, 1.65 and 2.0 molar, to which three different concentrations of potassium iodide were added in each of which the solubility of iodine was determined.

For each, the chloride-iodine complex and only the salting-out effect on the chloride ion on the iodine were considered, as suggested by Carter (4), but calculated according to the method of Kiss and Urmanczy (5). It is evident from figures 6 and 5 (curves 1 and 3, respectively), and tables 7 and 9 (column 5) that these data are in contradiction to the current idea. The work of Spivey and Dawson (30), which appeared after the completion of the experimental work for potassium chloride as solvent here reported, substantiates these values for the mass action expression representing the triiodide equilibrium. Curve 2 of figure 6 records the data of Spivey and Dawson.

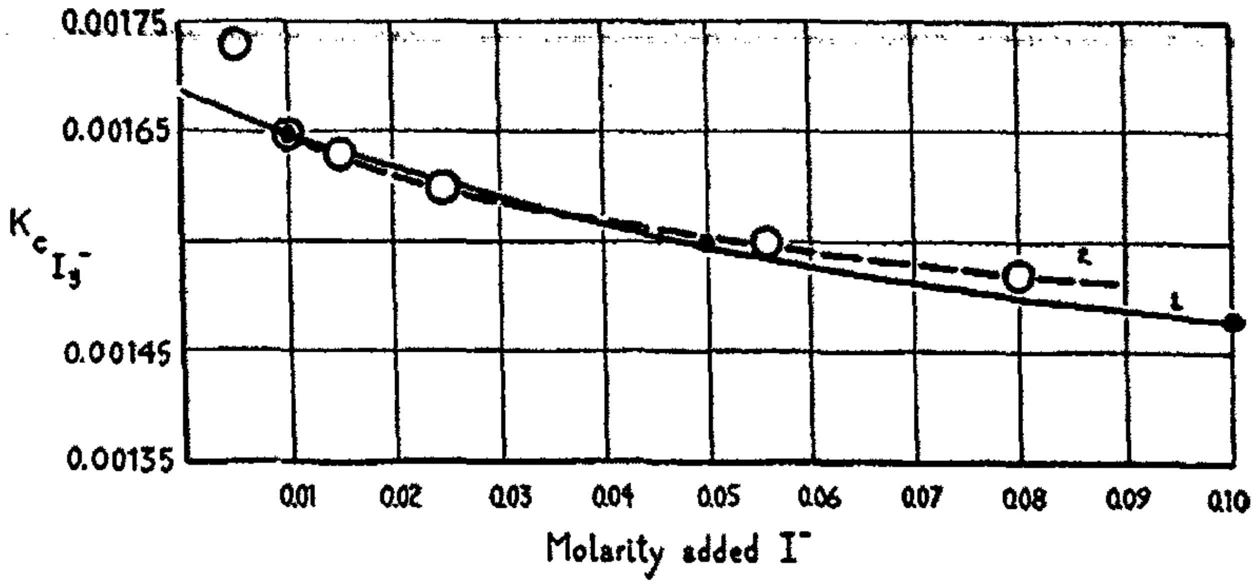

Fig. 6

● Present investigation.
○ Spivey and Dawson.

It was for this solvent, namely, 1.65 molar potassium chloride, that Brönsted and Pedersen (1) gave an extrapolated value for the $K_{a_{I_3^-}}$ at 25°C., called "L," as 0.00611. This value, correcting for the chloride-iodine complex and the salting-out effect of chloride ion on iodine, has been recalculated and found to be 0.00175, which agrees with the mean value of Spivey and Dawson (30) and that obtained by the present investigators.

Spivey and Dawson (30) in their calculations used the value for the salting-out constant k for the chloride ion on iodine as determined by Carter (4), to calculate the concentration of free iodine,—a procedure, which as previously pointed out, is questionable. In table 8, columns 3, 6, and 4, 7 show that this error is unimportant in this particular case. The more important factor in calculating the value for the $K_{c_{I_3^-}}$ relationship is that the ratio of c_{I^-} to $c_{I_3^-}$ shall be constant, and not whether the salting-out effect of the chloride ion on iodine has been correctly considered. The latter merely changes the numerical value of $K_{c_{I_3^-}}$ and does not here make for constancy of results. Therefore, this decided drift in the value of the constant for the mass law equilibrium probably is due to a factor other than the salting-out effect of the chloride ion on iodine.

TABLE 7

Solubility of iodine in 1.65 molar potassium chloride to which three different concentrations of potassium iodide were added

$k = 0.162$; $K_a = 0.00168$ (solvent as reference state)

KI ADDED	S	s	$c_{I_3^-}$	$K_{c_{I_3^-}}$	STATES OF REFERENCE H_2O f_{I_2}	 $f_{I_3^-}/f_{I^-}$	 1.65 M KCl f_{I_2}	 $f_{I_3^-}/f_{I^-}$
molar								
	3.533	1.012			1.30		0.766	
0.01	7.335	1.012	3.802	0.00165	1.30	1.54	0.766	0.757
0.05	23.32	1.012	19.78	0.00155	1.30	1.45	0.766	0.707
0.1	44.203	1.012	40.67	0.00148	1.30	1.37	0.766	0.675

TABLE 8

Comparison of the values for the $K_{c_{I_3^-}}$ expression in a 1.65 molar potassium chloride solution as solvent (obtained by Spivey and Dawson) with those in table 7

$k = 0.172$ (Spivey and Dawson); $k = 0.162$ (table 7)

The former's values were recalculated using $k = 0.162$

KI ADDED	s (TABLE 7)	SPIVEY AND DAWSON $k = 0.172$ s	 $k = 0.162$ s	$K_{c_{I_3^-}}$ (TABLE 7)	SPIVEY AND DAWSON $k = 0.172$ $K_{c_{I_3^-}}$	 $k = 0.162$ $K_{c_{I_3^-}}$
molar						
0.01	1.012	0.994	1.012	0.00165	0.00165	0.00168
0.05	1.012	0.994	1.012	0.00155		
0.056	1.012	0.994	1.012		0.00155	0.00157
0.08	1.012	0.994	1.012		0.00152	0.00154
0.1	1.012	0.994	1.012	0.00148		

There are three other possible reasons for the non-attainment of invariant values for the mass law expression representing the triiodide equilibrium in a chloride ion solvent.

(1) Probable failure of the Brönsted principle: If 2.0 molar potassium nitrate is a sufficiently concentrated solution to stabilize the environment, then the same should be true for 2.0 molar potassium chloride. To show that this failure to obtain constant values for the $K_{c_{I_3^-}}$ expression does not represent a failure, but rather a misinterpretation of the Brönsted principle, 2.0 molar potassium nitrate plus 1.0 molar potassium chloride was selected as solvent. In this solvent the values for the mass law expression and the ratio of the activity coefficients of the triiodide ion to the iodide ion follow the same drift, but to a less extent than they did in 2.0 molar potassium chloride solvent (figures 5 and 5a, curves 4 and 3). Table 10 cites the afore-mentioned values for this mixed solvent. Equivalent concentrations of potassium iodide were added. This indicates that the Brönsted principle must be carefully interpreted, i.e., a salt employed as solvent must be chemically inert with respect to the other solutes.

TABLE 9

Solubility of iodine in 2.0 molar potassium chloride to which three different concentrations of potassium iodide were added

$k = 0.162$; $K_a = 0.00140$ (water as reference state); $K_a = 0.0034$ (2.0 molar potassium chloride as reference state); all solubilities are multiplied by 10^3

KI ADDED	S	s	$c_{I_3^-}$	$K_{c_{I_3^-}}$	STATES OF REFERENCE			
					H₂O		2.0 M KCl	
					f_{I_2}	$f_{I_3^-}/f_{I^-}$	f_{I_2}	$f_{I_3^-}/f_{I^-}$
molar								
	3.829	0.956			1.37		0.725	
0.001	4.090	0.956	0.261	0.00271	1.37	2.67	0.725	0.576
0.0025	4.638	0.956	0.809	0.00200	1.37	1.97	0.725	0.425
0.005	5.560	0.956	1.731	0.00181	1.37	1.78	0.725	0.389

TABLE 10

Solubility of iodine in 2.0 molar potassium nitrate plus 1.0 molar potassium chloride to which three different concentrations of potassium iodide were added

$k = 0.162$; $K_a = 0.00184$ (solvent as reference state); $K_a = 0.00140$ (water as reference state); all solubilities are multiplied by 10^3

KI ADDED	S	s	$c_{I_3^-}$	$K_{c_{I_3^-}}$	STATES OF REFERENCE			
					H₂O		Solvent	
					f_{I_2}	$f_{I_3^-}/f_{I^-}$	f_{I_2}	$f_{I_3^-}/f_{I^-}$
molar × 10^3								
	2.285	0.882			1.50		0.668	
1.0	2.632	0.882	0.3467	0.00166	1.50	1.77	0.668	0.603
2.5	3.212	0.882	0.9274	0.00150	1.50	1.60	0.668	0.545
6.956	4.963	0.882	2.678	0.00141	1.50	1.51	0.668	0.512

(2) Formation of higher polyiodides. Heretofore this served as the answer. Similarly, Spivey and Dawson (30) ascribed this marked decrease in the values of the $K_{c_{I_3^-}}$ function to the formation of small quantities of I_5^- ion. The values for the $K_{c_{I_3^-}}$ function in solvents, potassium nitrate and sodium sulfate, show that the amount of I_5^- ion formed depended only upon the concentration of added iodide ion. Should one not then expect that the amount of I_5^- ion formed for a definite concentration of added iodide ion be independent of the salt used as solvent? But this is not true. From the summary of the concentrations of the triiodide ion formed on the addition of equivalent amounts of iodide ion in the three solvents, as presented in figure 7, it is evident: first, that the concentration of the triiodide ion formed decreases markedly with increasing molarity of added potassium chloride; secondly, that when potassium nitrate is present as solvent the values for the $K_{c_{I_3^-}}$ function are more nearly constant; and third, that whenever potassium chloride is present in the solvent the drift in the $K_{c_{I_3^-}}$ expression follows the same course (figure 5). Therefore, it is necessary to consider another hypothesis as an explanation for this drift in the values of the mass law expression representing the triiodide equilibrium in the presence of potassium chloride.

TABLE 11

Comparison chart

2.0 molar potassium nitrate as solvent

ADDED HALIDE	$c_{ClI_3^-}$	$c_{BrI_3^-}$	$c_{I_3^-}$	$K_{c_{ClI_3^-}}$	$K_{c_{BrI_3^-}}$	$K_{c_{I_3^-}}$
molar						
0.05	0.000083			0.6321		
0.025		0.00034			0.0752	
0.001			0.000436			0.00134
0.05		0.000686			0.0742	
0.5	0.000769			0.6244		
0.0025			0.0011			0.00132
1.0	0.001403			0.6299		
0.1079		0.001486			0.0732	
0.005			0.002217			0.00130
0.2		0.002753			0.0722	
0.5		0.006775			0.0701	
0.02			0.008907			0.00129
1.0		0.01316			0.0670	
K_a values				0.628	0.0759	0.00135

(3) Salting-out of ions on ions. It is evident from figure 7 that as the chloride ion concentration is increased, the amount of the triiodide ion formed on the addition of equivalent molarities of potassium iodide is

markedly decreased. The chloride ion or the chloride–iodine ion complex must have exercised a salting-out effect on the iodide ion whereby the concentration of the triiodide ion would be lessened. Unfortunately there is at the present time no adequate method (31) of calculating the salting-out effect of ions on ions. It must be sufficient to state that the salting-out effects of the chloride ion and the nitrate ion on the iodide ion are different, the effect of the latter being small in comparison with the chloride ion.

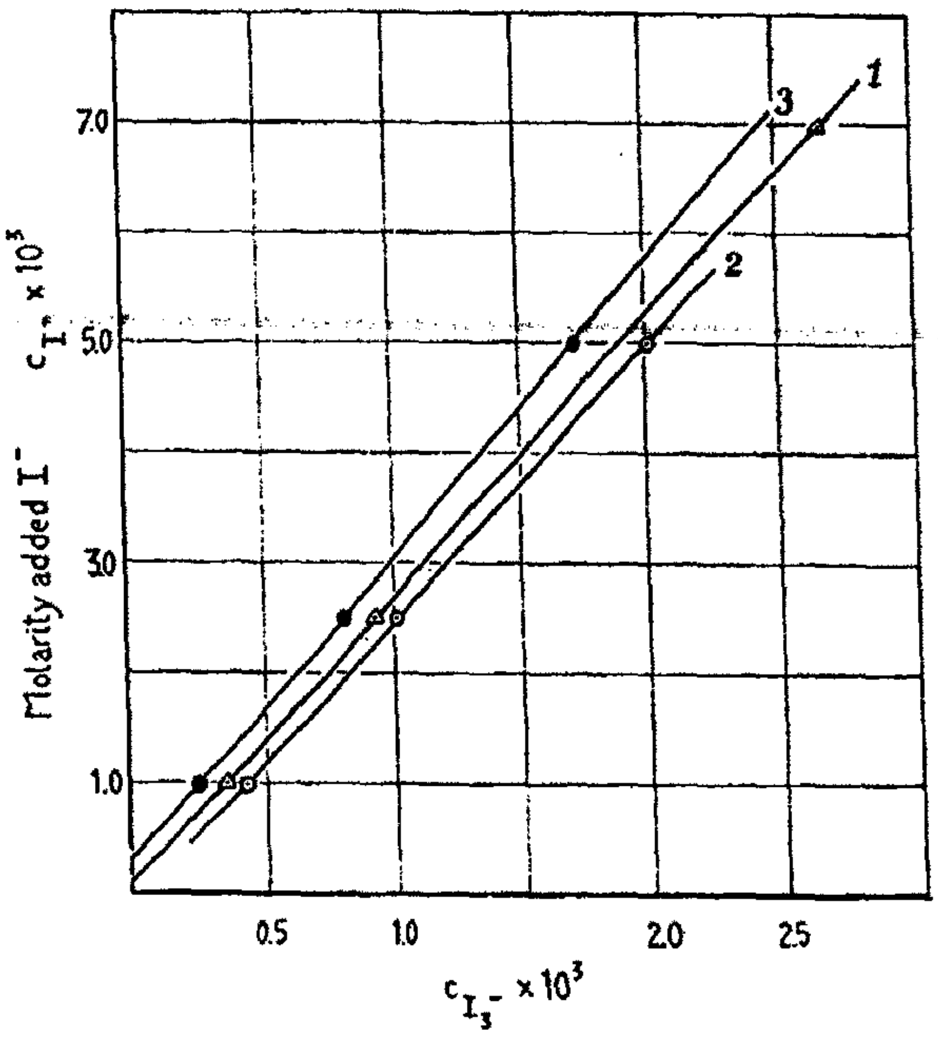

Fig. 7

● 2.0 *M* potassium chloride as solvent.
△ 2.0 *M* potassium nitrate plus 1.0 *M* potassium chloride as solvent.
⊙ 2.0 *M* potassium nitrate as solvent.

Therefore, the non-attainment of constant values for the $K_{c_{I_3^-}}$ expression in a solvent of constant but high chloride ion content appears to be due to a large salting-out effect of the chloride ion or of the chloride–iodine ion complex or of both on the iodide ion and not (a) to the changing environment produced by the addition of small concentrations of potassium iodide to the salt solvent, or (b) to the incorrect values for the salting-out constant for the chloride ion on the neutral molecule, iodine. Thus the concentration of the triiodide ion is small as compared with its value if the chloride ion exercises no salting-out effect on the iodide ion, and therefore the values for the mass action function representing the triiodide equilibrium in a chloride ion solvent here reported are high.

However, it is just possible that if one reads into the assertion made by Carter and Hoskins (4), the thought that the mutual salting-out effect of ions on ions must be considered, then constant values for the mass law expression representing the triiodide equilibrium may be obtained, regardless of the salt employed as solvent maintaining a constant ionic environment.

IV. SUMMARY

1. The solubility of iodine at 25°C. in water at a pH of 5, to prevent hydrolysis, has been established as 0.001321 ±2 × 10^{-6} moles per liter of solution.

2. The values for the mass action expressions for the three equilibria:

EQUILIBRIA	CONSTANTS FOR THE EQUILIBRIA IN	
	H_2O	2 *M* KNO_3
$ClI_2^- \rightleftharpoons I_2 + Cl^-$	0.629	0.628
$BrI_2^- \rightleftharpoons I_2 + Br^-$	0.0820[6]	0.0759
$I_3^- \rightleftharpoons I_2 + I^-$	0.00140	0.00135

are more nearly constant with changing halide concentration in the presence of 2 *M* potassium nitrate than in water. Potassium nitrate gives no evidence of combining chemically with iodine and is used to maintain constant ionic environment.

3. Values for the expression for $K_{c_{I_3^-}}$ deviate considerably from the $K_{a_{I_3^-}}$ value in a potassium chloride solution, a salt which maintains a constant ionic environment but reacts chemically with iodine. This indicates that the assertion made by Carter and Hoskins is neither correct nor complete.

4. In a solvent containing potassium chloride, to which small amounts of potassium iodide were added, the values for the expression for $K_{c_{I_3^-}}$ are more nearly constant in the presence of potassium nitrate than in its absence.

[6] Bell and Buckley (32) determined the solubility of iodine in solutions of potassium and sodium bromides, but did not attempt a quantitative interpretation. The values for the mass action function have been calculated and the value for K_a for potassium bromide has been found by extrapolation. The latter value is incorporated in the summary.

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THE HYDROLS

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Liquid water is recognized as being more or less polymerized (7), but very little use is made of this except to account for the temperature of maximum density of water and for its not boiling at 80–193°K. as calculated by van't Hoff, Walden, Tammann, and Sidgwick. In many thermodynamical reasonings the assumption is made tacitly that the degree of polymerization does not change. Very few people are interested in the probability of the different forms of liquid water having different properties. This is the more remarkable because we are quite used to marked changes with different metamers and polymers.

We have red NO_2 and colorless N_2O_4; soluble and insoluble sulfur; anthracene and dianthracene; red phosphorus and white phosphorus; diamond and graphite; cyanic acid, cyanuric acid, and cyamelid; acetaldehyde and paraldehyde; oxygen and ozone; ordinary and nascent hydrogen, oxygen, and nitrogen. The enol and keto forms can be distinguished. Polymerized alcohol peptizes pyroxylin while depolymerized alcohol does not. The two forms of chromic chloride and of benzaldoxime each lower the melting point of the other. The dielectric constant of solid nitrobenzene I is nearly four times that of solid nitrobenzene II.

The lyotropic or Hofmeister series of chloride, bromide, and iodide is found to hold both for true solutions and for colloidal solutions. In the case of true solutions the series holds for reaction velocity experiments (neutral salt effect), electromotive forces, boiling points, and displacements of the temperature of maximum density. Sodium chloride increases the dissociation constant (18) of carbonic acid one thousandfold. Sodium chloride increases the apparent strength of boric acid (16). The apparent molecular weights of sodium chloride, bromide, and iodide vary in that order. The potential difference between hydrogen and hydrochloric acid differs from that between hydrogen and hydrobromic acid (26). Richards and Rowe (19) found that the heats of neutralization of caustic soda and caustic potash decrease as the neutralizing acid changes from hydrochloric acid to hydrobromic acid and then to hydriodic acid. The solubility of gases in salt solutions, the heat capacity of water, the displacement of the temperature of maximum density of water, and the quenching of fluorescence in certain solutions by salts show the same general phenomenon.

The Hofmeister series holds in colloidal solutions for the peptization and precipitation of proteins, cellulose, and many other colloids. We do not at present consider adsorption as occurring in true solutions, though the conception of a water sheath on ions is practically adsorption. So long as we adopt the ordinary point of view, adsorption is not a necessary cause of the Hofmeister series. The Hofmeister series cannot be due to electrostatic effects because nitrates are very different from chlorides and bromides, though coming between them in molecular weights. It cannot be due to hydrated or hydrous ions because the boiling points are more abnormal than the freezing points and also because on that hypothesis hydrous or hydrated iodides should raise the setting points of gelatin jellies and should increase the rate of saponification of esters. The neutral salt effect cannot be due to an increased dissociation of the acid, because it is easy to get effects corresponding to many times 100 per cent dissociation. Many people have suggested an increased dissociation of water, but no one has maintained it seriously for any length of time. Sodium chloride alone does not invert sugar solution at an appreciable rate. Sodium chloride, bromide, and iodide decrease the rate of saponification of methyl acetate.

The only thing that is left is that the Hofmeister series is due in part to a change in the degree of polymerization of water (1). For the cases in which one can eliminate adsorption, the neutral salt effect is due exclusively to a change in the water equilibrium. For other cases selective adsorption may play the important part. With gelatin the order of effectiveness of the anions is the same on both sides of the isoelectric point and the amounts of chloride or iodide adsorbed are so small that nobody has ever measured them in aqueous solutions. With gelatin the change in the water equilibrium is the important one, and the effect due to adsorption of the anion is practically negligible for chlorides, bromides, and iodides, though it does exist. With albumin the order of the effectiveness of the anions reverses as one changes from acid to alkaline solutions. Here the adsorption is the important factor and the displacement of the water equilibrium is of much less importance. Gelatin and albumin may be taken as representing the two extremes. Hofmeister (11) deduced the Hofmeister series from experiments on proteins.

Since adsorption is selective, the order of the anions will not necessarily be the same in all cases and colloid chemists know that the Hofmeister series varies somewhat with different adsorbents, nitrate jumping around in an especially disturbing way. It has not yet been shown that all these cases are due to differences in selective adsorption, but that will come in time. We have already proved it for the two cases that we have studied. The boiling point curve for sodium thiocyanate is more nearly normal than that for sodium iodide, whereas sodium thiocyanate peptizes gelatin more strongly than does sodium iodide. By using 80 per cent and 95 per cent alcohol it was possible to show that sodium thiocyanate is adsorbed more strongly than sodium iodide. A similar explanation holds for sodium nitrate and sodium chloride. The nitrate has the more normal boiling point curve, peptizes gelatin a little better, and is adsorbed by gelatin more strongly.

The usual order of the anions in the Hofmeister series when adsorption is negligible is I^-, SCN^-, Br^-, NO_3^-, Cl^-, SO_4^{--}. When selective adsorption occurs, a common order is SCN^-, I^-, Br^-, NO_3^-, Cl^-, SO_4^{--}.

We have introduced a set of arbitrary assumptions for the effects of these six ions on water. This will make the discussion more definite and should be helpful.

1. Under ordinary conditions liquid water may be considered as essentially a mixture of trihydrol (or polyhydrols), dihydrol, and monohydrol coëxisting in reversible equilibrium.
2. Chloride, bromide, thiocyanate, and iodide ions tend to change dihydrol into monohydrol and have no especial effect on trihydrol beyond that which is a necessary consequence of the displacement of the equilibrium between dihydrol and monohydrol. The order of increasing effectiveness is chloride, bromide, thiocyanate, and iodide.
3. The nitrate ion tends to convert trihydrol into dihydrol, and dihydrol into monohydrol. For equivalent concentrations the amount of monohydrol is less with nitrate ion than with chloride ion.
4. The sulfate ion tends to convert trihydrol and monohydrol into dihydrol.
5. The electrolytic solution pressure of hydrogen is greater in dihydrol than in monohydrol, and that of oxygen is less.

Many years ago Kahlenberg (14) showed that potassium iodide gave a greater rise of boiling point than potassium bromide, and potassium bromide a greater rise than potassium chloride. He also showed that these results were distinctly more abnormal than those with potassium nitrate. We have confirmed and extended his results. The experiments were made at 760 mm. with the arrangement of the Davis-Brandt apparatus (8), which permits working at constant pressure irrespective of fluctuations in barometric pressure. The data obtained with this apparatus are given in table 1. The concentration of the solutions is expressed in moles of the solute per kilogram of water. By plotting molal concentrations against rise of boiling points, we eliminate all question of the applicability of any particular formula. One reason why Kahlenberg's results were ignored was because he calculated molecular weights and people said that the formula did not hold for such concentrations. The solutions of sodium chloride, sodium bromide, sodium iodide, and sodium thiocyanate were titrated with standard silver nitrate solution, using potassium chromate as an indicator. The solutions of sodium nitrate were analyzed gas-volumetrically with a Dennis nitrometer. The sodium sulfate solutions were determined by precipitating and weighing as barium sulfate.

TABLE 1

Boiling point data at 760 mm.

SALT	MOLES PER KILOGRAM OF WATER	RISE OF BOILING POINT	BOILING POINT RISE PER MOLE
		degrees C.	*degrees C.*
NaCl	4.404	5.16	1.17
	2.070	2.04	0.985
	1.456	1.38	0.948
	0.889	0.79	0.888
	0.382	0.34	0.895
NaBr	3.896	4.73	1.21
	1.932	2.01	1.04
	0.687	0.63	0.918
	0.272	0.26	0.954
NaI	3.875	5.15	1.33
	2.398	2.73	1.14
	2.043	2.21	1.08
	1.910	2.04	1.07
	1.010	1.01	1.00
	0.588	0.55	0.935
$NaNO_3$	4.04	3.65	0.903
	3.01	2.70	0.897
	1.81	1.69	0.935
	0.926	0.85	0.918
	0.547	0.53	0.970
NaSCN	4.28	5.25	1.22
	3.01	3.38	1.12
	1.96	2.07	1.06
	0.93	0.92	0.980
	0.75	0.73	0.974
Na_2SO_4	2.70	2.55	0.945
	2.09	1.99	0.952
	1.37	1.34	1.01
	0.892	0.90	1.01
	0.476	0.50	1.05
	0.232	0.26	1.12

In dilute solutions the results for all salts fall practically on the same line, as they should. In more concentrated solutions the curves diverge. These results do not check those of Johnston (13) for the sodium bromide solutions. His error is probably due to superheating, giving too high a boiling point.

There is a very real difference between such similar salts as sodium chloride and sodium iodide. At about 4 molal the rise of boiling point for sodium chloride is about 85 per cent of that for sodium iodide. This is a difference of about 0.7°C., which is far beyond the estimated experimental error of 0.03°C. There cannot be any such difference in dissociation. The difference cannot be due to adsorption in the ordinary sense of the word, because the salts are in true solution. Even at 3 normal the difference between sodium iodide and sodium nitrate is about 1°C.

Sidgwick and Ewbank (22) deduce from freezing point data that the lowering of the freezing point varies with the hydration of the ions. A similar conclusion has been drawn by Fajans and Karagunis (9). The difficulty with this is that in general the boiling points are more abnormal than the freezing points, whereas the degree of hydration must be greater at 0° than at 100°C., because the formation of hydrates is an exothermal process.

Arbitrary assumption No. 2 was based on the boiling point data. Iodides have the highest boiling points and then come thiocyanates, bromides, and chlorides. The differences between sodium thiocyanate and sodium bromide are very small. If iodides are the most effective in converting dihydrol into monohydrol, they are more soluble in monohydrol than in dihydrol and are consequently lowering the vapor pressure of the more volatile constituent. Therefore the rise of boiling point is abnormally large.

The temperature of maximum density of water is lowered by most salts. That means that these salts depolymerize water to some extent, thereby making it necessary to cool more before the expansion due to increased polymerization overbalances the contraction due to temperature contraction. On this basis iodide should have more effect than bromide and bromide more effect than chloride. This is the case. Unfortunately nitrate is more effective than iodide and sulfate more so than nitrate. Arbitrary assumptions Nos. 3 and 4 take care of the apparent exceptions.

Arbitrary assumption No. 5 is made to account for the apparent increase in concentration of hydrogen ion on addition of sodium chloride, bromide, or iodide to a solution of an acid. There can be no such change in concentration as there appears to be, and consequently the observed change in electromotive force must be due to a change in the so-called solution pressure. It would be much better if people would evaluate singly as many of the disturbing factors as possible instead of lumping them all under the purely formal term of activity.

As has been stated, the boiling points for sodium iodide are more abnormal than those for sodium thiocyanate, and the boiling points for sodium chloride are more abnormal than those for sodium nitrate. On the other hand, sodium thiocyanate is a better peptizing agent for gelatin than sodium iodide, and sodium nitrate than sodium chloride. It was therefore necessary to show that gelatin adsorbs thiocyanate somewhat more strongly than sodium iodide, and sodium nitrate more strongly than sodium chloride. Previous experiments at Cornell and elsewhere had shown the practical impossibility of getting the necessary data with water as solvent. The experiments were therefore made in alcoholic solutions in which the peptization of gelatin and the adsorption of alcohol by gelatin are practically negligible.

TABLE 2

Adsorption by gelatin

SALT	SOLVENT	MOLES PER LITER IN SOLUTION	MILLIMOLES ADSORBED PER GRAM OF GELATIN
NaSCN	95 per cent alcohol	0.0592	0.171
		0.040	0.123
		0.0173	0.059
		0.0059	0.020
NaI	95 per cent alcohol	0.0805	0.193
		0.0504	0.139
		0.0240	0.063
		0.0086	0.030
NaCl	80 per cent alcohol	0.0554	0.291
		0.0410	0.215
		0.0236	0.115
		0.0060	0.023
$NaNO_3$	80 per cent alcohol	0.0558	0.303
		0.0385	0.212
		0.0225	0.121
		0.0058	0.028

Three grams of Eastman's de-ashed gelatin was used as obtained, adding 35 cc. of the alcoholic solutions. Sodium thiocyanate and sodium iodide were dissolved in 95 per cent alcohol; since sodium nitrate and sodium chloride are less soluble, 80 per cent alcohol was used for them. Trial runs showed that it was necessary to wait thirty-six hours in order to be sure of reaching equilibrium. At the end of that time 25 cc. of the supernatant liquid was titrated with a known silver nitrate solution, using potassium chromate as indicator. The data are given in table 2.

The results show that sodium thiocyanate is adsorbed more strongly by gelatin than sodium iodide is, and that sodium nitrate is adsorbed more strongly than sodium chloride. There is therefore no necessary reason why the order of peptization should be identical with the order of boiling points.

Bowe (5) has used the theory of the water equilibrium to explain the neutral salt effect. If neutral salts cause a shift in the water equilibrium, we then have different solvents in which solubilities, reaction velocities, and degrees of ionization may be different from those in the original solvent. He showed that the equation for the electromotive forces postulates the constancy of the solution pressure of hydrogen. This is not true experimentally for hydrochloric acid, hydrobromic acid, and hydriodic acid.

Bowe showed that the addition of sodium chloride, sodium bromide, and sodium iodide to 0.1 *N* hydrochloric acid increased the apparent concentration of hydrogen ion in each case, the increase being greatest for sodium iodide and least for sodium chloride. Making the solution 4 normal with respect to sodium iodide increased the apparent concentration of hydrogen ion tenfold. To account for the facts we postulate that the solution pressure of hydrogen is less in monohydrol than in dihydrol. All determinations of hydrogen-ion concentration in halide solutions are therefore in error to some extent. Since all determinations of pH in biological systems are made in the presence of chlorides, all these determinations are in error to some extent, unless some other unsuspected error counteracted the first one.

These experiments suggested an even more striking one. The cell H_2 | HCl | KCl Hg_2Cl_2 | Hg should have a higher electromotive force than the cell H_2 | HBr | KCl Hg_2Cl_2 | Hg, provided the molal concentrations of hydrochloric acid and hydrobromic acid are the same. The corresponding cell with hydriodic acid should have the lowest electromotive force of the three.

The electromotive forces of these three cells were measured, using a saturated calomel half-cell. After the electromotive forces had been determined, the solutions were analyzed volumetrically by titration with silver nitrate, using potassium chromate as indicator. It was not possible to run up to high concentrations of hydriodic acid, because under ordinary conditions iodine is set free and poisons the electrode. The results are given in table 3.

With strong acids of the same type, such as these, the percentage dissociation should not differ appreciably. The migration velocities are practically identical. At 8 normal concentration the difference between hydrochloric acid and hydrobromic acid is about 40 millivolts, which is far beyond the experimental error and which must therefore be due to a difference in solution pressure. These results agree with those of Wilke and Schränkler (26), who measured the cell H_2 | HCl | HX | H_2.

From a consideration of the boiling points of salt solutions and from the displacement of the water equilibrium by salts, we deduced (arbitrary assumption No. 4) that the sulfate ion tends to convert trihydrol and monohydrol into dihydrol. In this reaction heat is evolved, which accounts for the fact that the solubility curve for anhydrous sodium sulfate shows a decreasing solubility with rising temperature along the first part of this curve. The heat of formation of sodium sulfate decahydrate is sufficient to change the sign of the heat of solution, and consequently this salt shows an increasing solubility with rising temperature. At higher temperatures the effect of sodium sulfate in displacing the water equilibrium will probably become less, and therefore there may come a temperature at which this heat effect will just equal the algebraic sum of the heat of fusion plus the heat of dilution not due to displacement of the water equilibrium. At this temperature anhydrous sodium sulfate will have a minimum solubility. Experimentally the solubility curve for anhydrous sodium sulfate does have a minimum in it. With the exception of potassium and rubidium sulfates, most sulfates do show a minimum solubility at some temperature.

TABLE 3

Electromotive forces

$H_2 \mid HX \mid \underline{KCl},\ \underline{Hg_2Cl_2} \mid Hg$

ACID	NORMALITY	E.M.F.	ACID	NORMALITY	E.M.F.
HCl	1.148	0.237	HBr	1.09	0.233
	2.900	0.215		2.06	0.212
	4.636	0.197		2.76	0.202
	6.415	0.181		6.08	0.153
	8.136	0.162		6.66	0.142
HI	0.800	0.240		6.91	0.140
	1.430	0.217		8.72	0.110

For the present, we offer no explanation of the fact that calcium hydroxide shows a decreasing solubility with rising temperature.

The data in the literature on the solubility of gases in aqueous salt solutions are incomplete for most gases, but sulfur dioxide will serve as an example. The solubility is given in table 4 in terms of the Bunsen absorption coefficient, which is the volume of gas at 0°C. and 760 mm. that is dissolved in one volume of water when the partial pressure of the gas is 760 mm. The temperature is 25°C. and the salt concentration is 0.5 molar.

We see here the clearly defined series: SO_4^{--}, NO_3^-, Cl^-, Br^-, SCN^-, I^-, sulfate ion decreasing and iodide ion increasing the solubility of the gas. With regard to the water equilibrium we can see that an increased solubility will result if the gas and the salt tend to shift the equilibrium in the same direction, whereas the gas will be less soluble in water if the effects of the gas and the salt are opposed. It is not claimed that the displacement of the water equilibrium is the sole factor determining the change of solubility of a gas on adding salt. The solubility or insolubility of the salt in the liquefied gas and the solubility or insolubility of the gas in the liquefied salt are very real factors which are not being discussed in this article.

Since potassium iodide depolymerizes water and increases the solubility of sulfur dioxide, we conclude that sulfur dioxide depolymerizes water to some extent, provided we are justified in ignoring all the other factors. Since potassium sulfate increases the polymerization of water, we should expect it to decrease the solubility of the gas in water and this actually happens. For the other gases the agreement is fairly good, although the solubility in nitrate solutions seems out of line occasionally.

Bancroft and Butler (2) have shown that the solubility of succinic acid in binary mixtures of methyl, ethyl, and propyl alcohols is very nearly a straight line function of the composition of the alcohol mixture. This shows that any change in polymerization of the alcohols has little or no effect. In mixtures of water with any one of these alcohols there is a maximum solubility, which cannot be due entirely to compound formation, because the position of the maximum is displaced sideways with changing temperature. Assuming that the effect of the alcohol is additive, it is possible to calculate the apparent solvent action of water in any mixture. It was found that the water was more effective in dilute solutions. From this it seems to follow that succinic acid is much more soluble in depolymerized water than in polymerized water. The only objection to this is that, if so, the rise of boiling point for succinic acid solutions should be abnormally large, just as it is for potassium iodide solutions. This proved not to be the case and no explanation of this discrepancy is forthcoming at present.

TABLE 4

Solubility of sulfur dioxide in salt solutions at 25°C.

SOLVENT	COEFFICIENT	SOLVENT	COEFFICIENT
Water	32.76	K_2SO_4	30.42
Na_2SO_4	29.28	KNO_3	30.97
NaCl	29.74	KCl	31.53
NaBr	30.93	KBr	32.97
NaSCN	32.47	KSCN	34.42
		KI	35.42

In recent papers Barnes (4) describes experiments designed to measure the physiological effect of trihydrol in water. By freezing and melting, a water was obtained which increased the rate of growth and multiplication of spirogyra to nine times the value observed in distilled water. The explanation offered is a displacement of the water equilibrium, with trihydrol promoting growth. We should of course like to believe this, but the evidence is unsatisfactory as yet. If this explanation is true, it means that equilibrium is reached slowly, in which case water would be a substance with a variable freezing point like acetaldoxime and benzaldoxime. Until Barnes can show that this happens, his conclusion should not be accepted by chemists. A possible explanation would be an increase in the relative amount of "heavy water." That might have a physiological effect, but in previous experiments the "heavy water" has been unfavorable to growth. An unsuspected impurity in the melted ice or in the distilled water is the most probable explanation.

Urban (25) has shown that the Hofmeister series holds for the variation of the heat capacity of water caused by the ions in a solution. All salts lower the heat capacity compared with the value for pure water. Iodides lower it least and tartrates most. Urban implies that the heat capacity will be lowered if a salt depolymerizes water, and he therefore concludes that tartrates depolymerize water the most and iodides the least, which is the reverse of what we postulate. A possible flaw in Urban's reasoning is his assumption as to the relative heat capacities of polymerized and depolymerized water. If a salt increases the relative concentration of trihydrol and if trihydrol has a lower specific heat than dihydrol, we might expect polymerization to lead to a lowering of the specific heat.

Sutherland (21) was bold enough to calculate the specific heats of trihydrol and dihydrol. While his method is not perfect, the best guess that he could make for the specific heats at 0°C. was 0.6 calorie for trihydrol and 0.8 calorie for dihydrol. Therefore polymerization does lead to a lower specific heat than depolymerization, and iodides depolymerize water more than tartrates do.

It is worth noting that Urban places the thiocyanate ion between the bromide ion and the iodide ion, just as our boiling point experiments do.

In a paper on the heats of neutralization of strong acids by strong bases, Richards and Rowe (20) point out that hydrobromic acid gives a higher heat of neutralization than hydriodic acid with lithium, sodium, or potassium hydroxide. Some data are given in table 5. The difference between hydrobromic acid and hydriodic acid with potassium hydroxide is 70 calories as against an experimental error of only 10 calories, so the difference is a real one. With sodium hydroxide the order of acids in decreasing heats of neutralization is hydrochloric, hydrobromic, nitric, and hydriodic. With potassium hydroxide the order is nitric, hydrochloric, hydrobromic, and hydriodic acid. The results are consistent for chlorides, bromides, and iodides. We do not know why sodium nitrate is out of line.

Everyone agrees that the polymerization of water increases with falling temperature and that the reaction is therefore exothermal. The formation of water from hydrogen and hydroxyl ions is also exothermal. We can predict therefore that neutralization accompanied by polymerization will give an apparently high heat of neutralization, while the heat of neutralization will be smaller the less the polymerization. Thus we see that hydriodic acid should have a smaller heat of neutralization than hydrobromic acid, and hydrobromic acid a smaller one than hydrochloric acid, which is what Richards and Rowe found.

Another occurrence of the Hofmeister series for true solutions is the quenching of the fluorescence of various dyes by addition of salts. Jette and West (12) found that the fluorescence of aqueous solutions of quinine bisulfate, the sodium salt of fluorescein, and uranyl sulfate is extinguished by anions in the order: I^-, SCN^-, Br^-, Cl^-, NO_3^-, the iodide ion being the most effective and the nitrate the least. They say that "the order in which ions suppress the fluorescence of the substances discussed in this report is very similar to the well-known lyotropic series of ions [Hofmeister series] which appear in many diverse fields of physical chemistry. . . . The parallelism between the lyotropic series as usually found and that observed in fluorescence is, however, not exact. Thiocyanate in the lyotropic series usually comes beyond iodide, while we have consistently found its effect on fluorescence to be between that of bromide and iodide; and nitrate, which occurs in the lyotropic series between bromide and iodide, is in ours at the opposite end of the series from iodide. As we shall indicate, we believe these differences to be significant.

TABLE 5

Heats of neutralization at 20°C.

$HX \cdot 100H_2O + MOH \cdot 100H_2O \rightarrow MX \cdot 201H_2O$

	KOH	NaOH	DIFFERENCE
HNO_3	14086	13837	249
HCl	14014	13895	119
HBr	13988	13843	145
HI	13915	13780	135

"In 1913 Heydweiller (10) pointed out that the order of the optical dispersions of negative ions for visible light was parallel to that of their precipitating power in colloid chemistry, *except that thiocyanate, instead of being beyond iodide, was intermediate between bromide and iodide.*"

Since thiocyanate ion belongs properly between bromide and iodide, and since it only comes beyond iodide when there is abnormal absorption, the objection raised by Jette and West is not sound. It seems to us that the quenching of the fluorescence may be due to the shift in the water equilibrium produced by the ions. On this basis it would seem either that trihydrol was necessary for fluorescence in aqueous solution or that monohydrol acts against fluorescence. Iodide should therefore be most effective in extinguishing fluorescence, as it actually is. On the other hand, ethyl alcohol increases the trihydrol concentration, as is shown by the fact that in dilute solutions ethyl alcohol raises the temperature of maximum density of water (15) and therefore increases fluorescence.

This can be shown so as to prove two points. A moderately concentrated solution of fluorescein does not fluoresce, and some physicists have postulated that the high concentration of ions changed the absorption of the solution so that the fluorescent light is absorbed. No independent proof was ever given for this. If one takes a sufficiently concentrated solution of fluorescein and dilutes one half with a suitable volume of water and the other half with an equal volume of alcohol, the alcohol solution will fluoresce and the water solution will not. The concentration of ions has nothing necessarily to do with the phenomenon. The fluorescein concentration was 0.108 *N* in both cases and the alcohol concentration was 7 per cent.

West and Jette ascribe the occurrence of the Hofmeister series to the deformability of the ions; Banow (3) attributes it to hydration of ions; Perrin (17) accounts for the quenching of fluorescence on the basis of "collisions of the second kind"; while Büchner, Voet, and Bruins (6) believe that the Hofmeister series is related in some way to the ionic radius.

Tammann and Diekmann (23) consider that the effect of neutral salts on the electromotive force of the hydrogen electrode is due to a change in the chemical potential of the hydrogen ion and to a change in the internal pressure of the liquid. They show that a change in the salt concentration produces a change in the internal pressure.

These different explanations are incomplete but not necessarily incompatible. Tammann is ascribing the neutral salt effect in great part to a change in the solvent. A displacement of the water equilibrium would necessarily change the internal pressure. Of course it is not claimed that the change in internal pressure is due exclusively to a displacement of the water equilibrium. What is assumed to be the deformability of the ions or a hydration of the ions may perfectly well be in whole or in part a false interpretation of the phenomena accompanying the displacement of the water equilibrium. "Collisions of the second kind" is merely a phrase.

There is a great deal of work to be done in correlating the change of different properties with the displacement of the water equilibrium. For instance, Tammann and Rabe (24) show that, for the change of viscosity of salt solutions with the pressure, we get the order: nitrate, chloride, bromide, and iodide, the nitrate solution having the highest viscosity and the iodide the least. This apparently means that depolymerized water has a lower viscosity than polymerized water. This is in accord with the behavior of pure water. At 0°C. pressures up to about 1000 kg. per square centimeter cause a decrease in the viscosity, because the displacement to the form having the smaller volume and the lower viscosity overbalances the normal increase in viscosity due to the increased pressure. At higher pressures the second factor predominates and the pressure-viscosity curve shows a minimum. At 75°C. the displacement of the water equilibrium is relatively so unimportant that no minimum shows on the curve as reproduced by Tammann and Rabe.

SUMMARY

1. The Hofmeister series holds in one form or another both for true solutions and for colloidal solutions. It must be dependent at least in part on changes in the solvent.

2. When adsorption can be excluded, the order of anions is usually sulfate, nitrate, chloride, bromide, thiocyanate, and iodide.

3. When selective adsorption comes in, the order of the anions may change. It is usual for thiocyanate and iodide to be transposed, while nitrate very often comes between chloride and bromide, and occasionally between bromide and iodide.

4. The two factors determining the Hofmeister series are the displacement of the water equilibrium and selective adsorption.

5. With gelatin the order of the anions is the same on both sides of the isoelectric point, and consequently displacement of the water equilibrium is the major factor and selective adsorption the minor factor.

6. With albumin the order of the anions reverses as the system passes from one side to the other of the isoelectric point. Consequently, displacement of the water equilibrium is the minor factor and selective adsorption the major factor.

7. The order of boiling points for equimolal solutions is sodium nitrate, sodium chloride, sodium bromide, sodium thiocyanate, and sodium iodide, the iodide solutions having the highest boiling points.

8. The order of boiling points cannot be due primarily to hydrated or hydrous ions, because the boiling point curves are more abnormal than the corresponding freezing points. Also, if we assume that the iodides are more hydrated or hydrous than the chlorides, they should peptize gelatin less readily, whereas the reverse is the case.

9. The following arbitrary assumptions have been made in order to account for the behavior of certain anions.

a. Under ordinary conditions liquid water may be considered as essentially a mixture of trihydrol, dihydrol, and monohydrol coëxisting in reversible equilibrium.

b. Chloride, bromide, thiocyanate, and iodide ions tend to change dihydrol into monohydrol and have no especial effect on trihydrol beyond that which is a necessary consequence of the displacement of the equilibrium between dihydrol and monohydrol. The order of increasing effectiveness is chloride, bromide, thiocyanate, and iodide.

c. The nitrate ion tends to convert trihydrol into monohydrol. For equivalent concentrations the amount of monohydrol is less with nitrate ion than with chloride ion.

d. The sulfate ion tends to convert trihydrol and monohydrol into dihydrol.

e. The electrolytic solution pressure of hydrogen is greater in dihydrol than in monohydrol, and that of oxygen is less.

10. The order of anions in lowering the temperature of maximum density of water is chloride, bromide, iodide, nitrate, and sulfate, the sulfate being the most effective.

11. Alcohol raises the temperature of maximum density of water and therefore increases the trihydrol concentration.

12. Working in 80 to 95 per cent alcohol it was possible to show that thiocyanate is adsorbed more strongly by gelatin than iodide and nitrate than chloride.

13. The neutral salt effect occurs both with strong and with weak acids when sodium chloride or sodium bromide is used as the neutral salt. The dissociation constant of carbonic acid has been increased one thousandfold and this is not the limiting value.

14. The single potential difference $H_2 \mid HCl$ is greater than that for $H_2 \mid HBr$ when the two acids are equimolal.

15. The decreasing solubility of anhydrous sodium sulfate with rising temperature is due to displacement of the water equilibrium.

16. On adding salts to a solution of sulfur dioxide in water, the solubility changes in the order: SO_4^{--}, NO_3^-, Cl^-, Br^-, SCN^-, and I^-, sulfate ion causing a decrease in solubility and iodide ion an increase. From this we deduce that sulfur dioxide tends to depolymerize water.

17. Succinic and adipic acids are apparently more soluble in depolymerized water than in polymerized water, but the boiling point curve for succinic acid in water is not as abnormal as it should be and some factor may have been overlooked.

18. There is no satisfactory evidence as yet to show that spirogyra grows more rapidly in polymerized than in depolymerized water.

19. The heat capacities of salt solutions and the heats of neutralization vary from chloride to bromide as they should, but the heat of neutralization of sodium hydroxide by nitric acid is apparently out of line.

20. The fluorescence of aqueous solutions of quinine bisulfate, the sodium salt of fluorescein, and uranyl sulfate can be extinguished by addition of salts. The order of decreasing effectiveness of the anions is: I^-, SCN^-, Br^-, Cl^-, and NO_3^-.

21. A concentrated solution of fluorescein does not fluoresce. This is not due to an electrostatic effect changing the absorption, because it is possible to dilute to a certain extent with water without bringing back the fluorescence, while diluting with the same volume of alcohol causes fluorescence. That seems to indicate that trihydrol promotes fluorescence and monohydrol checks it.

22. The displacement of the water equilibrium changes the internal pressure, iodide raising it more than chloride.

23. The phenomena now ascribed to deformability of ions and to hydration of ions can probably be better ascribed, at least in part, to displacement of the water equilibrium.

24. The changes in viscosity of water and of salt solutions with changing pressure fit in very well under the concept of displacement of the water equilibrium by pressure and by salts.

25. Since the Debye-Hückel theory postulates interaction of the ions as the only disturbing factor, this theory must break down for all concentrations at which the displacement of the water equilibrium is a disturbing factor.

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ELECTROKINETIC PROPERTIES OF PROTEINS. II

ADSORPTION OF GLIADIN AT GLASS–LIQUID INTERFACE AS INFLUENCED BY HYDROGEN-ION CONCENTRATION[1,2]

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In the streaming potential studies reported in an earlier paper (11), the isoelectric points of some of the wheat proteins were interpolated from the values for the ζ-potential of the protein–liquid interface. The latter were calculated from the streaming potential data by the formula for diaphragms developed by Briggs (2)

$$\zeta = \frac{4\pi\eta\kappa_s H}{P\epsilon} \tag{1}$$

in which η is the viscosity of the liquid, κ_s the electrical conductance across the diaphragm, H the streaming potential, P the hydrostatic pressure, and ϵ the dielectric constant of the liquid.

At the isoelectric point the value for ζ is zero, and since the properties of the liquid represented by η, κ_s, and ϵ, and the hydrostatic pressure P have definite values, the streaming potential H is also equal to zero. The isoelectric point is thus the hydrogen-ion concentration at which no electromotive force is produced by streaming the solution through a diaphragm on which the protein is adsorbed.

Inasmuch as it was desired to use the isoelectric point as a differentiating property in the study of proteins, an attempt was made in this investigation to devise a convenient and rapid method for determining the electroneutral point of a protein by adsorbing it on a fritted glass diaphragm and then varying the hydrogen-ion concentration of the solution until its streaming potential fell to zero.

Preliminary experiments showed, however, that the hydrogen-ion concentration of the solution could not be experimentally adjusted to maintain the streaming potential at zero, but that a positive potential was gradually

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developed. It was evident from these experiments that either the adsorption equilibrium, or the chemical equilibrium, of the proteins was disturbed by changes in the hydrogen-ion concentration of the streaming solutions. The adsorption equilibrium would, obviously, be influenced by the magnitude and sign of the charge of the protein micelles in relation to that of the adsorbent (glass particles in diaphragm), and in consequence this phase of the problem has been studied in the present work.

EXPERIMENTAL

Preparation of gliadin

Two kilograms of patent flour, from which the fatty materials had been removed by extraction with anhydrous diethyl ether, was made into a pliable dough and allowed to stand under water for 1 hour. The starch was then washed from the gluten by kneading in a stream of tap water. It was then finely divided and added to sufficient pure ethyl alcohol to form a solution containing 60 per cent of alcohol and 40 per cent of water by volume. The mixture was then placed in a mechanical shaker for 10 hours, after which it was centrifuged, filtered, and the filtrate reduced to a sirupy consistency by evaporating under reduced pressure. The gliadin was precipitated by pouring the cooled sol into a 1 per cent sodium chloride solution at 0°C., filtered, and thoroughly washed with distilled water. The precipitate was redissolved in a 60 per cent alcohol solution, its volume reduced by evaporating under reduced pressure, and again precipitated by pouring into cold 1 per cent sodium chloride solution. The re-solution and reprecipitation was repeated four times, the final precipitation being accomplished by pouring the concentrated sol into a mixture of 1 part of absolute alcohol and 1 part of anhydrous diethyl ether, after which the precipitate was washed with anhydrous ether and dried in a vacuum oven at 80°C.

Streaming potential measurements

The apparatus shown diagrammatically in figures 1 and 2 was designed to measure, by the streaming potential method, the progressive change in the potential across a solid–liquid interface when proteins, acids, alkalis, or other reagents were added to the liquid phase. Inasmuch as slight traces of electrolytes, or surface-active substances dissolved in the liquid or adsorbed at the solid–liquid interface, were readily detected by a marked change in the streaming potential, it was necessary to eliminate every possible source of contamination. Atmospheric gases such as carbon dioxide, ammonia and acid fumes were excluded from the apparatus by a counter-current of air which had been purified by bubbling successively through sulfuric acid, sodium hydroxide, and distilled water. All parts of the apparatus coming in contact with the liquid were cleaned with hot chromic acid and rinsed with conductivity water.

The streaming cell 2 shown in figures 1 and 2 consists of a fritted glass filter crucible (Jena Glass Works No. lbG4) with sheet platinum electrodes 1 cm. square on each side of the diaphragm. The crucible is attached at the top to an outlet receptacle bearing the upper electrode and closed at the bottom with a two-hole rubber stopper carrying the inlet tube and lower electrode.

The liquid in reservoir 1, the hydrogen-ion concentration of which is adjusted experimentally by adding acid or alkali from burettes 11 and 12, is streamed through the diaphragm of cell 2 into flask 3 by suction. The air in flask 3 is exhausted through needle valve 6 into tank 5 which is evacuated by a water pump. The hydrostatic pressure under which the liquid streams through the diaphragm may be measured by either the mercury manometer 7 or the water manometer 8, or both, by adjusting the three-way stopcock 9, the pressure being maintained constant by the automatic regulator 10. Stopcock 4 is closed when it is desired to stop the streaming liquid without readjusting the hydrostatic pressure.

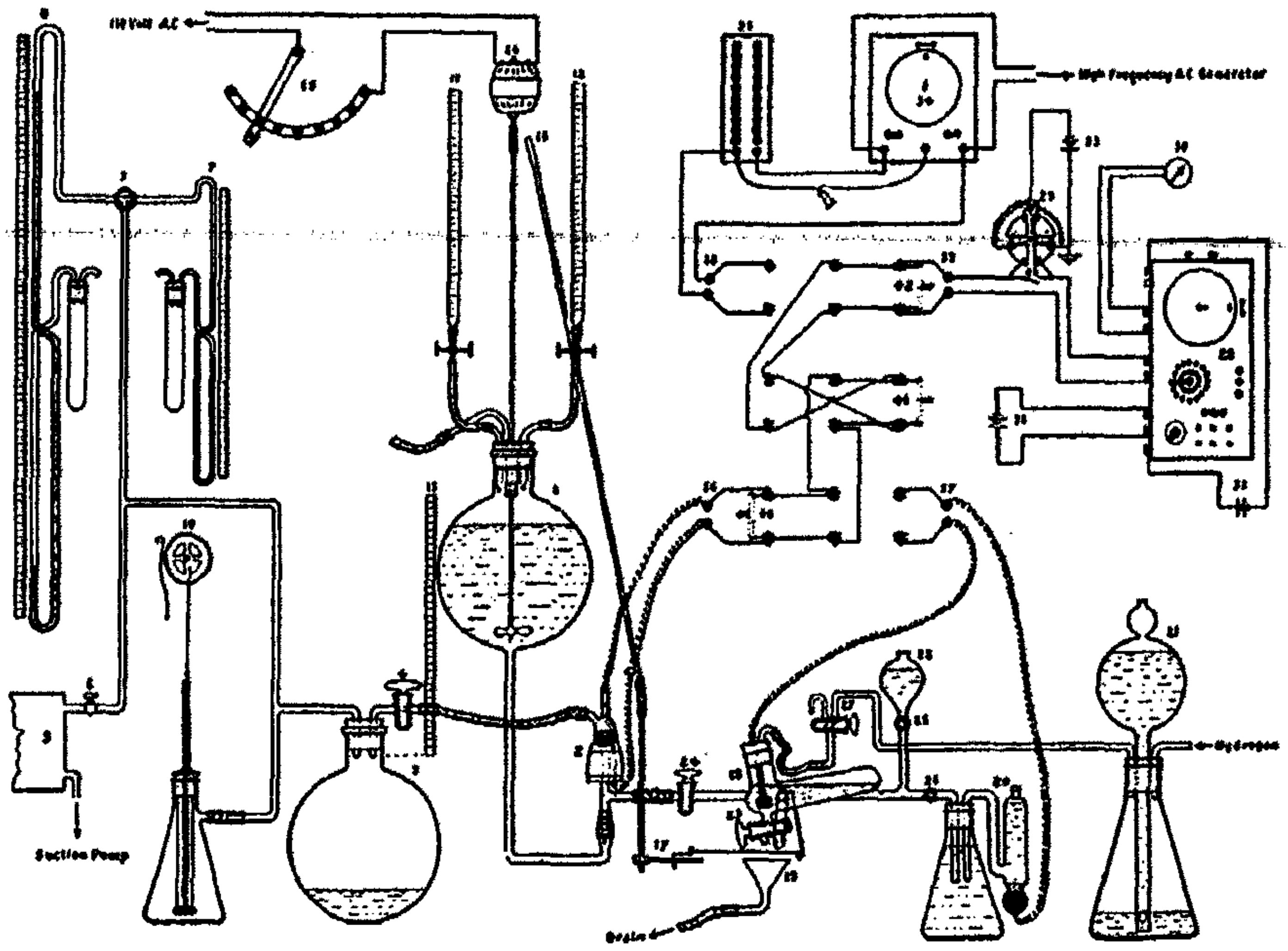

FIG. 1. STREAMING POTENTIAL APPARATUS

The electromotive force produced by streaming the liquid through the fritted glass diaphragm in cell 2 is measured by connecting the electrodes in circuit with the potentiometer (28) and Compton electrometer (29). Switches 40 and 42 are set in contact with 36 and 39, respectively, and the reversing switch 41 is set so that the positive electrode of the streaming cell is connected to the positive binding post of the potentiometer. The electromotive force supplied to the potentiometer by the 2-volt lead storage cell (31) is balanced against that of the standard cadmium cell (32), the null-point being indicated by the galvanometer (30). The electrometer, which is used to indicate the null-point in balancing the electromotive force from the potentiometer against the streaming potential, is operated on a charge of 90 volts by connecting two radio "B" batteries (33) in series between the needle and one pair of quadrants.

After adjusting the electrometer to its zero-point, switch 43 connecting the two pairs of quadrants is opened and the liquid caused to stream through the diaphragm by opening needle valve 6. The hydrostatic pressure gradually increases to that automatically maintained by regulator 10, while at the same time the increasing potential across the diaphragm is balanced by adjusting the potentiometer experimentally. The applied hydrostatic pressure may be increased or decreased by changing the tension of the helical spring of the pressure regulator, after which it remains constant during the progress of the experiment. The effective hydrostatic pressure decreases slightly, however, owing to the lowering of the liquid in reservoir 1. This difference in level between the liquid in 1 and the end of the discharge tube in 3 is read directly from scale 13 in millimeters, divided by 13.6, and added to the pressure indicated by the manometers.

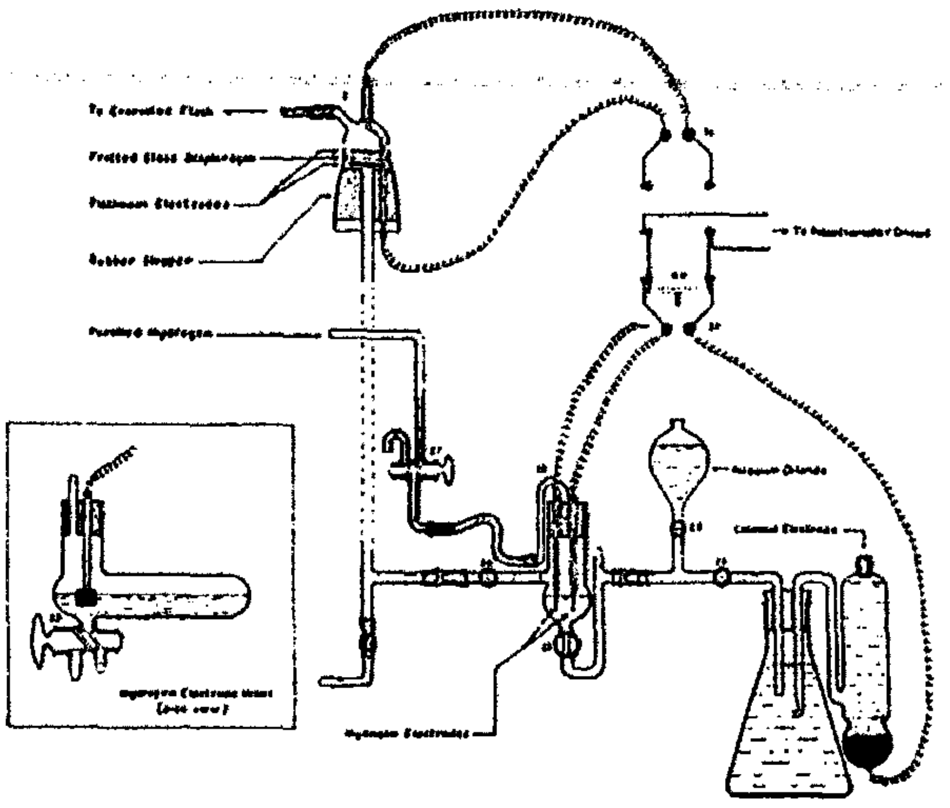

FIG. 2. STREAMING-CELL AND HYDROGEN ELECTRODE APPARATUS

If the diaphragm or the streaming liquid have not been contaminated in any way, the system will come to equilibrium in one or two minutes, and the streaming potential will remain constant except for a slight gradual decrease due to the lowering of the level of the liquid in the reservoir.

The system being in equilibrium and the streaming potential constant, except for the slight change explained above, a measured volume of standard gliadin solution containing 0.002 g. of gliadin for each liter of streaming liquid is added and the solution quickly homogenized by the mechanical stirrer 14, the speed of which is regulated by rheostat 15. The time of adding the gliadin is recorded and the change in streaming potential measured at 2-minute intervals for 10 minutes, and at 5-minute intervals thereafter.

Electrical resistance across diaphragm

With the liquid still flowing, switch 43 is closed and the streaming cell thrown in circuit with the conductivity apparatus by setting switches 40 and 42 in contact with 36 and 38, respectively. The resistance across the diaphragm is then balanced against the adjustable resistances 35 by means of the Kohlrausch slide wire 34, a pair of ear-phones being used to detect the null-point. With solutions of high resistance in the streaming cell, the slide wire could not be accurately balanced by the telephone detector, and in consequence three or more determinations were made and the average of these used in the calculations. Bull and Gortner (6) overcame this difficulty by using an alternating current galvanometer instead of the telephone detector.

After completing the streaming potential, hydrogen-ion concentration, and electrical resistance measurements, the cell constant was determined by replacing the liquid in the cell with a standard solution (10) composed of 0.7476 g. of potassium chloride and 1000 g. of redistilled water. The resistance of the cell was measured with the standard solution streaming through the diaphragm under the same hydrostatic pressure used in making streaming potential measurements.

Hydrogen-ion concentration of streaming liquid

Although the glass electrode might have been used advantageously in determining the hydrogen-ion concentration of the extremely dilute unbuffered solutions, it has not, perhaps, been investigated sufficiently to justify its use as a routine method. The better known hydrogen electrode was therefore used in the apparatus shown in figures 1 and 2.

The hydrogen electrode vessel (18) is filled by closing stopcock 23, opening 24 and 27 and tilting it so that it is filled with the liquid, thereby displacing the air upward and out through stopcock 27. Stopcock 24 is then closed, 23 opened and the vessel tilted down, after which 27 is turned to permit hydrogen gas to displace the liquid from the vessel into drain 19. These operations are repeated several times to free the system from oxygen.

All stopcocks are finally closed with the vessel about one-quarter filled with liquid. Stopcock 27 is then turned so that the hydrogen pressure from reservoir 21, which is equal to about 15 cm. of water above that of the atmosphere, is maintained within the hydrogen electrode vessel. This not only saturates the platinum electrodes more quickly, but prevents the atmospheric gases from diffusing into the system. It also causes the films of liquid in the ground glass joints of stopcocks 23 and 24 to move outward instead of inward, thus reducing error from this source.

The vessel is then gently shaken by the geared mechanism 17 by connecting shaft 16 to the motor 14 with a short piece of rubber tubing, the speed of the motor being regulated by the rheostat 15. The system is saturated with hydrogen within four minutes, after which the motor is stopped with the liquid in the electrode end of the vessel. With the system still under pressure from the hydrogen reservoir, stopcock 23 is turned to discharge from the bore of the stopcock plug, and from the tube between the stopcock and the vessel, the solution which has not been saturated with hydrogen. The pressure within the vessel is then released through 27, after which 23 is carefully turned to connect the vessel with the calomel electrode 20. Stopcock 25 is then carefully opened and saturated potassium chloride solution flows from reservoir 22 and rises slowly in the tube above the stopcock, forming a well defined and easily reproducible liquid junction. When the liquid junction has risen to a mark on the tube midway between stopcock 23 and the vessel, 27 is closed to prevent the potassium chloride from rising too high and mixing with the liquid. The plug in 26 is greased only at the ends to facilitate electrical conductance when the stopcock is closed. The difference in potential between the hydrogen and the calomel electrodes is measured by throwing switches 40 and 42 in contact with 37 and 39, respectively. The electromotive force is then balanced with the potentiometer, using the quadrant electrometer as a null-point instrument. The potential of each of the twin hydrogen electrodes is measured and two complete determinations made on each solution.

Calculation of the electric moment of the double layer

From the streaming potential data may be calculated either the ζ-potential or the electric moment of the double layer. For the reasons set forth by Bull and Gortner (7) the electric moment is preferable, and accordingly the data obtained in the present work have been computed to this basis. The formula for the electric moment given by Bull and Gortner is

$$qd = \frac{\eta \kappa_s H}{P} = \mu \tag{2}$$

where q is the charge per unit area of the double layer in electrostatic units, d the thickness of the double layer in centimeters, η the viscosity of the streaming liquid in poises, κ_s the electrical conductance across the diaphragm in reciprocal ohms, H the streaming potential in volts, and P the hydrostatic pressure in centimeters of mercury. The product qd (charge × distance) is the electric moment per square centimeter of the double layer and is represented by μ. Remembering, however, that one C.G.S. electrostatic unit of potential is equal to 299.86 absolute volts, and that the C.G.S. electrostatic unit of conductance is equal to 1.112151×10^{-12} ohm^{-1} $cm.^{-1}$ (9); and that the density of mercury is 13.6, and the force of gravity 981 dynes, the different quantities in the above equation are converted to C.G.S. units by evaluating the constants to give the simplified expression:

$$\mu = 224755.22 \times \eta \times \frac{\kappa_s H}{P} \tag{3}$$

For convenience in comparing the data presented in this paper with the more familiar ζ-potential in the literature, the relation of the two may be expressed by substituting the ζ-potential formula developed by Briggs (2).

$$\zeta = 847{,}649{,}450 \times \frac{\eta}{\epsilon} \times \frac{\kappa_s H}{P} \tag{4}$$

in equation 3, which gives

$$\zeta = \frac{3771.43\ \mu}{\epsilon} \tag{5}$$

or

$$\mu = 2.65 \times 10^{-4} \times \epsilon\zeta \tag{6}$$

where ϵ is the value for the dielectric constant used in the original calculations. Although the value for ϵ generally used in calculating the ζ-potential from streaming potential data is probably incorrect, as explained by Bull and Gortner (7), expressions 5 and 6 may be used to convert the data of this and other papers to a comparable basis.

DISCUSSION

Fritted glass discs on filter crucibles are satisfactory diaphragms for streaming potential measurements, because they are composed of glass particles of uniform size and are of sufficient porosity to produce results not in error due to "back-pressure" effects. The importance of uniformity of size of particles in streaming potential diaphragms has been emphasized by Bull and Gortner (6), whose experiments showed that the streaming potential was a linear function of hydrostatic pressure only when the particles in the diaphragms were homogeneous in size. The effect of size of pores on the streaming potential has also been investigated by Bull (4), whose experimental data showed that an appreciable "back-pressure" was developed by electroösmotic flow if the radius of the capillaries was 1 μ or smaller.

The data in table 1 and the graphs in figures 3 and 4 show that the glass diaphragms were negatively charged in both acidic and basic solutions. The magnitude of the charge, however, was a function of the total ionic concentration rather than of the concentration of hydrogen ions. This is shown by the relation of the values for the electric moment to those for the specific electrical conductivity of the solution, a relationship similar to that observed by Bull and Gortner (5) for cellulose in aqueous solutions of inorganic salts.

TABLE 1

Electric moment of the double layer at the solid–liquid interface of a fritted glass diaphragm as influenced by hydrogen-ion concentration

STREAMING LIQUID	pH	$\kappa_s \times 10^{-6}$	η	TEMPERATURE	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
		ohms^{-1}	*poises*	*degrees C.*	*mm. Hg*	*millivolts*	*e.s.u.* $\times 10^{-}$
HCl	5.69	1.76	0.0089	25.2	124	−1230	−3.49
HCl	5.22	3.02	0.0084	27.9	124	−874	−4.02
HCl	4.82	5.96	0.0085	27.4	125	−643	−5.86
HCl	4.43	12.62	0.0087	26.2	124	−380	−7.69
HCl	4.25	17.48	0.0087	26.1	125	−320	−8.75
HCl	3.20	36.43	0.0093	23.5	125	−257	−15.67
NaOH	7.76	2.42	0.0088	25.0	125	−1315	−5.04
NaOH	8.16	3.82	0.0086	26.9	125	−1134	−6.70
NaOH	9.06	10.22	0.0084	27.7	126	−724	−11.10
NaOH	9.44	17.68	0.0084	27.8	124	−524	−14.12
NaOH	9.65	23.71	0.0087	26.4	123	−434	−16.37
NaOH	9.74	43.81	0.0089	25.3	124	−237	−16.76
NaOH	9.94	48.19	0.0085	27.1	125	−244	−17.99

The results of the adsorption studies given in table 2 and presented graphically in figures 5 and 6 show that the electrostatic charge of the double layer at the glass–liquid interface is reversed upon adding protein to the streaming liquid if its hydrogen-ion concentration is on the acid side of the isoelectric point of the protein. The negatively charged glass surface apparently adsorbs a layer of positively charged protein and assumes its electrokinetic properties. The behavior of the glass is thus similar to that of quartz particles used by Briggs (3), Freundlich and Abramson (8), and by Svedberg and Tiselius (12). Recently Abramson (1) has shown that the isoelectric point, the cataphoretic mobility, and the dissociation constant of serum albumin and egg albumin are very nearly the same when adsorbed on quartz as when dispersed in solution. The

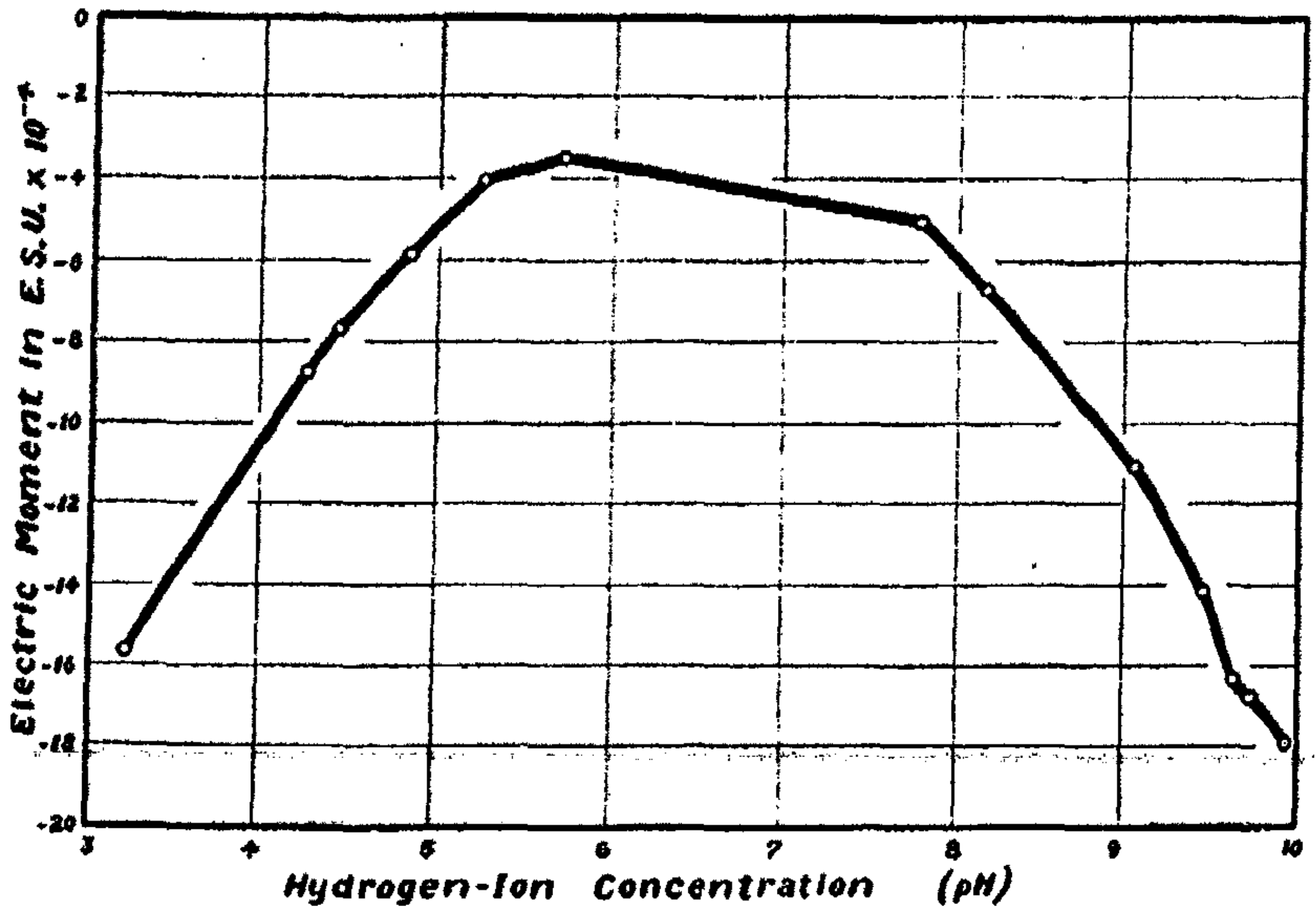

FIG. 3. ELECTRIC MOMENT OF DOUBLE LAYER AT GLASS-LIQUID INTERFACE AS INFLUENCED BY HYDROGEN-ION CONCENTRATION

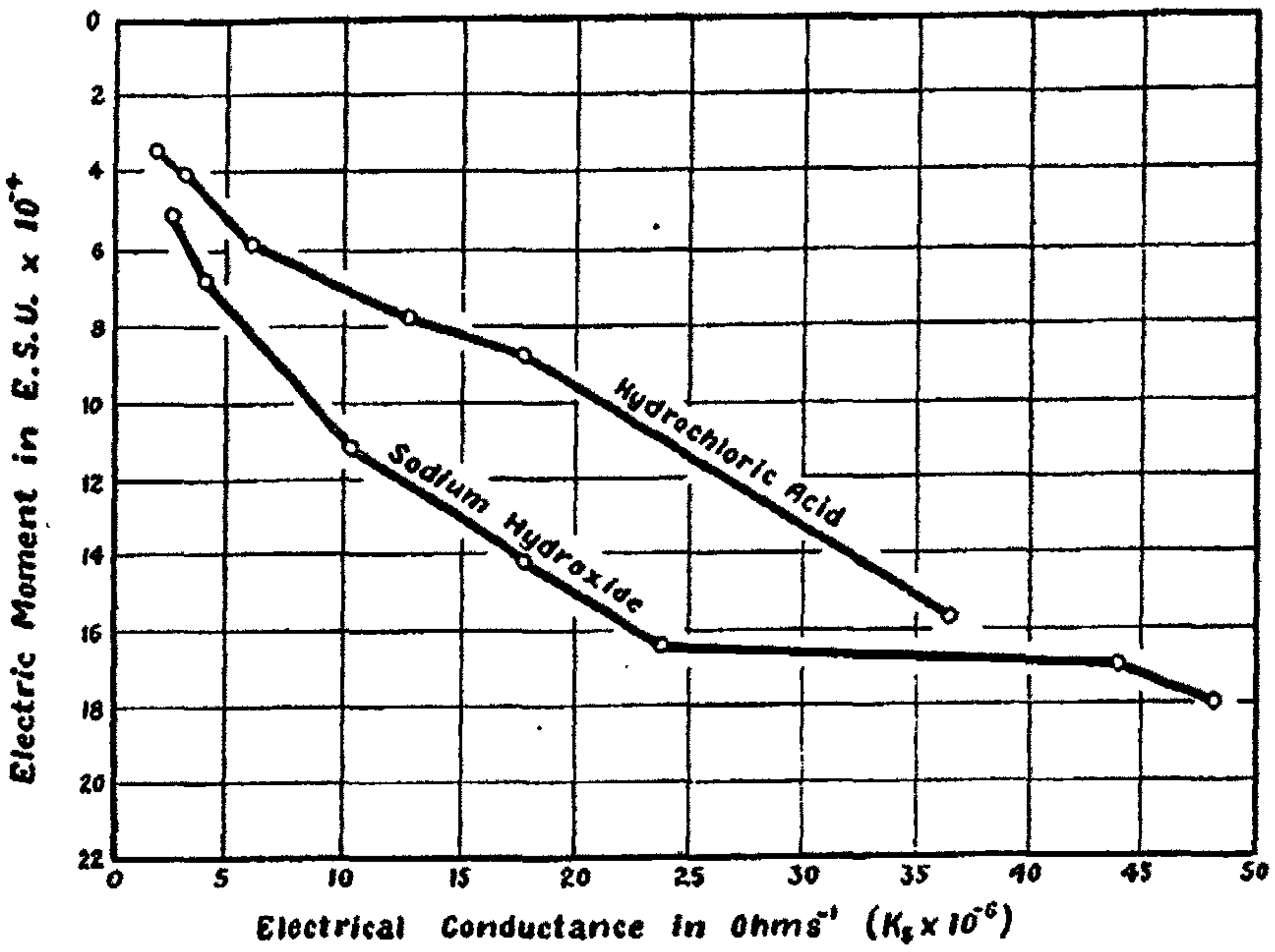

FIG. 4. ELECTRIC MOMENT OF DOUBLE LAYER AT GLASS-LIQUID INTERFACE AS INFLUENCED BY TOTAL IONIC CONCENTRATION (ELECTROLYTIC CONDUCTIVITY OF SOLUTION)

TABLE 2

Influence of hydrogen-ion concentration on the rate of adsorption of gliadin at a glass–liquid interface as indicated by change in the electric moment of the double layer

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
Distilled water; pH = 6.41; κ_s = 1.59 × 10^{-6}; η = 0.0090; T = 24.9°C.			
minutes	*mm. Hg*	*mv.*	*e.s.u.* × 10^{-4}
0	127	−1316	−3.33
5	126	−1304	−3.33
10	125	−1297	−3.34
15	124	−1290	−3.35
20	124	−1285	−3.34
0.002 g. gliadin per liter added			
22	123	−920	−2.41
24	123	−638	−1.67
26	122	−390	−1.03
28	122	−195	−0.51
30	121	−38	−0.10
35	120	+325	+0.87
40	120	+558	+1.50
45	119	+738	+2.00
50	118	+862	+2.32
55	118	+956	+2.61
60	117	+1007	+2.77
65	116	+1053	+2.92
70	115	+1084	+3.03
75	115	+1102	+3.08
HCl solution, pH = 5.69; κ_s = 1.76 × 10^{-6}; η = 0.0089; T = 25.2°C.			
0	126	−1246	−3.49
5	125	−1237	−3.49
10	124	−1231	−3.50
15	124	−1222	−3.48
20	123	−1215	−3.49
0.002 g. gliadin per liter added			
22	123	−809	−2.32
24	122	−402	−1.16
26	122	−51	−0.15
28	122	+299	+0.86
30	121	+538	+1.57
35	121	+911	+2.66
40	120	+1134	+3.33
45	119	+1269	+3.76
0.002 g. gliadin per liter added—*Cont'd*			
minutes	*mm. Hg*	*mv.*	*e.s.u.* × 10^{-4}
50	118	+1355	+4.05
55	117	+1410	+4.25
60	117	+1453	+4.38
65	116	+1494	+4.54
70	115	+1517	+4.65
75	114	+1526	+4.72
80	113	+1528	+4.77
85	112	+1525	+4.80
HCl solution; pH = 5.22; κ_s = 3.02 × 10^{-6}; η = 0.0084; T = 27.9°C.			
0	126	−884	−4.01
5	125	−879	−4.02
10	124	−874	−4.03
15	123	−869	−4.04
20	123	−863	−4.01
0.002 g. gliadin per liter added			
22	122	−208	−0.97
24	122	+154	+0.72
26	121	+321	+1.52
28	121	+401	+1.89
30	121	+459	+2.17
35	120	+530	+2.52
40	119	+563	+2.70
45	118	+593	+2.87
50	118	+616	+2.98
55	117	+631	+3.08
60	116	+644	+3.17
65	115	+657	+3.26
70	115	+663	+3.29
75	113	+669	+3.38
80	111	+666	+3.43
HCl solution; pH = 4.82; κ_s = 5.96 × 10^{-6}; η = 0.0085; T = 27.4°C.			
0	127	−651	−5.84
5	126	−648	−5.86
10	125	−643	−5.86
15	124	−639	−5.87
20	124	−635	−5.84

TABLE 2—*Continued*

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
0.002 g. gliadin per liter added			
minutes	*mm.* Hg	*mv.*	*e.s.u.* × 10^{-4}
22	123	−241	−2.23
24	123	+63	+0.58
26	122	+204	+1.90
28	122	+264	+2.47
30	121	+291	+2.74
35	121	+322	+3.03
40	120	+342	+3.25
45	119	+350	+3.35
50	118	+356	+3.44
55	117	+360	+3.51
60	117	+364	+3.55
65	116	+362	+3.56
70	115	+367	+3.64
75	114	+366	+3.66
80	113	+363	+3.66
HCl solution; pH = 4.43; κ_s = 12.62 × 10^{-6}; η = 0.0087; T = 26.2°C.			
0	126	−392	−7.68
5	125	−389	−7.68
10	124	−386	−7.69
15	124	−383	−7.63
20	123	−382	−7.67
0.002 g. gliadin per liter added			
22	123	−14	−0.28
24	123	+97	+1.95
26	122	+128	+2.59
28	122	+169	+3.42
30	122	+195	+3.95
35	121	+204	+4.16
40	121	+207	+4.22
45	120	+210	+4.32
50	119	+211	+4.38
55	119	+215	+4.46
60	118	+218	+4.56
65	117	+217	+4.58
70	117	+222	+4.69
75	116	+225	+4.79
HCl solution; pH = 4.25; κ_s = 17.48 × 10^{-6}; η = 0.0087; T = 26.1°C.			
0	127	−325	−8.76
5	126	−322	−8.74
10	125	−319	−8.73
HCl solution; pH = 4.25; κ_s = 17.48 × 10^{-6}; η = 0.0087; T = 26.1°C.—*Cont'd*			
minutes	*mm.* Hg	*mv.*	*e.s.u.* × 10^{-4}
15	124	−317	−8.75
20	123	−315	−8.76
0.002 g. gliadin per liter added			
22	123	−3	−0.08
24	122	+139	+3.90
26	122	+175	+4.91
28	122	+182	+5.10
30	121	+200	+5.66
35	121	+209	+5.91
40	120	+206	+5.87
45	120	+205	+5.85
50	119	+201	+5.78
55	118	+197	+5.71
60	118	+193	+5.60
65	117	+189	+5.53
70	116	+186	+5.49
75	115	+186	+5.53
HCl solution; pH = 3.20; κ_s = 36.43 × 10^{-6}; η = 0.0093; T = 23.5°C.			
0	127	−260	−15.61
5	126	−259	−15.67
10	125	−256	−15.61
15	125	−255	−15.55
20	124	−253	−15.55
0.002 g. gliadin per liter added			
22	124	−100	−6.15
24	123	+46	+2.85
26	123	+95	+5.89
28	122	+106	+6.62
30	122	+112	+7.00
35	121	+113	+7.12
40	120	+115	+7.30
45	120	+115	+7.30
50	119	+114	+7.30
55	118	+117	+7.56
60	118	+113	+7.30
65	117	+115	+7.49
70	117	+116	+7.56
75	116	+115	+7.56
80	115	+117	+7.75
85	114	+115	+7.69

TABLE 2—*Continued*

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
NaOH solution; pH = 7.53; κ_s = 2.84 $\times 10^{-6}$; η = 0.0089; T = 25.2°C.			
minutes	*mm.* Hg	*mv.*	*e.s.u.* $\times 10^{-4}$
0	125	−1167	−5.27
5	125	−1158	−5.27
10	124	−1150	−5.27
15	123	−1144	−5.29
20	123	−1137	−5.26
0.002 g. gliadin per liter added			
22	122	−1264	−5.89
24	122	−1375	−6.41
26	122	−1451	−6.76
28	121	−1519	−7.14
30	121	−1560	−7.28
35	120	−1579	−7.48
40	119	−1593	−7.61
45	118	−1596	−7.69
50	118	−1590	−7.66
55	117	−1581	−7.68
60	116	−1561	−7.65
65	115	−1549	−7.66
70	114	−1538	−7.67
75	114	−1531	−7.64
NaOH solution; pH = 7.14; κ_s = 2.04 $\times 10^{-6}$; η = 0.0089; T = 25.4°C.			
0	124	−1215	−4.00
5	123	−1207	−4.01
10	123	−1198	−3.98
15	122	−1191	−3.99
20	121	−1186	−4.00
0.002 g. gliadin per liter added			
22	121	−1239	−4.18
24	121	−1272	−4.29
26	120	−1285	−4.37
28	120	−1296	−4.41
30	120	−1302	−4.43
35	119	−1304	−4.47
40	118	−1295	−4.48
45	117	−1288	−4.50
50	117	−1281	−4.47
55	116	−1277	−4.50
60	115	−1272	−4.52
65	114	−1267	−4.54
70	113	−1255	−4.54
75	112	−1242	−4.53
NaOH solution; pH = 7.76; κ_s = 2.42 $\times 10^{-6}$; η = 0.0088; T = 25.0°C.			
minutes	*mm.* Hg	*mv.*	*e.s.u.* $\times 10^{-4}$
0	122	−1330	−5.02
5	126	−1323	−5.04
10	125	−1316	−5.05
15	124	−1307	−5.06
20	124	−1299	−5.03
0.002 g. gliadin per liter added			
22	123	−1597	−6.23
24	122	(exceeded range of potentiometer)	
NaOH solution; pH = 8.16; κ_s = 3.82 $\times 10^{-6}$; η = 0.0086; T = 26.9°C.			
0	126	−1138	−6.67
5	125	−1135	−6.70
10	125	−1135	−6.70
15	124	−1132	−6.74
20	124	−1130	−6.73
0.002 g. gliadin per liter added			
22	124	−1294	−7.70
24	123	−1423	−8.54
26	123	−1520	−9.12
28	123	−1555	−9.33
30	122	−1573	−9.52
35	121	−1599	−9.76
40	120	−1604	−9.87
45	119	−1598	−9.91
50	119	−1589	−9.86
55	118	−1559	−9.75
60	117	−1525	−9.62
65	117	−1511	−9.53
70	116	−1499	−9.54
75	114	−1468	−9.51
NaOH solution; pH = 9.06; κ_s = 10.22 $\times 10^{-6}$; η = 0.0084; T = 27.7°C.			
0	127	−726	−11.04
5	127	−725	−11.02
10	126	−724	−11.10
15	126	−724	−11.10
20	125	−722	−11.15

TABLE 2—*Continued*

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
0.002 g. gliadin per liter added			
minutes	*mm. Hg*	*mv.*	*e.s.u.* × 10^{-4}
22	125	−738	−11.40
24	125	−750	−11.59
26	124	−762	−11.87
28	123	−759	−11.92
30	123	−759	−11.92
35	122	−756	−11.97
40	121	−752	−12.00
45	121	−748	−11.94
50	120	−748	−12.04
55	119	−734	−11.91
60	118	−720	−11.78
65	117	−710	−11.72
70	116	−701	−11.67
75	115	−691	−11.60
80	114	−682	−11.55
NaOH solution; pH = 9.44; κ_s = 17.68 × 10^{-6}; η = 0.0084; T = 27.8°C.			
0	126	−532	−14.10
5	125	−527	−14.08
10	124	−523	−14.09
15	123	−521	−14.15
20	122	−519	−14.21
0.002 g. gliadin per liter added			
22	122	−514	−14.07
24	122	−509	−13.94
26	121	−505	−13.94
28	121	−498	−13.75
30	120	−492	−13.70
35	120	−478	−13.31
40	119	−468	−13.14
45	118	−461	−13.05
50	117	−450	−12.85
55	117	−443	−12.65
60	116	−439	−12.64
65	115	−434	−12.61
70	114	−429	−12.57
75	113	−423	−12.51
NaOH solution; pH = 9.65; κ_s = 23.71 × 10^{-6}; η = 0.0087; T = 26.4°C.			
0	124	−437	−16.35
5	124	−436	−16.32
NaOH solution; pH = 9.65; κ_s = 23.71 × 10^{-6}; η = 0.0087; T = 26.4°C.—*Cont'd*			
minutes	*mm. Hg*	*mv.*	*e.s.u.* × 10^{-4}
10	123	−434	−16.37
15	123	−432	−16.30
20	122	−430	−16.35
0.002 g. gliadin per liter added			
22	122	−425	−16.16
24	122	−414	−15.74
26	121	−405	−15.53
28	121	−397	−15.22
30	120	−392	−15.16
35	120	−375	−14.50
40	119	−366	−14.27
45	118	−357	−14.04
50	117	−349	−13.84
55	116	−346	−13.84
60	116	−340	−13.60
65	115	−335	−13.52
70	114	−330	−13.43
75	112	−324	−13.42
NaOH solution; pH = 9.74; κ_s = 43.81 × 10^{-6}; η = 0.0089; T = 25.3°C.			
0	126	−241	−16.78
5	125	−239	−16.77
10	124	−237	−16.76
15	123	−235	−16.76
20	122	−233	−16.75
0.002 g. gliadin per liter added			
22	122	−210	−15.10
24	122	−198	−14.23
26	121	−182	−13.19
28	121	−174	−12.61
30	121	−167	−12.11
35	120	−159	−11.62
40	119	−152	−11.20
45	118	−144	−10.70
50	118	−140	−10.41
55	117	−140	−10.49
60	117	−138	−10.35
65	116	−135	−10.21
70	115	−131	−9.99
75	114	−131	−10.08
80	113	−129	−10.01

TABLE 2—*Concluded*

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
NaOH solution; pH = 9.94; κ_s = 48.19 × 10^{-6}; η = 0.0085; T = 27.1°C.			
minutes	*mm. Hg*	*mv.*	*e.s.u. × 10^{-4}*
0	127	−249	−18.07
5	126	−246	−17.99
10	125	−244	−17.99
15	124	−242	−17.98
20	123	−240	−17.98
0.002 g. gliadin per liter added			
22	122	−212	−16.01
24	122	−195	−14.73
26	122	−187	−14.12
0.002 g. gliadin per liter added.—*Cont'd*			
minutes	*mm. Hg*	*mv.*	*e.s.u. × 10^{-4}*
28	121	−180	−13.71
30	121	−177	−13.48
35	120	−166	−12.75
40	119	−160	−12.39
45	118	−156	−12.18
50	118	−152	−11.87
55	117	−146	−11.50
60	116	−141	−11.20
65	115	−135	−10.82
70	114	−131	−10.59
75	113	−125	−10.19

reversal of the charge of the fritted glass diaphragm when protein was added to the streaming liquid, therefore represents the transition from a glass–liquid to a protein–liquid system; and the rate of change, as indicated by the electric moment of the double layer, is an index of the rate of adsorption of the protein.

As shown by the slopes of the curves in figure 5 for the acid solution, the rate of adsorption was most rapid for the highest hydrogen-ion concentrations and slowest for the low. The adsorption rate appears to be dependent upon the difference in the charge on the glass particles composing the diaphragm and that of the protein micelles. For example, the charge at the glass–liquid interface is −3.34 × 10^{-4} E.S.U. at pH 6.41 and −15.60 × 10^{-4} E.S.U. at pH 3.20, while that at the protein–liquid interface is +3.08 × 10^{-4} and +7.56 × 10^{-4} E.S.U., respectively, for the same two solutions. The latter two values are those for the electric moment of the double layer 55 minutes after adding the protein to the streaming liquid, or 75 minutes after beginning the experiment. Although the system had not attained equilibrium, as shown by the slope of the curves in figure 5, the above values are relative. The electrostatic charge of the protein–liquid interface with respect to that of the glass–liquid interface is thus 6.42 × 10^{-4} E.S.U. at pH 6.41 and 23.16 × 10^{-4} E.S.U. at pH 3.20. The rates of adsorption were approximately in the proportion of 23 to 6, as indicated by the slopes of the curves, that for pH 3.20 approaching as nearly to a constant value in 15 minutes as did that for pH 6.41 in 55 minutes. The other curves for the acid solution show a similar relationship.

In alkaline solutions the glass diaphragm and the protein micelles are both negatively charged, and in consequence the electrical forces of repulsion tend to prevent adsorption. The effect of adding proteins to the alkaline solutions on the electric moment of the double layer at the glass-liquid interface must, therefore, be attributed to changes in the composition of the liquid phase due to the binding of some of the alkali by the protein. Obviously, the removal of the alkali ions from solution would reduce the total ionic concentration and increase the hydrogen-ion concentration,

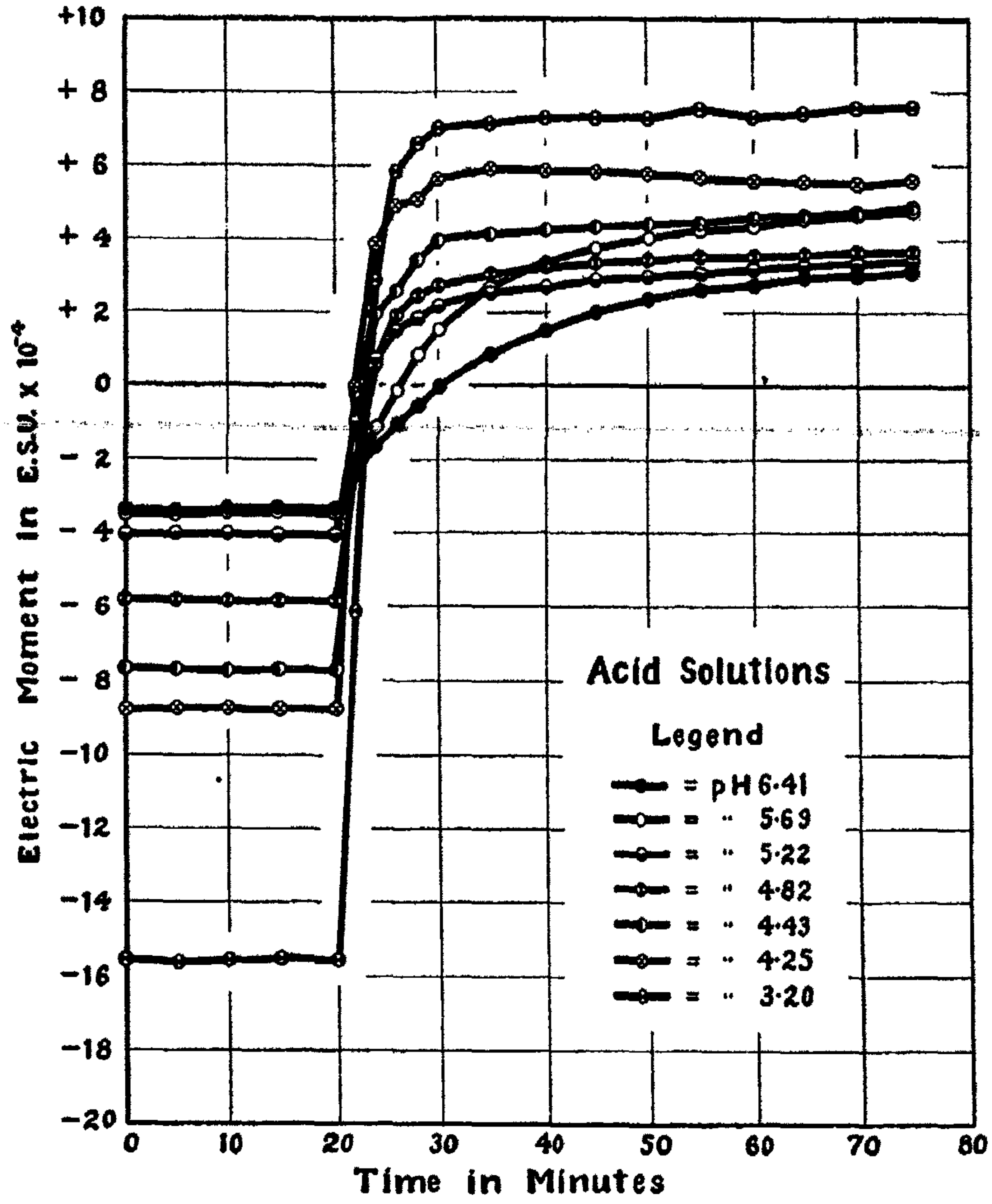

FIG. 5. RATE OF ADSORPTION OF GLIADIN AT A GLASS-LIQUID INTERFACE FROM ACIDIC SOLUTIONS AS INDICATED BY CHANGE IN THE ELECTRIC MOMENT OF THE DOUBLE LAYER

As shown by the curves in figure 6 the addition of protein to solutions of pH 7.14, 7.53, 8.16, and 9.06 increased the electric moment of the double layer, whereas it decreased that in solutions more alkaline than pH 9.44,

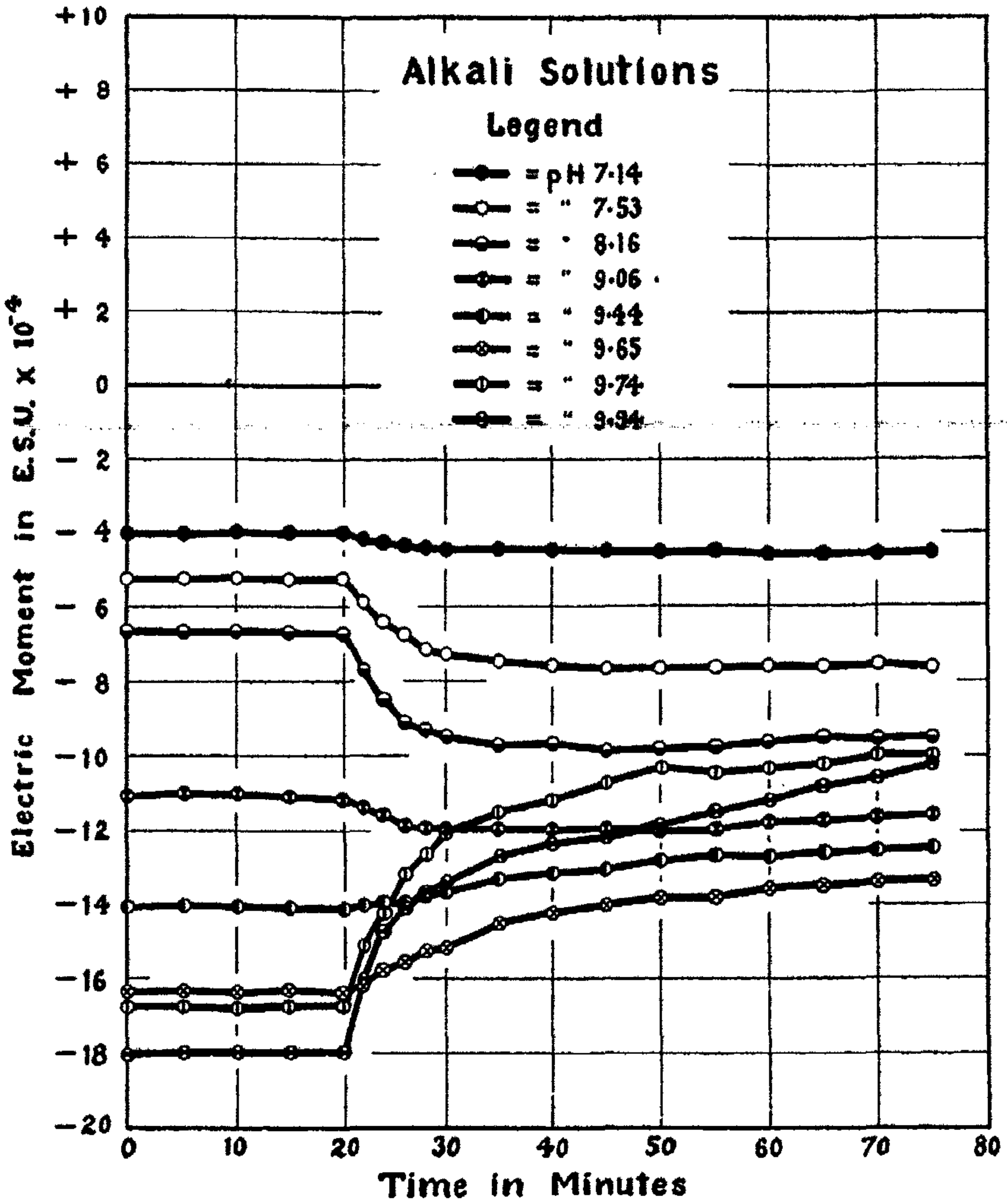

Fig. 6. Rate of Adsorption of Gliadin at a Glass-Liquid Interface from Alkaline Solutions as Indicated by Change in the Electric Moment of the Double Layer

there apparently being a hydrogen-ion concentration between pH 9.04 and pH 9.44 at which no change would have occurred. That the protein was not adsorbed on the glass from alkaline solutions was also indicated by adding increments of dilute acid to the system and observing the change in the streaming potential. At first the potential increased rapidly with successive additions of acid, then more slowly; and finally, when the isoelectric range of the protein was reached, it fell rapidly to zero and reversed in sign. The increase in the streaming potential with the addition of acid was undoubtedly due to an increase in total ionic concentration similar to that shown in figure 3, and the break and reversal of the potential in the isoelectric region apparently marked the beginning of adsorption.

SUMMARY

1. Streaming potential apparatus and methods for measuring the rate of adsorption of proteins or other substances at a glass-liquid interface are described.

2. A fritted glass diaphragm used in the streaming cell was negatively charged in both acidic and basic solutions, the magnitude of the charge being a function of the total ionic concentration rather than of concentration of hydrogen ions.

3. The rate of adsorption of gliadin at the glass-liquid interface was determined by the sign and the magnitude of the difference in the charge of the glass and of the protein micelles.

4. In the region of the isoelectric point of gliadin the adsorption equilibrium was disturbed by changes in the hydrogen-ion concentration, indicating either structural transformation of the adsorbed protein micelles, or displacement by micelles or fragments having different isoelectric points.

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THE SURFACE TENSION OF MERCURY IN A VACUUM AND IN THE PRESENCE OF HYDROGEN

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Recent determinations of the surface tension of mercury show considerable discrepancy. Popesco (11) gave a value of approximately 400 dynes per centimeter at 15°C. (corrected by Burdon (4)), Cook (6) gave 515 dynes per centimeter at 31°C., Kernaghan (8) 436.1 dynes per centimeter at 20°C., Bircumshaw (2) 480 dynes per centimeter at 20°C. The most recent value, 488 dynes, with a maximum of 491 at 25°C., observed by R. S. Burdon (4), appeared while this work was in progress. In the following paper a new modification of the flat drop method for measuring the surface tension of mercury is described. The top of the drop was located by the style of a Bourdon gauge. In addition, the variation in surface tension in the presence of hydrogen was determined. This is important in view of the recent work on activated adsorption (14). Various workers have disputed whether slow adsorption is due to the fact that only activated molecules are adsorbed, or whether solution in the bulk phase occurs through diffusion into the interior along microcapillaries. A clean mercury surface would seem, therefore, an ideal system with which to study slow adsorption, as the latter factor is absent.

THE FLAT DROP METHOD

A number of formulas have been given for deriving the surface tension σ from measurements on a flat drop. If h is the height from the top to the plane of greatest section, ρ the density, and r the radius of the above plane, then Worthington (16) found for a flat drop

$$\sigma = \tfrac{1}{2} h^2 g\rho \frac{1}{1 + 0.609\, h/r}$$

Ferguson (7 and 1) found

$$\sigma = \tfrac{1}{2} h^2 g\rho - \frac{0.609}{r} \cdot \left(\frac{g\sigma^3\rho}{2}\right)^{\frac{1}{2}}$$

For mercury these differ under the conditions below by about 0.2 per cent, and as Worthington's formula is easier to use (Ferguson's formula requires successive approximation), and as h is uncertain to 0.05 per cent, Worthington's formula will be adopted. Porter (12) has shown that for mercury drops of radius greater than 2 cm. the above formulas agree well with the results obtained by graphical integration (Bashforth and Adams). No correction need be applied for the curvature at the top of the drop, as $\frac{h^2}{r^2}$ is only 0.01.

THE APPARATUS

The apparatus (figure 1) was made of Pyrex glass, and consists of a hemispherical cup A, 5.5 cm. in diameter, sealed into a vessel B with a window C. The cup was lipped on the inside and the edge was free from chippings.

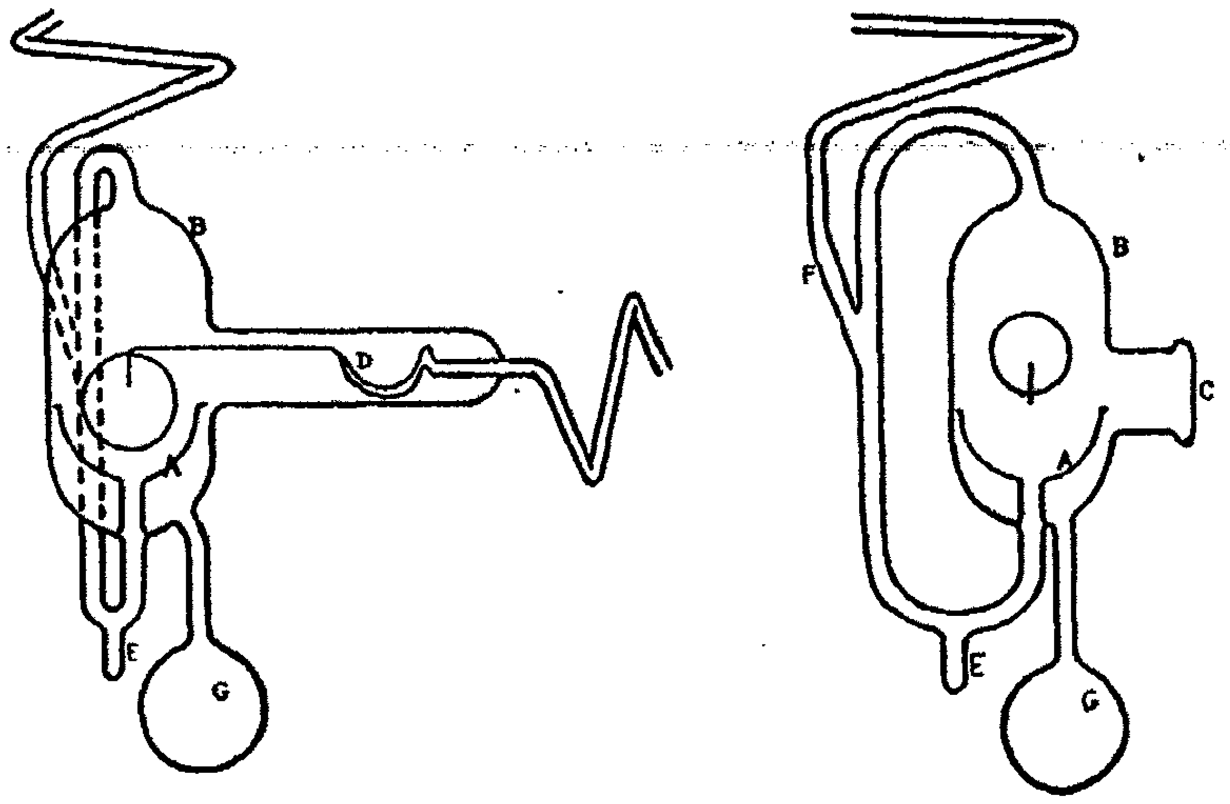

Fig. 1. Detail of the Apparatus Used

The window was tested before it was sealed in, and no difference, to 0.001 mm., could be detected between the distance apart of two points viewed through the central portion of the window and through air. The Bourdon gauge D was arranged so that the fine tip comes just above the middle of the top surface of the cup. It would stand a pressure difference of 10 mm., and had a sensitivity of 2 mm. per millimeter change of pressure. A smooth adjustment could be made without agitating the mercury surface. Any overflow of mercury was caught in G, which could be cut off, and the mercury could easily be returned to the still. A tungsten wire could be sealed in at E. The mercury was admitted from the still at F, the spirals allowing adjustments to be made in the level of the apparatus without disconnecting.

The complete apparatus is shown in figure 2. The mercury was washed with sodium hydroxide, air was bubbled in under a layer of dilute nitric acid and mercurous nitrate, it was distilled twice in a current of air, and then in a vacuum. It was distilled over into the cup from B. The cut-off C and the McLeod gauge were constructed so that the mercury was not fouled by rubber. There was no tap between the cut-off and the measuring apparatus, and since liquid air was always placed round the trap D when C was open, no grease vapor should have entered the apparatus; as an extra precaution a fresh sample of Apiezon grease was used in the taps, which were not exposed to strong sunlight. The Bourdon gauge could be adjusted, C being closed, by filling the space between the taps F and G with air, which was then admitted to the gauge, while the compression of the gas in the gauge by lifting the column of mercury in E gave a very fine adjustment. To prevent the bursting of the gauge, taps F, G, J, also C were opened when gas was admitted. The tip of the style was adjusted to give an image the width of a very fine cross hair (a thin thread pulled out from rubber solution) below itself. Pressures from 1 to 15 mm. could be read on the Hamblin gauge H. With practice, readings on the mercury surface could be repeated to 0.001 mm.

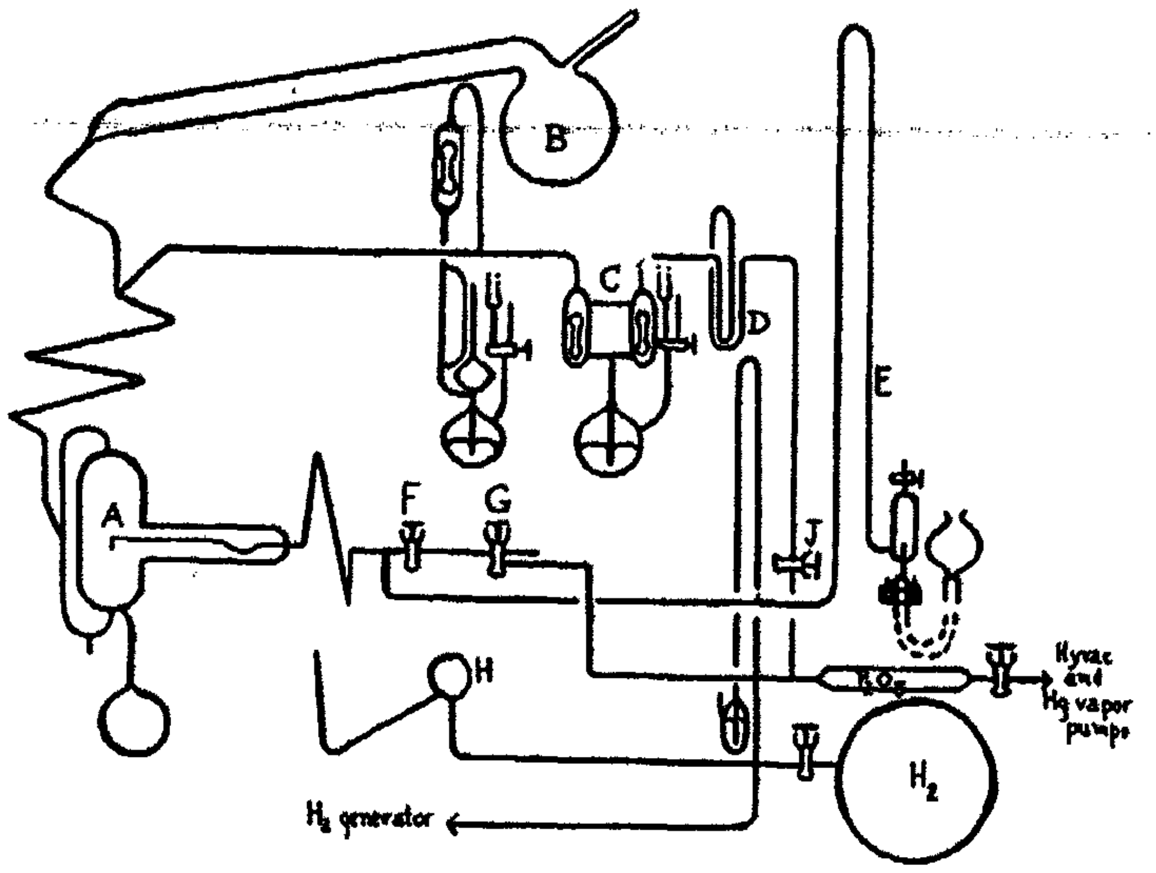

Fig. 2. The Complete Apparatus

The whole apparatus was washed with a solution of potassium permanganate in concentrated sulfuric acid, then with distilled water, and allowed to drain. It was joined in a moist condition, using a liquid air trap, and then pumped out and degassed by playing over it the blowpipe flame. The mercury surface was illuminated by a flash-lamp bulb, and was observed through a microscope which read to 0.001 mm. The latter was carefully levelled and was adjusted so that the barrel racked horizontally (lycopodium powder dusted on to a flat mercury surface was observed). A flash-lamp bulb illuminated a horizontal slit which gave an image in the mercury surface at the point of largest section in the usual manner, care being taken to ensure that the slit and its image were on the same level. The room, a cellar, was constant in temperature to a degree during the winter months.

The surface tension was found to be constant over long periods of observation lasting several weeks, but for fresh distillations of mercury differed by about 1 dyne from the mean, 500.3 dynes per centimeter at 16.5°C.; this value lies between those of Burdon and Cook.

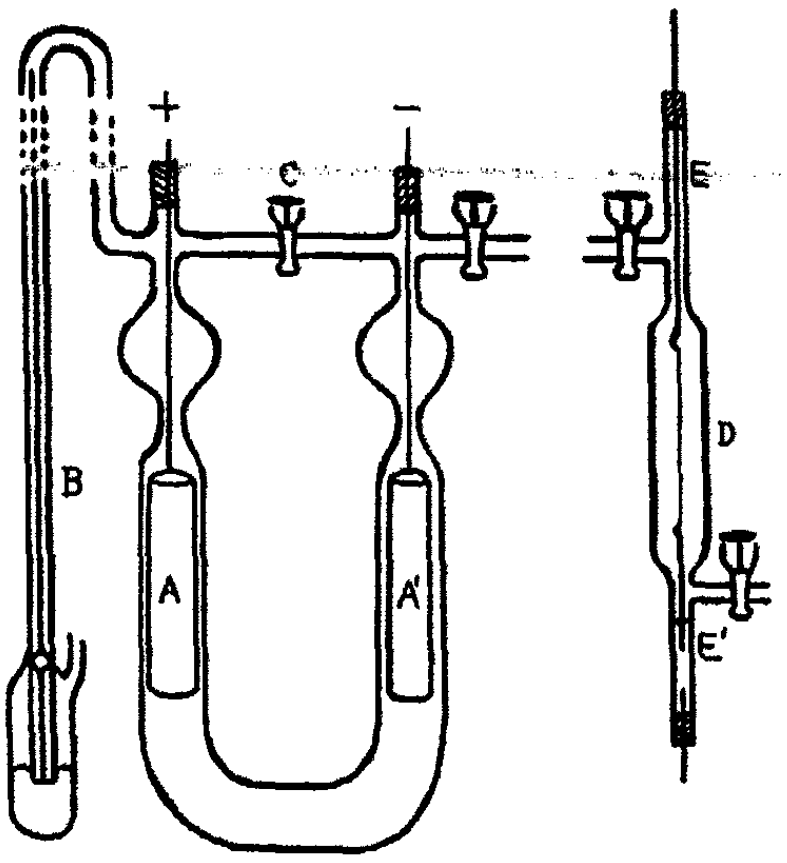

FIG. 3. APPARATUS FOR THE PREPARATION OF PURE HYDROGEN

A tungsten wire fused in at E (figure 1) was earthed, as it was thought that in the process of distillation, during which the mercury ran over glass surfaces, a charge might have been acquired. This would be dissipated only very slowly in a glass apparatus. No difference, however, was observed.

THE SURFACE TENSION OF MERCURY IN HYDROGEN

The author has experienced considerable difficulty in preparing pure hydrogen for density work, using the ordinary type of electrolytic cell. A modification was therefore devised by which the electrolyte could be thoroughly degassed before the run was made; moreover no air came in contact with it during the preparation of the gas (figure 3). The electrolyte was a solution of pure sodium hydroxide and recrystallized barium hydroxide; the cylindrical electrodes were made from nickel sheet. The capillary tube dipped only 0.5 cm. under the surface of the mercury, so that the oxygen generated escaped at a pressure only slightly greater than atmospheric. Tap C was opened and the whole degassed with a Hyvac and mercury diffusion pump, the water finally boiling over into tubes containing sodium hydroxide. Tap C was then closed and the current passed, no difficulty being experienced in adjusting the levels of the electrolyte round A and A′, since the hydrogen comes off twice as fast as the oxygen.

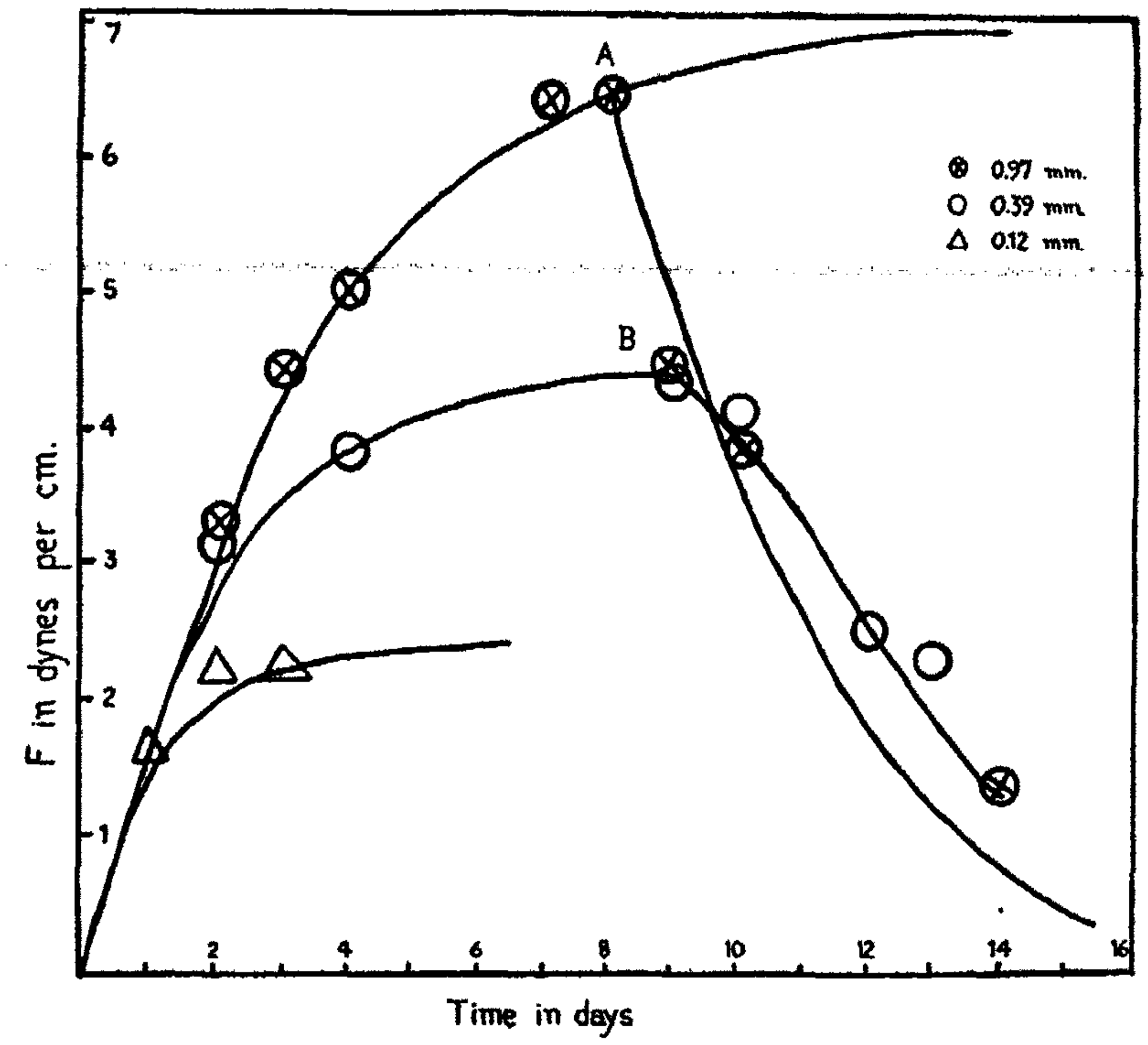

Fig. 4. The Surface Tension of Mercury in Hydrogen

The hydrogen was passed over the glowing platinum wire D, joined to steel electrodes E E′, the lower one of which hung in mercury; in this way no sag occurs when the wire is heated. On leaving D the gas passed over phosphorus pentoxide and then through a tube immersed in liquid air.

Hydrogen was admitted to the drop at various pressures and the surface tension was measured as before. Between each run the whole apparatus was thoroughly degassed (heated as before), a fresh mercury surface was prepared, and the constancy of the surface tension of the latter was checked. It was found that a very slow decrease in surface tension occurred, the experiments lasting several days. At low pressures the final value of the surface tension decreased with increasing pressure, but as the pressure of hydrogen was increased the rate of decrease fell off, and from 8 to 100 mm. no change was observed (figure 4). A number of runs were made at these higher pressures, and no fall in surface tension occurred during a week's observation.

THE THEORY OF THE FALL OF SURFACE TENSION IN HYDROGEN

The simplest assumption is that the slow fall in surface tension is accompanied by a slow adsorption, i.e., that not all the hydrogen molecules which strike the surface are adsorbed. We may speak therefore of an activation necessary for adsorption. Various possibilities may then be considered: a molecule may require activation before it is adsorbed, necessary to mount the energy hump on the intermolecular energy distance diagram (2); ~~since mobility is possible on the surface, molecules may become adsorbed~~ by striking those already on the surface, so that adsorption would be possible on other than the free space of Langmuir's theory; similarly, collisions between molecules on the surface may cause desorption, which may also result from collisions between molecules in the bulk and surface phases, if the pressure is sufficient. The bulk material of the adsorbent is usually looked upon as a perfect energy reservoir, but an important factor will be the rate of interchange of energy between the molecules of adsorbent and the adsorbed molecules.

If we consider the most probable of these possibilities, we may suppose that a fraction θ of the surface is covered, and that there are n molecules per square centimeter when the gas pressure is p. The rate of adsorption in molecules per second is then

$$(1-\theta)p(2\pi mkT)^{-\frac{1}{2}}\alpha + \theta p(2\pi mkT)^{-\frac{1}{2}}\beta$$

where the first and second terms refer to the bare and covered surface, respectively, and where α and β are the fractions of the impinging molecules which are adsorbed. If the activation is thermal, α and β will be of the form $e^{\frac{-k_1}{T}}$, $e^{\frac{-k_2}{T}}$, where k_1 and k_2 are constants. Similarly the rate of desorption is $\gamma\theta$, where γ, for activated desorption, is of the form $Be^{\frac{-k_3}{T}}$, where B and k_3 are constants.

If A is the area occupied by a molecule for a condensed film, then $\theta = nA$, and

$$\frac{dn}{dt} = (1-nA)\alpha p(2\pi mkT)^{-\frac{1}{2}} + nA\beta p(2\pi mkT)^{-\frac{1}{2}} - \gamma nA$$

or

$$\frac{dn}{C-Dn} = dt$$

where

$$C = \alpha p(2\pi mkT)^{-\frac{1}{2}}$$

$$D = \alpha pA(2\pi mkT)^{-\frac{1}{2}} + \gamma A - p(2\pi mkT)^{-\frac{1}{2}}A\beta$$

Hence

$$n = \frac{C}{D}(1 - e^{-Dt})$$

since $n = 0$ when $t = 0$ 1

Let F be the lowering of the surface tension of the mercury. Then $F = \sigma_0 - \sigma$, i.e., F is the surface pressure of the hydrogen film (σ_0 and σ are the surface tensions of pure mercury and of mercury in the presence of hydrogen). We may suppose that the surface film of gas behaves as a two-dimensional gas, which, owing to the surface forces, is more imperfect than the bulk material. Thus we may write

$$F = nkT + \delta n^2 + \ldots\ldots\ldots\ldots 2$$

The first term in the expansion may be called the kinetic pressure, the second the cohesive pressure (actually a tension). For the analogous case of a three-dimensional gas we may write

$$p = \frac{kT}{V - b} - \frac{A}{V^2}$$

where V is the volume per molecule, and b and A are constants. Phillips (10) has shown that the last term retains the same form independently of the law of force assumed. Thus n in equation 2 will be the true surface concentration only when this is small; moreover δ will be negative, and this is the result obtained below. It is interesting to note that for most pure liquids σ is expressible in the form

$$-\sigma = nkT - \delta n^2$$

where n is of the right order (10^{15}), the decrease in surface tension as temperature is increased being due, on this view, to the increase in surface pressure and to a smaller extent to the change in cohesion.

On inserting the value of n found in equation 1 in equation 2 we obtain

$$F = \frac{C}{D}kT(1 - e^{-Dt}) + \delta\frac{C^2}{D^2}(1 - e^{-Dt})^2$$

The experimental results for low pressures can in fact be fitted to a curve of the type

$$F = H(1 - e^{-Dt}) + J(1 - e^{-Dt})^2$$

This gives

$$\frac{dF}{dt} = De^{-Dt}\left[H + 2J(1 - e^{-Dt})\right]$$

Hence $\frac{dF}{dt} = 0$ when $t = \infty$, F having then the value $H + J$, or when

$$e^{-Dt} = 1 + \frac{H}{2J}$$

When $H = -2J$ these two points coincide; in other cases there is a small hump in the curve, giving

$$F_{\max} = -\frac{H^2}{4J}$$

Since this does not correspond to anything physical and is due to the omission of higher terms in the equation for F, a better fit can be obtained by making $H = -2J$; this limitation is supported by the fact that on solving the curves without it a rough fit is obtained, except for the region of the hump, giving values of $-H$ between 1.5 and 2. When $H = -2J$ a good fit is secured throughout.

Hence we shall take

$$\begin{aligned} F &= -2J(1 - e^{-Dt}) + J(1 - e^{-Dt})^2 \\ &= -J(1 - e^{-2Dt}). \end{aligned}$$

This is easily solved by taking two points at times t_1 and t_2, such that $t_2 = 2t_1$. Then if

$$e^{-2Dt_1} = x$$

$$F_1 = J(x - 1) \qquad F_2 = J(x^2 - 1)$$

or

$$x = \frac{F_2 - F_1}{F_1} \qquad J = \frac{F_1^2}{F_2 - 2F_1}$$

The smooth curves in figure 4 were obtained in this way. The values of J, D, and $n_\infty = -2J/kT$ are given in table 1. The trend of D is interesting; it shows that $\beta > \alpha$.

The free motion of hydrogen on mercury is very probable, especially in view of the other evidence which shows that adsorbed molecules have a lateral mobility (5, 15). Burdon states that "it is difficult to picture the mechanism by which anything much less than a contiguous layer of molecules could appreciably affect the surface tension." This, however, neglects the motion of the adsorbed molecules in the surface.

At a pressure of 6 mm. a curve was obtained below that at a pressure of 0.39 mm., and above 8 mm. no change in surface tension was observed. This unexpected result can perhaps be interpreted in terms of deactivation by collision, and bears an apparent analogy to explosion limits. It would seem that no hypothesis other than some type of activation can account for the slow fall of surface tension in hydrogen. For even if slow solution occurred, and the surface film were rapidly established, there would be no reason why the composition of the surface should not remain the same, and presumably the surface tension would be constant. There is the possibility that a film is held by weak adsorption, and that this then forms a stronger union with the mercury, when equations similar to the above would be obtained, the weakly adsorbed film replacing the bulk gas as a reservoir of molecules. Mercury and hydrogen combine only when the molecules are excited, but when once formed the molecule HgH is fairly stable, with an energy of dissociation of 8500 calories per gram-molecule (9). It is possible that the activation is due to external radiation.

TABLE I

p	J	D	$n \times 10^{-14}$
mm.			
0.97	−6.94	0.1623	3.56
0.39	−4.41	0.2458	2.26
0.12	−2.39	0.4380	1.23

A study was also made of desorption from the surface. According to the above, if adsorption is stopped at the point t_1,

$$F_{t_1} = -2J(1 - e^{-Dt_1}) + J(1 - e^{-Dt_1})^2$$
$$= n_{t_1}kT + \delta n_{t_1}^2$$

If now t is measured from this point as a new zero,

$$\frac{dn}{dt} = -Gn$$

where $G = \gamma A$. Hence

$$n = n_0e^{-Gt}$$

where n_0 is the value of n at the point $t = 0$, the point at which desorption began. As before, equation 2 gives

$$F = n_0kTe^{-Gt} + \delta n_0^2e^{-2Gt}$$

Since n_0 for the desorption is the same as n_{t_1} for the adsorption curve, the equation for desorption will therefore be

$$F = H'e^{-Gt} + J'e^{-2Gt}$$

where

$$H' = -2J(1 - e^{-Dt_1})$$

and

$$J' = J(1 - e^{-Dt_1})^2$$

it is asymptotic to the axis of time.

The desorption curve contains therefore only one unknown constant, G, as the others can be calculated from the adsorption curve. G is easily found by taking one point on the desorption curve at t_2, and solving for

$$e^{-Gt_2} = x$$

as the admissible root of the equation

$$F_{t_2} = H'x + J'x^2$$

TABLE 2

p	H'	J'	G
mm.			
0.97	10.09	3.67	0.4311
0.39	8.82	4.41	0.3575

In this way the curves for 0.97 and 0.39 mm. were obtained, desorption starting at the points A and B, when the apparatus was pumped down to a hard vacuum, and it is noteworthy that in these curves H' and J' were calculated from the curves for adsorption. Moreover it will be seen from table 2 that the G's are nearly the same, as they should be, and that they are greater than the corresponding D's, as they should be if $\beta > \alpha$.

THE EFFECT OF ILLUMINATION

Mercury vapor excited by light of wave length 2536 A.U. can dissociate hydrogen to atoms by a mechanism which is probably represented by

$$Hg' + H_2 \rightarrow HgH' + H$$

the dashes indicating excited molecules. The HgH' reverts to the normal state with the emission of a band spectrum, and may then dissociate. A tube was fitted on the apparatus at right angles to the mercury surface and the end was blown out very thin. This thin spherical end was surrounded by a tube which could be evacuated, and to the end of this tube was waxed a quartz plate. By adjusting the pressure on the outside of the thin end, collapse was avoided. Light was shone on to the mercury surface from a Pyrex mercury vapor lamp with a thin window (13). The lamp was cooled by a strong air blast, as the cold mercury vapor absorbs only the center of the line, and the waxed quartz plate was also cooled. No immediate effect was observed, but the rate of decay after illumination was greater than normally; thus with a pressure of 1 mm. the surface tension fell 7 dynes in three days instead of 4.5 dynes, after 10 minutes illumination; after an hour's illumination it fell 7 dynes in one day. It seems probable that this effect is due to HgH molecules which have reverted to the normal state. These would be easily adsorbed as one end would be "soluble" in mercury.

SUMMARY

The surface tension of mercury was determined by measurements on a flat drop, using a method of defining the top surface of the drop which was free from error. The mean value of 500.3 dynes per centimeter at 16.5°C. was obtained. The fall of the surface tension in hydrogen at pressures from 0 to 100 mm. was studied and interpreted theoretically. The surface was illuminated with light from a mercury vapor lamp. No immediate effect was noticed, but the surface tension fell more rapidly than normally.

My thanks are due to Professor Whytlaw Gray, F.R.S., for encouragement and to Imperial Chemical Industries Ltd. for a grant which defrayed part of the cost of the apparatus.

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COMMUNICATION TO THE EDITOR

EFFECT OF SULFATED FATTY ALCOHOLS IN THE COLORIMETRIC DETERMINATION OF pH

In This Journal (J. Phys. Chem. **37**, 1001 (1933)) Neville and Jeanson state that they used standard indicators to determine colorimetrically the pH of solutions containing Gardinol CA. Since no mention is made of the errors which may be encountered in utilizing this method, it appears advisable to point out certain limitations which exist.

We have examined the effect of Gardinol CA (sodium salt of sulfated technical oleyl alcohol), and Gardinol WA (sodium salt of sulfated technical lauryl alcohol), on a number of common indicators in buffered solutions and have found that the fat alcohol sulfates exert a specific effect on most indicators, which is frequently a source of appreciable error. Our method was as follows: 5 cc. of the buffer solution, prepared by the specifications of Clark and Lubs (W. M. Clark: The Determination of Hydrogen Ions, pp. 192–202. Williams & Wilkins Co., Baltimore (1928)), was diluted with 5 cc. of water and 0.5 cc. of the indicator solution (La Motte) and the pH observed in the La Motte comparator. For comparison, 5 cc. of the buffer solution was diluted with 5 cc. of a fat alcohol sulfate solution and 0.5 cc. of the indicator and the apparent pH determined as above. Measurements were made at three or more values in the range covered by each indicator.

The observed errors in all of the determinations made in the presence of fat alcohol sulfates were on the acid side of the values obtained for the corresponding buffer solutions free of the fat alcohol sulfates. The comparisons show that in 0.5 per cent sodium lauryl sulfate solutions the error in the observed pH value, using cresol red (acid), methyl red, bromthymol blue, and thymol blue, is greater than 1.0; using meta cresol purple, bromcresol green, and bromcresol purple, is greater than 0.5; using La Motte yellow, and chlorphenol red, is greater than 0.2; using cresol red (alkaline), is less than 0.2; and using phenol red and La Motte purple, is negligible. At a 5.0 per cent concentration of this fatty alcohol sulfate, all of the indicators are in error. With 0.5 per cent sodium oleyl sulfate solutions, the error in the observed pH value, using bromthymol blue, is greater than 1.0; using cresol red, methyl red, and thymol blue, is greater than 0.5; using meta cresol purple, bromcresol green, bromcresol purple, and chlorphenol red, is greater than 0.2; using phenol red and cresol red, is less than 0.2; and using La Motte yellow and La Motte purple, is negligible. Electrometric measurements have shown that no change in pH occurs when a fatty alcohol sulfate solution is added to a buffer solution in the manner used in obtaining these results. The technical sodium lauryl sulfate used in these experiments was of 75 per cent and the technical sodium oleyl sulfate was of 50 per cent strength. Both products were slightly alkaline to phenol red, but the amount of alkali present was negligible when compared with the concentration of the buffers.

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NEW BOOKS

Les fondements de la théorie de la relativité générale. Théorie unitaire de la gravitation et de l'electricité. Sur la structure cosmologique de l'espace. By A. Einstein. Translated from the German by Maurice Solovine. 111 pp. Paris: Hermann et Cie, 1933. Price: 35 francs.

The first two sections of this small volume dealing with general relativity and with the unitary theory of electricity and gravitation are translations of two papers published, the first one in 1916, the second one in 1931. As far as these two articles are concerned, the present volume will be of use mainly to those who prefer French to German or to whom this translation is more easily accessible than the original publications.

The third section on the cosmological structure of space is translated from a manuscript prepared in September, 1932. Einstein concludes that in a dynamic theory of the universe, the existence of an average density of matter different from zero must not be related theoretically to a curvature of space but to a spatial expansion. In the light of our present knowledge, there is no sure indication of spatial curvature, positive or negative.

F. H. MacDougall.

Die physikalische Chemie der Kesselstein Bildung und ihrer Verhütung. Second revised and enlarged edition. By R. Stumper. 74 pp.; 18 illustrations. Stuttgart: Ferdinand Enke, 1933. Price: paper, 5.30 R.M.; as part of collection, 4.80 R.M.

It is only three years since the first edition of this pamphlet appeared, which is an indication of how well it has been received. In it the author has collected the most plausible theories of boiler scale formation and methods of combatting it. It is a clear exposition of the physico-chemical equilibria of scale formation, the formation of solid and crystalline phases in supersaturated solutions, and an explanation of the effect of evaporation and colloids on scale formation. This edition discusses silicate scales, the solubility of scale constituents at operating boiler temperatures and pressures, and the dynamics of carbonate scale formation.

Old and new methods of scale prevention by shifting of chemical equilibria, by means of colloids, mechanically, and electrically are critically considered.

Throughout this pamphlet are given excellent tables of data, graphs, illustrations, some calculations, and many literature references. The subject matter is very well treated from the theoretical standpoint. Practical calculations and applications would make the pamphlet more useful to the practicing engineer.

Charles A. Mann.

The Conductivity of Solutions. Second edition. By Cecil W. Davies. viii + 281 pp.; 32 figs. New York: John Wiley and Sons, Inc., 1933. Price: $4.00.

This book may be recommended as an interesting, easily readable, but hardly adequate presentation of modern theories of the electrical conductance of solutions. The standpoint of the author seems to be that chemists need not understand the equations of Debye or of Onsager but should only be concerned with their success in predicting experimental results. In harmony with this is the fact that the author evidently does not require his readers to possess mathematical knowledge beyond algebra and analytic geometry. In spite of the importance of the subject in connection with the measurement of conductivity, the book does not contain anything approaching an adequate treatment of inductance, capacity, and polarization effects.

Nevertheless there is much in this text book that deserves high praise and that can be read with profit by both beginners and advanced students. We refer to the many applications of Onsager's equation, the discussion of the solvent correction, the evaluation of the equivalent conductance at zero concentration and finally the use of conductance methods in solving analytical problems in pure and technical chemical research.

F. H. MacDougall.

Bearing Metals and Bearings. American Chemical Society Monograph Series, No. 53. By W. M. Corse. 6 x 9 in.; 383 pp. New York: The Chemical Catalog Company, Inc., 1930. Price: cloth, $7.00.

The author has surveyed the literature on bearing metals and bearings and has collected into one volume bibliographic references to the widely scattered publications in different languages and in many journals, the more important articles being abstracted. Part I (25 pages) presents a brief but interesting history of the development of bearing metals and bearings. This part serves to acquaint those not familiar with this field of work with some of the important subjects.

Part II (106 pages) contains more than a thousand bibliographic references to articles on bearing metals, sliding-contact bearings, friction, and lubrication. The metals included are the white metals, the bronzes, and the graphite bearing metals. The bibliographic references are arranged under appropriate main and subheadings and cover the literature through 1928.

Part III (108 pages) contains two hundred thirty-four abstracts of selected papers. These abstracts were specially prepared and give quite completely the important information in the original articles. Part IV contains sixteen tables showing the properties of bearing metals.

This volume is a valuable contribution to workers and students in this field. In looking up the published information on this whole field or on any special phase of it, much time can be saved by making use of the material which Corse has collected and put into convenient and usable form. The author index contains about seven hundred names, and the subject index provides an easy means of finding the information on some two hundred subjects.

Oscar E. Harder.

Grundlagen der Photochemie. By K. F. Bonhoeffer and P. Harteck. 295 pages; 73 figures; 30 tables. Dresden and Leipzig: Theodore Steinkopff, 1933. Price: bound, 25 R.M.; unbound, 24 R.M.

In the three or four decades during which the study of chemical kinetics has been intensively pursued, it has become increasingly evident that there is no golden road to knowledge along which progress takes an easy course. This is equally or more true of photochemical kinetics. The technique is difficult; the theory, involving several domains of physics and chemistry, is complicated and incomplete. The Einstein law of photochemical equivalence and its experimental verification marked a milestone of substantial achievement; the application of the principles of modern spectroscopy to photochemical phenomena ushers in the newest phases of photochemistry.

It is these principles and their detailed application to various photochemical reactions that are admirably introduced and treated in the present work. Experimental procedure is wholly omitted nor is any attempt made to give a complete citation of all photochemical reactions that have been investigated, though the most important ones, naturally, are discussed in applying theoretical considerations to them.

The first chapter contains a list of gaseous and liquid reactions of which the quantum yields have been determined both in direct and in sensitized photochemical reactions. The second chapter, entitled "The Photochemical Primary Process," is introduced by a splendidly condensed general treatment of atomic and molecular light absorption, continuous and discrete spectra, dissociation and predissociation, followed by the application of these principles to many photochemically important substances for which tables of absorption spectra and diagrams of energy levels are given. The third chapter deals with the photochemical secondary or thermal reactions that follow the primary act. The final chapter treats rather fully the complete kinetics of about a dozen of the most fully investigated photochemical reactions.

After examining this excellent treatment of photochemistry from the modern standpoint, one cannot fail to be impressed by the fact that in spite of its greater experimental difficulties photochemistry has not only repaid thermal kinetics for all that was borrowed, but has enriched it with a knowledge of atomic chemistry that will enable both to advance with enhanced certainty and rapidity, arduous though the way may be.

S. C. LIND.

Liquid Crystals and Anisotropic Melts. A General Discussion held by the Faraday Society. 25 x 16 cm.; iv + 204 pp. London: Gurney and Jackson, 1933. Price: 12/6d.

The present volume, reprinted from the *Transactions of the Faraday Society*, contains twenty-four papers and a general discussion. Two papers, that on the connection between the x-ray patterns of gases and true liquids, and the contribution of Bernal and Fowler on water, are particularly interesting. Water is, we presume, nearly as good a liquid as ever was, and our feeling is that the subject matter of the volume should have been extended to include the most interesting question of structure in so-called isotropic liquids. The book would then have possessed a uniformity which its contents at present belie.

There is no question about the value of the book as a whole. The subject has previously received attention from Continental scientists alone, as reference to a recent volume of the *Zeitschrift für Kristallographie* shows. The names of Vorländer, Kast, Ornstein, Rinne, Zocher, and Ostwald are sufficient guarantee to the authoritative nature of the volume under review. In addition there are the English contributors, Bernal, W. H. Bragg, Crowfoot, Fowler, Malkin, and Lawrence.

Ornstein and Zocher discuss rival theories of liquid crystals; Rinne emphasizes their biological importance. Lawrence makes a valuable contribution to the study of the lyotropic mesomorphs. Until these discussions, little or no study of the true crystalline phases of liquid-crystal forming substances had been made. Bernal and Crowfoot have performed a valuable service in remedying this state of affairs. It is only by comparison of the densities in the solid and liquid phases that one may obtain clues as to the modifications of grouping which take place on melting. If the arrangements in the true solid are unknown, speculations about arrangements in true liquids or the mesophases of liquid crystals become mere guess work.

The work of Bernal and Fowler is of far-reaching importance. Lack of space prevents anything like an adequate summary of their paper; briefly, however, their achievements are these. The accepted crystalline structure of ice has been modified. The unit cell is very much bigger than that found by Barnes and the structure is molecular: four molecules are arranged in rough tetrahedral fashion round a central fifth. This arrangement and various developments of it in space, is, in conjunction with Prins's theory, the basis of their explanation of the x-ray diffraction patterns of water and their variation with temperature. Water changes from something roughly ice-like at low temperatures to a quartz-like structure at ordinary temperatures. Further heating tends to produce close packing.

The whole volume is of great value to those interested in structural physics and chemistry, particularly from the point of view of the transition from solid to liquid. Need the binding of the *Discussions* be quite so flimsy?

J. T. RANDALL.

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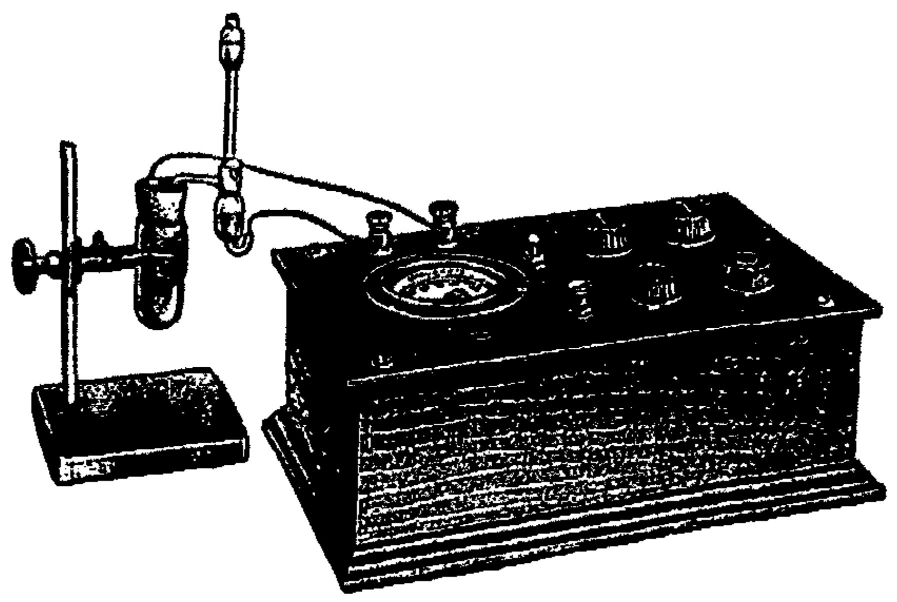

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*Bureau of Standards Journal of Research, V. 12, p. 67 (1934).

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I. THE ADSORPTION OF ALKALI HYDROXIDES BY SILICA GEL IN THE PRESENCE OF AMMONIA AND AMMONIUM SALTS[1]

I. M. KOLTHOFF AND V. A. STENGER[2]

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received July 24, 1933

In a preliminary communication (4) various factors affecting the adsorption of cations from ammoniacal solution by silica gel have been mentioned. It has been pointed out that equilibrium may not be reached even after a long time of shaking, and that during the experiment the external and internal surface of the gel may change, owing to the dissolving effect of the alkali. Since the alkali hydroxides form soluble silicates, it might be expected that with these bases adsorption equilibrium is attained more quickly than in cases where the cations form slightly soluble silicates. In this paper the adsorption of sodium and potassium hydroxides, also in the presence of ammonia and ammonium salts, and of ammonia by silica gel is described.

SILICA GEL USED

The same gel was used as in the previous work (4). It was purchased from the Silica Gel Corporation and had originally been prepared by a modification of McGavack and Patrick's method (5). It was purified in this laboratory with nitric acid and finally by electrodialysis as described before (4). After drying at 350°C. it contained 3 per cent of water. In agreement with results of Bartell and Almy (1) it was found that on heating the gel to 900°C. its activity decreased considerably (40 to 50 per cent). In addition, its speed of solution in alkaline liquids had decreased markedly. In agreement with van Bemmelen's work (7) no indication was obtained that adsorbed water is chemically bound, but rather that it covers the surface of capillary walls as a result of capillary action and then fills the capillaries themselves. Figure 1 gives the results of experiments in which the gel was kept at various water vapor tensions for different times. The typical S shaped curves are found only at or close to equilibrium conditions; with

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[1] From a thesis submitted by Vernon A. Stenger to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1933.

[2] J. T. Baker Fellow in Analytical Chemistry, 1932–1933.

insufficient time of standing the curves representing the amount of water adsorbed at various vapor tensions have a different shape. The ordinate in figure 1 indicates the number of moles of water adsorbed per mole of silica gel; the abscissa gives the relative vapor tension.

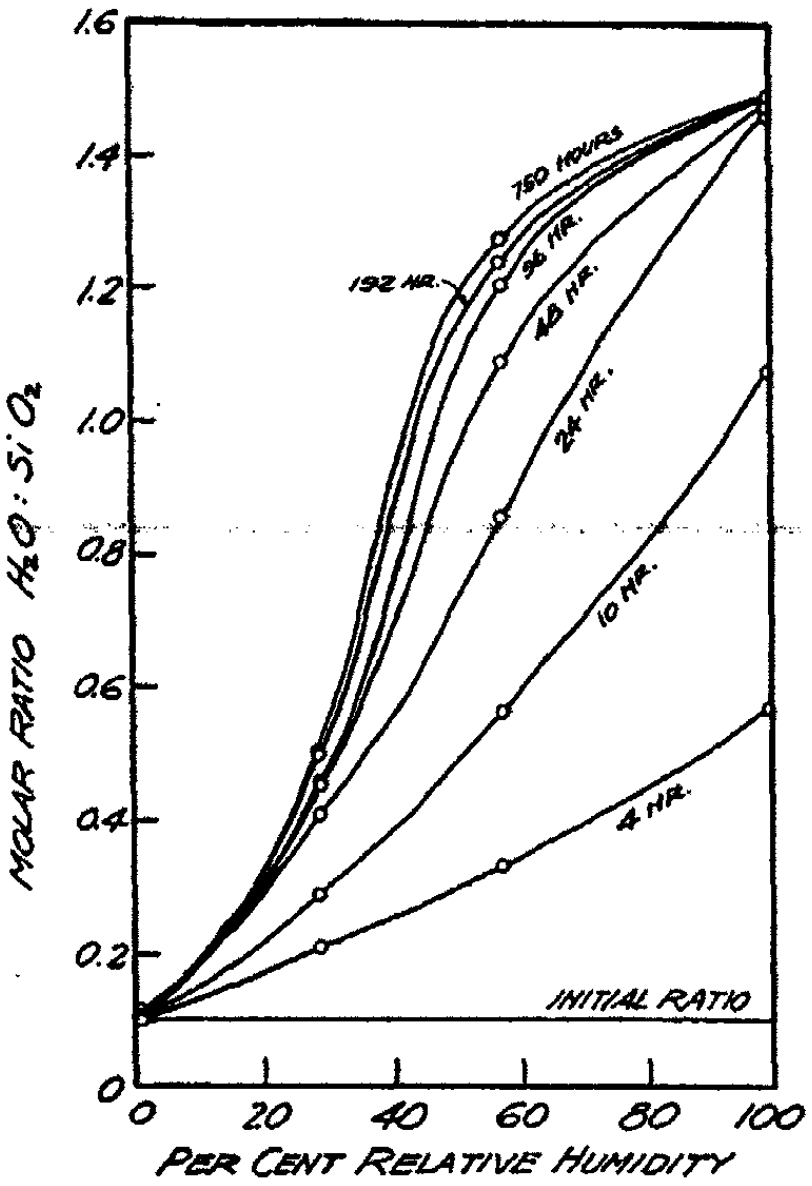

FIG. 1. ADSORPTION OF WATER

PROCEDURE AND ANALYSIS

The experiments were carried out as described before (4), the samples being shaken at room temperature (around 25°C.) on an eccentric rotary shaker revolving at 160 R.P.M.

The amount adsorbed was determined by analysis of the supernatant liquid or by extraction of the quickly washed gel with a known volume of standard acid; usually both procedures were followed. The total amount of base adsorbed was found by standard volumetric procedures, whereas ammonia in the presence of other bases was determined by oxidation with a new stable standard reagent, calcium hypochlorite. The details of this method will be described elsewhere.

Former workers who have studied the adsorption of bases by silica gel have not considered the amount of adsorbent going into solution during the experiments. In all our work the amount dissolved has been determined by transferring the sample of gel, after extraction with acid and rinsing, to a porcelain crucible and igniting for 1½ hours at 900°C. The water content of the original sample was determined in a similar way.

EXPERIMENTAL

In order to get comparable results the same speed of shaking, the same size of the gel, and the same temperature should be maintained during the work. The speed of adsorption and of solution appeared to increase with increasing speed of shaking and decreasing size of the particles of the gel. The adsorption of ammonia and the solubility in dilute ammonia solutions were determined at 5°, 25°, and 45°C., respectively. The adsorption of the base decreases, but the speed of solution increases much more markedly with increasing temperature.

Adsorption of sodium hydroxide and potassium hydroxide

Some results on the relation between the time of shaking and the amount of base adsorbed and amount of gel gone into solution are given in table 1. The number of milliequivalents of base adsorbed per 1 g. of original gel have been corrected for the amount of gel dissolved during the experiment.

With the 0.0057 *N* sodium hydroxide solution, adsorption equilibrium seems to be reached after one hour of shaking, although more gel is going into solution on prolonged time of contact. With the stronger solution equilibrium has not been attained even after four hours of shaking, whereas more than 50 per cent of the gel had gone into solution after that time. With potassium hydroxide similar results were obtained.

In the final experiments the adsorption isotherm was determined after four hours of shaking. The results plotted in figure 2 show the abnormal shape of the curve, if the data are not corrected for the amount of gel dissolved. In figure 3 the amounts of sodium and potassium hydroxides, ammonia, and calcium hydroxide adsorbed after four hours of shaking and corrected for the dissolved gel are plotted.

Adsorption of ammonium hydroxide

The adsorption of ammonium hydroxide was studied in considerable detail, since in later experiments the adsorption of cations from ammoniacal solution was investigated. Preliminary experiments showed that adsorption equilibrium is virtually established within two hours, although on longer shaking more gel is going into solution.

Table 2 gives the percentage of gel going into solution and the amount of ammonia adsorbed after two hours of shaking. The reported adsorption data have been corrected for the dissolved amount of gel.

The desorption of the ammonia was studied by washing the gels continuously with water for various periods of time. Even after sixty days all the gels contained some ammonia, but only of the order of 3 to 4 per

TABLE 1

Adsorption of sodium hydroxide and solubility of gel in the alkaline solution

0.5 g. of gel; 100 cc. of solution

TIME SHAKEN	FINAL CONCENTRATION OF NaOH	GEL DISSOLVED	NaOH ADSORBED (NOT CORRECTED FOR SOLUBILITY OF GEL) MILLIEQUIVALENTS PER GRAM OF GEL		NaOH ADSORBED (CORRECTED FOR SOLUBILITY) MILLIEQUIVALENTS PER GRAM OF GEL	
			From analysis of solution	From extraction of gel	From analysis of solution	From extraction of gel
Original concentration of NaOH = 0.00566 *N*						
hours	*N*	*per cent*				
0.5	0.0033	1.8	0.48	0.47	0.49	0.48
1	0.0030	2.85	0.54	0.54	0.55	0.56
2	0.0030	4.8	0.54	0.54	0.57	0.56
4	0.0032	6.5	0.50	0.50	0.53	0.53
6	0.0031	6.75	0.51	0.50	0.55	0.54
12	0.0031	7.3	0.51	0.51	0.55	0.55
Original concentration of NaOH = 0.0566 *N*						
0.5	0.0513	7.0	1.07	1.00	1.15	1.08
1	0.0509	18.9	1.14	1.09	1.41	1.34
2	0.0511	32.7	1.10	1.04	1.64	1.55
4	0.0525	56.4	0.82	0.77	1.89	1.77

TABLE 2

Adsorption of ammonia

0.5 g. of gel per 100 cc. of solution; 2 hours of shaking

FINAL CONCENTRATION OF NH_3	GEL DISSOLVED	NH_3 ADSORBED IN MILLIEQUIVALENTS PER GRAM (CORRECTED FOR SOLUBILITY)	
		From analysis of solution	From extraction of gel
N	*per cent*		
0.00680	4.1	0.52	0.51
0.0119	5.0	0.68	0.67
0.0207	4.4	0.85	—
0.0443	5.7	1.12	—
0.0696	7.2	1.29	1.28
0.0923	7.4	1.56	1.48
0.1625	9.2	1.74	1.74
0.24	10.0	2.05	1.96
0.49	12.3	2.14	2.31
0.99	14.4	—	2.80
1.98	17.9	—	3.48

cent of the original amount adsorbed. It is interesting that especially in the first periods of the desorption the gels lost fairly much in weight, thus showing that the adsorbed ammonia is given off in the form of ammonium silicate.

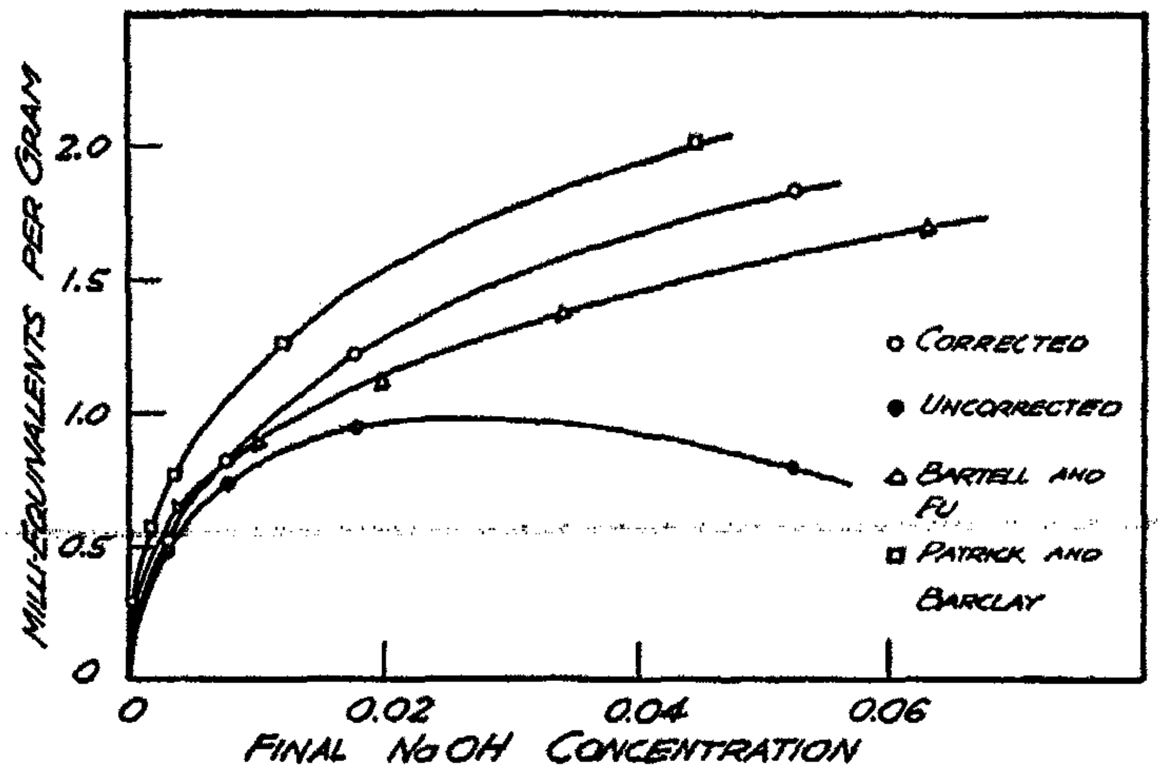

FIG. 2. ADSORPTION OF SODIUM HYDROXIDE

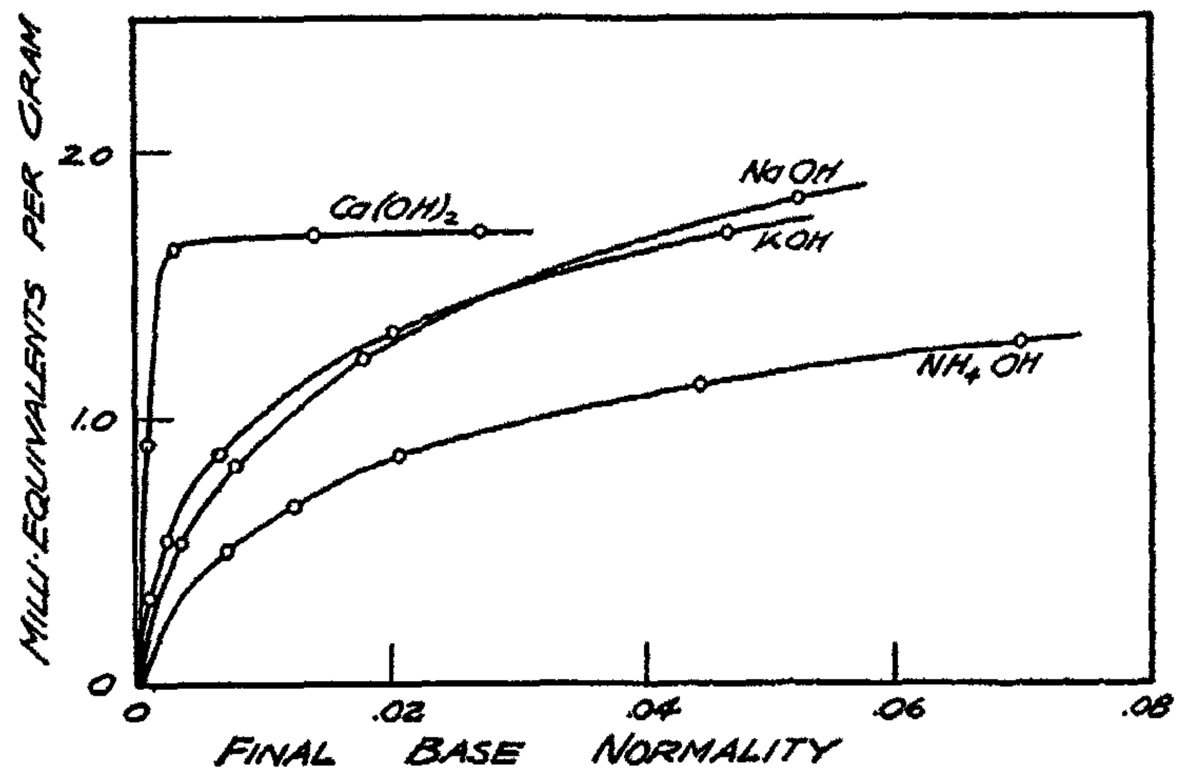

FIG. 3. ADSORPTION OF VARIOUS BASES

Experiments have been made in which the adsorption of ammonia at various concentrations was determined in the presence of varying amounts of ammonium chloride. The adsorption of ammonia (no chloride is removed from the solution) appeared to be entirely independent of the ammonium salt concentration in the solution, although, as might be expected, the solubility of the gel is markedly decreased in the presence of an excess of ammonium ions.

The adsorption of potassium hydroxide in the presence of potassium and ammonium salts

Potassium salts favor the adsorption of potassium hydroxide, as is shown by some figures given in table 3.

Ammonia and potassium chloride. On shaking an aqueous solution of potassium chloride with silica gel a slight hydrolytic adsorption of the base takes place, no chloride being removed from the solution. This result is in agreement with the findings of Bartell and Fu (2). In the presence of ammonium hydroxide a strong adsorption of potassium hydroxide is found, whereas the ammonia adsorption decreases markedly. Experiments have been carried out in various mixtures of ammonia and potassium chloride over periods of time up to twelve hours. Adsorption equilibrium was attained after four hours of shaking. The results of 4-hour experiments are given in table 4 and plotted in figure 4.

TABLE 3

Adsorption of potassium hydroxide in the presence of potassium chloride

(4 hours)

CONCENTRATION OF KOH		CONCENTRATION OF KCl	GEL DISSOLVED	KOH ADSORBED IN MILLIEQUIVALENTS PER GRAM (CORRECTED FOR SOLUBILITY)	
Original	Final			From analysis of solution	From extraction of gel
N	*N*	*N*	*per cent*		
0.005	0.0025	0	5.8	0.55	0.55
0.005	0.0010	0.1	4.4	0.85	0.85
0.005	0.00067	0.5	3.6	0.91	0.94
0.05	0.0466	0	55.7	1.78	1.65
0.05	0.0468	0.1	58.4	1.76	1.69
0.05	0.0464	0.5	61.8	2.12	2 03

It is evident that the potassium and ammonium ions compete for positions at the surface of the gel. If the concentration of the ammonium ions is increased, the adsorption of potassium hydroxide is strongly reduced. Comparison of the results given in tables 4 and 5 brings this fact out very clearly.

If, on the other hand, the concentration of the ammonium ions is strongly decreased by working with mixtures of potassium hydroxide and ammonia, the adsorption of the latter is reduced markedly. The adsorption of ammonia from a 0.05 *N* solution, for example, was 1.12 milliequivalents per gram; in the presence of 0.025 *N* potassium hydroxide it amounted to 0.35.

The adsorption of the potassium hydroxide increased from 1.32 milliequivalents in the absence of ammonia to 1.43 milliequivalents in the presence of 0.05 N ammonia.

DISCUSSION OF THE RESULTS

It is evident that in the adsorption of potassium and sodium hydroxides a primary adsorption of hydroxyl ions takes place, the latter ionize the surface of the gel, and a secondary adsorption of the alkali ions takes place. If the concentration of the alkali ions is increased by adding them in the form of a neutral salt to the alkaline solution, an increased adsorption of the base is noticed (see table 3), since less energy is required to withdraw the alkali ions from the solution. The adsorption curves as determined by Patrick and Barclay (6) and by Bartell and Fu (2) have no exact significance, since their data have not been corrected for the loss in solubility of the gel. It should be mentioned that this correction is smaller under their experimental conditions than in our work, however. In solutions of the bases more concentrated than about 0.03 N, the solubility is so pronounced that no adsorption equilibrium can be attained. The surface of the gel is changing constantly and new layers of the gel are exposed continuously to the solution. In addition, it should be realized that the dissolved silicate is hydrolyzed, resulting in a decrease of the hydroxyl ion concentration of the alkali hydroxide in the solution. From our results one may infer that the adsorptions of sodium and potassium hydroxides by silica gel are of the same order, but no more exact conclusions can be drawn.

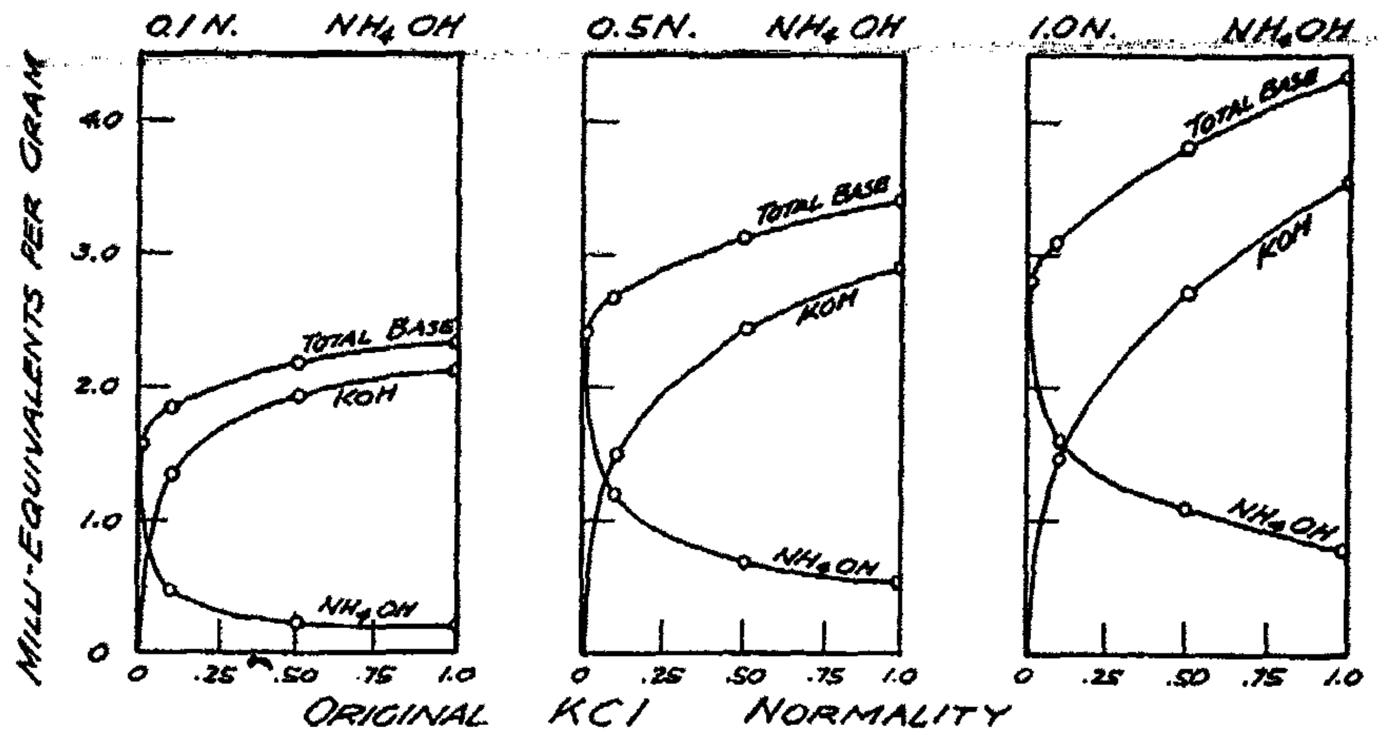

FIG. 4. ADSORPTION FROM AMMONIUM HYDROXIDE–POTASSIUM CHLORIDE MIXTURES

The speed of adsorption of ammonia is greater than that of the strong alkali hydroxides. This might be caused by a more rapid diffusion of the

TABLE 4

Adsorption from ammonia-potassium chloride mixtures

0.5 g. of gel; 100 cc. of solution; 4 hours of shaking

ORIGINAL CONCENTRATION OF NH_3	KCl CONCENTRATION	FINAL CONCENTRATION OF BASE	GEL DISSOLVED	BASE ADSORBED IN MILLIEQUIVALENTS PER GRAM (CORRECTED)				MOLAR RATIO NH_3:KOH ADSORBED
				Total base		NH_3	KOH	
				From solution	From extraction			
N	*N*	*N*	*per cent*					
0.099	0	0.0914	9.5	1.66	1.56	1.56	0	
0.099	0.1	0.0904	9.8	1.88	1.84	0.49	1.35	0.36
0.099	0.5	0.0893	11.2	2.16	2.18	0.24	1.94	0.12
0.099	1.0	0.0886	11.4	2.33	2.32	0.20	2.12	0.09
0.50	0		17.5		2.42	2.42		
0.50	0.1		21.3		2.67	1.19	1.48	0.80
0.50	0.5		26.3		3.12	0.67	2.45	0.27
0.50	1.0		27.9		3.42	0.51	2.91	0.17
1.0	0		23.2		2.80	2.80		
1.0	0.1		30.0		3.08	1.61	1.47	1.1
1.0	0.5		37.7		3.80	1.09	2.71	0.40
1.0	1.0		41.9		4.35	0.79	3.56	0.22

TABLE 5

Adsorption from ammonia-ammonium chloride-potassium chloride mixtures

0.5 g. of gel; 100 cc. of solution, 4 hours of shaking

ORIGINAL CONCENTRATION OF NH_3	CONCENTRATION OF NH_4Cl	CONCENTRATION OF KCl	GEL DISSOLVED	BASE ADSORBED IN MILLIEQUIVALENTS PER GRAM (CORRECTED FOR SOLUBILITY)			MOLAR RATIO NH_3:KOH ADSORBED
				Total base	NH_3	KOH	
N	*N*	*N*	*per cent*				
0.099	0.1	0	3.4	1.48	1.48		
0.099	0.1	0.1	4.0	1.61	1.10	0.51	2.15
0.099	0.1	0.5	4.4	1.77	0.64	1.13	0.57
0.099	0.5	0	2.3	1.48	1.48		
0.099	0.5	0.1	3.1	1.59	1.49	0.10	14.9
0.099	0.5	0.5	3.3	1.65	1.18	0.47	2.5
0.5	0.1	0	3.5	2.31	2.31		
0.5	0.1	0.1	7.9	2.42	1.88	0.54	3.5
0.5	0.5	0	2.9	2.35	2.35		
0.5	0.5	0.1	4.8	2.41	2.29	0.12	19.1
0.5	0.5	0.5	5.0	2.52	1.97	0.55	3.6
0.5	1.0	0	3.5	2.32	2.32		
0.5	1.0	0.5	3.9	2.50	2.28	0.22	10.4
1.0	0.5	0	4.7	2.80	2.80		
1.0	0.5	0.1	6.0	3.03	2.90	0.13	22.3
1.0	0.5	0.5	6.4	3.04	2.49	0.55	4.5
1.0	1.0	0	4.1	2.80	2.80		
1.0	1.0	0.5	4.9	2.98	2.74	0.24	11.4

ammonia into the interior of the gel. Some experiments were made in which the dried gels (containing 3 per cent of water) and those previously saturated with water vapor (containing 42 per cent of water) were used. After short periods of shaking, more ammonia was adsorbed by the dry gels, indicating that the ammonia diffuses more rapidly into the gel than water does. After two hours of shaking the same amounts of ammonia were adsorbed by both kinds of gel. Whereas addition of potassium chloride increases the adsorption of potassium hydroxide very markedly, no such effect was noticed upon adding an ammonium salt to the ammonia solution. The adsorption of the ammonia was found to be independent of the concentration of the ammonium salt. The adsorption is primarily a function of the hydroxyl ion concentration; by addition of an ammonium salt to the ammonia solution this concentration is strongly reduced. However, the product of $(OH^-)(NH_4^+)$ remains practically constant. From the fact that the ammonia adsorption is not affected by the concentration of ammonium salt in the solution, one might infer that the adsorption of the base is primarily a molecular and not an ionic one. However, the results of various experiments point in the direction that the ammonia is held in the ionized state. In the desorption experiments, for example, the ammonia was washed out in the form of ammonium silicate. The data presented in tables 4 and 5 show a primary adsorption of hydroxyl ions to take place, whereas the ammonium and potassium ions compete in the secondary adsorption. After this work had been concluded M. Berthon (3) published a note in which he mentioned that sodium hydroxide was adsorbed by silica gel from a mixture containing ammonia and sodium chloride. However, he did not consider the effect of the salt upon the adsorption of ammonia. It is seen from the figures in table 4 that the adsorption of the weak base is strongly reduced in the presence of potassium chloride. This does not necessarily mean that the potassium ions are more strongly adsorbed than the ammonium ions, because the latter are greatly outnumbered by the former. For example, in the experiment with 0.1 N ammonia and 0.1 N potassium chloride the ratio of NH_4^+ to K^+ is approximately 1:75. If the ammonium ion concentration is increased by addition of ammonium chloride (see table 5), about two to three times more ammonium than potassium hydroxide is adsorbed at the same ammonium and potassium ion concentration in the solution. This indicates that ammonium ions actually are more strongly held by the ionized silica surface than potassium ions.

It is interesting to notice that at a given ammonia concentration the ratio of ammonia to potassium hydroxide adsorbed is nearly a linear function of the ratio of ammonium to potassium ions in the solution (table 5), hence the total effect is mainly determined by the competition between the ammonium and potassium ions. However, table 5 also furnishes some evidence that part of the ammonia is adsorbed in the molecular form. The molar ratio of ammonia to potassium hydroxide adsorbed with the same ratio of ammonia to potassium ions in the solution increases slightly but regularly with increasing ammonia concentration in the solution. The changes, however, are small, indicating that the ratio in which the two bases are adsorbed at the same hydroxyl ion concentration is mainly determined by the ratio of the concentration of the ammonium and potassium ions in the solution. It is easily understood then that in mixtures of potassium and ammonium hydroxides the adsorption of the latter is so strongly reduced.

SUMMARY

1. It is impossible to determine the adsorption of strong alkali hydroxides by silica gel with any degree of exactness, owing to their dissolving effect upon the gel. Our results indicate that the adsorption of potassium hydroxide is of the same order as that of sodium hydroxide.

2. The adsorption of ammonia is primarily ionic. Owing to the fact that it is a weak base, its adsorbability is found to be less than that of sodium or potassium hydroxide at the same analytical concentration in the solution.

3. Potassium salts increase the adsorption of potassium hydroxide, whereas ammonium salts do not affect the adsorption of ammonia.

4. The amount of total base adsorbed from a mixture containing ammonium and potassium ions is primarily a function of the hydroxyl ion concentration of the solution. The ratio in which ammonium and potassium hydroxides are adsorbed is mainly determined by the ratio of ammonium to potassium ions in the solution.

5. The secondary adsorption of ammonium ions is stronger than that of potassium ions.

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THE SOLUBILITY OF PHENOLS IN PROTEINS

E. A. COOPER AND MARJORIE TREADGOLD

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Received July 7, 1933

The investigations so far carried out on this subject (1) have shown that the germicidal power of a disinfectant is not determined by the magnitude of the partition coefficient, which measures the ratio of its solubilities in a *protein sol* and water. Thus, *p*-chlorophenol is five times as efficacious in disinfecting power as phenol, and yet the partition coefficients

$$\frac{\text{solubility in protein sols}}{\text{solubility in water}}$$

are of much the same order of magnitude, e.g., 4 and 3, respectively.

In the case of proteins in the precipitated or coagulated state, however, it has been found that there is a general parallelism between the germicidal powers of the phenols and their partition coefficients between proteins and water. This result was unexpected, as the normal physiological state of proteins in the cell is not a coagulum, but a *sol* or *gel*. Furthermore, the partition coefficients are much higher with protein coagulae than with colloidal solutions, such as egg albumin sols, or gels, e.g., ordinary gelatin; in the case of phenol the partition coefficient is 3 with sols and gels, and 12 with albumin coagulated by heat or by phenol itself. Similar results were obtained with cresol and chlorophenols.

The experimental work described in the present paper has been carried out with the object of discovering an explanation of these unexpected physico-chemical observations.

I. DISTRIBUTION OF CHLORAL HYDRATE AND PICRIC ACID BETWEEN PROTEINS AND WATER

In the first place, we have endeavored to ascertain whether such abnormalities apply to disinfectants and physiologically active substances other than phenols and cresols, and their halogen derivatives. For this purpose chloral hydrate and the nitrophenols were selected.

a. Chloral hydrate and gelatin

Weighed amounts of gelatin (1 g.) were immersed in aqueous solutions of chloral hydrate varying from 5 to 20 per cent. The strengths of the solutions were estimated at the beginning of the experiment and then after standing at 15°C. for three days, by adding a known volume of N sodium hydroxide to a measured portion of the solution and titrating the excess of unused alkali with N sulfuric acid.

$$Cl_3C\cdot CH(OH)_2 + NaOH = CHCl_3 + HCOONa + H_2O$$

The results are given in table 1.

b. Chloral hydrate and egg albumin

Similar experiments were carried out with colloidal solutions of egg albumin. Ten cc. of water, in which 1 g. of the protein had been dissolved, were introduced into a series of viscose dialyzers, and these were then respectively immersed in solutions of chloral hydrate, varying from 0.5 to 10 per cent in strength (50 cc.). By this means it was possible to analyze the water phase in the complete absence of the protein phase after equilibrium had been attained (three days). The results are set out in table 2.

TABLE 1

Chloral hydrate and gelatin

1 g. of gelatin to 60 cc. of chloral hydrate solution

WATER PHASE		WEIGHT OF CHLORAL HYDRATE TAKEN UP BY 1 G. OF PROTEIN	DISTRIBUTION RATIO	CONDITION OF PROTEIN
Initial concentration per cc.	Final concentration per cc. *A*	*B*	*B/A*	
grams	*grams*	*grams*		
0.1920	0.1853	0.402	2.1	Precipitated
0.1440	0.1407	0.198	1.4	Unaffected
0.0960	0.0960	0	0	
0.0480	0.0480	0	0	

Parallel experiments were then set up with picric acid, the strengths of the aqueous solutions being estimated by titration with standard alkali (methyl red as indicator). Tables 3 and 4 give the results of these experiments.

The following conclusions may be drawn from these results. (1) In the case of chloral hydrate with gelatin there is a slightly increased value of the distribution ratio at precipitation, but with egg albumin no increase at all is apparent. (2) With picric acid, the distribution ratio also increases slightly when the precipitation of the gelatin first commences, but as the concentration of the picric acid rises, the ratio again falls rapidly in magnitude, although the protein remains permanently in the coagulated state.

The results are thus quite different from those observed in the case of phenol and cresol, and it may be concluded that the marked increase in the magnitude of the partition coefficient at precipitation observed with these substances is not general for all hydroxy compounds.

TABLE 2

Chloral hydrate and egg albumin

1 g. of albumin to 60 cc. of chloral hydrate solution

WATER PHASE		WEIGHT OF CHLORAL HYDRATE TAKEN UP BY 1 G. OF PROTEIN B	DISTRIBUTION RATIO B/A	CONDITION OF PROTEIN
Initial concentration per cc.	Final concentration per cc. A			
grams	*grams*	*grams*		
0.0834	0.0810	0.1380	1.7	Precipitated
0.0331	0.0314	0.1020	3.2	Unaffected
0.0081	0.0079	0.0120	1.5	Unaffected
0.0041	0.0039	0.0120	3.0	Unaffected

TABLE 3

Gelatin and picric acid

0.5 g. of gelatin to 40 cc. of picric acid solution

WATER PHASE		WEIGHT OF PICRIC ACID TAKEN UP BY 1 G. OF PROTEIN B	DISTRIBUTION RATIO B/A	CONDITION OF PROTEIN
Initial concentration per cc.	Final concentration per cc. A			
grams	*grams*	*grams*		
0.0112	0.0085	0.2154	25.3	Precipitated
0.0056	0.0033	0.1814	55.0	Precipitated
0.0028	0.0009	0.1527	158.5	Precipitated
0.0019	0.0005	0.1069	214.0	Precipitated
0.0011	0.0004	0.0534	133.5	Unaffected
0.0006	0.0004	0.0133	33.2	Unaffected

TABLE 4

Gelatin and edestin with phenol

CONDITION OF PROTEIN	WATER PHASE		AMOUNT OF PHENOL DISSOLVED BY 1 G. OF PROTEIN B	PARTITION COEFFICIENT B/A
	Initial concentration of phenol per cc.	Final concentration of phenol per cc. A		
(a) Gelatin. 1 g. of gelatin to 40 cc. of phenol solution				
	grams	*grams*	*grams*	
Precipitated by dialyzed iron..........	0.0023	0.0020	0.0124	6.2
"Sol"................................	0.0023	0.0021	0.0090	4.3
(b) Edestin. 1 g. of edestin to 40 cc. of phenol solution				
"Sol"................................	0.0032	0.0031	0.0040	1.3
Insoluble edestin chloride..............	0.0032	0.0031	0.0040	1.3

II. SOLVENT POWER OF COAGULATED PROTEINS FOR PHENOL

Experimental work has also been carried out with the object of ascertaining whether the increased solvent power for phenol, which is observed when proteins are coagulated by heat, or by the action of phenol itself, also takes place when precipitation of the protein is effected by other means.

In the first place, a comparison has been instituted between the solvent powers for phenol of a gelatin sol and gelatin precipitated by the addition of a colloid of opposite electric charge, e.g., dialyzed iron. And, in the second place a similar comparison has been made in the case of edestin dissolved in salt solution and the insoluble edestin chloride formed by adding a drop of hydrochloric acid to edestin solution.

a. Gelatin sols

Gelatin (1 g.) was introduced into viscose dialyzers, containing 15 cc. of ~~a dilute phenol solution and immersed in 25 cc. of the same phenol solution.~~ The experiment was carried out at 37°C., so that the gelatin dissolved and formed a "sol." Into one of the dialyzers sufficient dialyzed iron was added to precipitate the "sol," and after three days for equilibrium to be attained the phenol concentration in the protein-free water phase (outside the dialyzers) was estimated by Lloyd's method (3), which depends on the formation of tribromophenol from the interaction of bromine and phenol.

In the experiment with edestin 10 cc. of a 5 per cent salt solution in which 1 g. of the protein had been dissolved was introduced into dialyzers, which stood in 30 cc. of a phenol solution of known strength. To one of the dialyzers one drop of concentrated hydrochloric acid was added. After three days the phenol in the water phase was estimated as before.

The results of these experiments are shown in table 4. The observations show that in the case of gelatin the partition coefficient is slightly raised by precipitation with dialyzed iron, but the increase is small compared with that caused by precipitation of the gelatin by phenol itself (Cooper, 1912). In this case the partition coefficient rises as high as 30.

The results obtained in the edestin experiment indicate that the solvent power of an edestin "sol" for phenol is not increased at all by conversion into the precipitated chloride.

The increased solvent power is thus only manifested under certain experimental conditions, and is restricted to the particular cases of coagulation by heat and the action of phenols, i.e., it is associated strictly with the specific change induced in proteins by the process of "denaturation."

III. THE SIGNIFICANCE OF THE WATER FACTOR

Early in these researches (Cooper, 1923) it was realized that in a colloidal solution of a protein a portion of the water present is probably associated or imbibed with the protein phase, and this question was considered in relation to the problems under investigation. Possibly the imbibed water might possess less marked solvent properties than normal water. Hence when the protein was dehydrated by coagulation, the associated water thrown out would dilute the water phase, and as a result the increased solvent power for phenol observed when a protein is coagulated might be merely apparent, and the calculations fictitious. Experiments carried out at the time, however, suggested that this was not the case, and the results supported the view that the calculated partition coefficients were real. Since then considerable progress has been made in the field of colloidal chemistry, and in view of the new data now available further experimental work has been carried out.

a. Experiments with red cells

According to Krevisky (2) the amount of free water in the red cell is equal to one-third of the cell volume, whilst an equal proportion of water is *bound* water, i.e., associated with the protein and hence forming part of the disperse phase.

By carrying out distribution experiments with red cells and phenol on the lines of those already described in this paper, it has therefore been possible to calculate the partition coefficients by two different methods: (1) assuming that the water imbibed in the protein phase is *normal* water and thus for purposes of calculation may be regarded as part of the water phase; (2) assuming that the association with the proteins renders the bound water abnormal in solvent properties and such that it must be regarded as an intimate constituent of the protein phase and not to be calculated as an integral part of the water phase.

Red cells were obtained by centrifuging ox and pig blood. Fifteen cubic centimeters were introduced into a series of viscose dialyzers, which were immersed in varying concentrations of phenol (25 cc.), and after three days for equilibrium the phenol solutions outside the dialyzers were again analyzed. The percentage of protein in red cells is 30 per cent.

The results have been calculated by the two different methods already mentioned, the respective data being as follows: (1) Protein 4.5 g. (30 per cent of red cells); water phase 25 cc. + 10 cc. (two-thirds of red cells) = 35 cc. (2) Protein 4.5 g.; water phase 25 cc. + 5 cc. (one-third of red cells) = 30 cc. (See tables 5A and 5B, respectively.)

b. Experiments with egg white

St. John (4) has shown that the amount of water bound with the proteins of egg white is equal to 20 per cent of the total water content.

Similar experiments to those carried out with red cells have therefore been made with egg white and phenol, and the partition coefficients have been calculated as before in two ways, (1) assuming the whole water content

TABLE 5A

Experiments with red cells

WATER PHASE		AMOUNT OF PHENOL DISSOLVED BY 1 G. OF PROTEINS *B*	DISTRIBUTION RATIO *B/A*
Initial phenol concentration per cc.	Final phenol concentration per cc. *A*		
	Ox		
grams	*grams*	*grams*	
0.0043	0.0031	0.0093	3
0.0064	0.0040	0.0187	4.7
0.0071	0.0044	0.0209	4.7
0.0107	0.0074	0.0256	3.4
0.0150	0.0097	0.0412	4.2
0.0164	0.0103	0.0475	4.6
0.0236	0.0159	0.0599	3.6
0.0257	0.0162	0.0739	4.6
	Pig		
0.0088	0.0055	0.0256	4.6
0.0267	0.0178	0.0692	3.8
0.0381	0.0198	0.1423	7.2

TABLE 5B

Experiments with red cells

WATER PHASE		AMOUNT OF PHENOL DISSOLVED BY 1 G. OF PROTEINS *B*	DISTRIBUTION RATIO *B/A*
Initial phenol concentration per cc.	Final phenol concentration per cc. *A*		
	Ox		
grams	*grams*	*grams*	
0.0050	0.0031	0.0126	4.1
0.0075	0.0040	0.0233	5.8
0.0083	0.0044	0.0260	5.9
0.0125	0.0074	0.0340	4.6
0.0175	0.0097	0.0520	5.4
0.0192	0.0103	0.0593	5.7
0.0275	0.0159	0.0773	4.8
0.0300	0.0162	0.0920	5.7
	Pig		
0.0103	0.0055	0.0320	5.8
0.0312	0.0178	0.0893	5.0
0.0445	0.0198	0.1646	8.3

of egg white is normal water and thus counted as water phase, and (2) assuming the bound water to be abnormal and thus regarded as part of the protein phase. Calculated in the ordinary way, the partition coefficients

$$\frac{\text{amount of phenol dissolved in protein sol}}{\text{amount of phenol dissolved in water}}$$

were on the average 3.7. Calculated in the alternative way by regarding the proportion of bound water as a constituent of the disperse phase, the mean coefficient was 5.0. In the case of the coagulated protein, the partition coefficient was, however, 12.

From the experimental results with red cells and egg white it is seen that the particular method of calculation makes very little difference in the actual value of the distribution ratios. By introducing the correction for the amount of imbibed water, the distribution ratios only increase by about one-third. Yet the partition coefficient in the case of a coagulated protein is approximately four times as great as that for the protein in a state of colloidal solution. The increased solvent power for phenol noticed when a protein is coagulated is thus a reality, and is not due to fictitious calculations arising out of movements of water from one phase to the other.

A comparison was next made of the uptake of phenol by the moist and dry clot of egg white. Water is imbibed to a certain degree in a moist clot obtained by boiling a solution of egg white, but not by the clot after it has been dried at 100°C.

Thirty-five cubic centimeters of phenol solution were mixed with 10 cc. of half-strength eggwhite (i.e., egg white diluted with an equal volume of water and containing 6.0 per cent protein) for the moist clot experiment, the egg white then being coagulated in situ in the bottle by heat. For the dry clot experiment, 35 cc. of solution was used with 10 cc. of water and the *dried* and powdered clot from 10 cc. of diluted egg white was then added.

This experiment thus afforded a further simple method of studying the significance of the water factor.

WATER PHASE		AMOUNT OF PHENOL IN 1 G. OF PROTEIN B	B/A
Initial concentration per cc.	Final concentration per cc. A		
grams	*grams*	*grams*	
0.01027	0.00729	0.2233	30.6 Moist clot
0.01027	0.00699	0.2460	35.2 Dry clot

The dry clot of egg white absorbs slightly more phenol than the moist clot from solutions of the same strength. Thus, in the case of phenol, it makes very little difference whether the water in the system is entirely in one phase or whether it is present in the protein phase as well. The manner of distribution of the water hence does not affect the value of the partition coefficients to any appreciable extent, and the results are confirmatory of those already described in this section.

Although the rise in the value of the partition coefficient at coagulation is not due to errors in calculation introduced by transfer of water from one phase to another, yet this water factor may be of real significance in another way. The solubility of phenol in proteins will probably be diminished by the presence of bound or imbibed water, and the normal solvent power of proteins for phenol will hence not be manifested until the phenol replaces the associated water, which it will drive out through its dehydrating action, thus causing coagulation. According to this view the partition coefficients obtained with *coagulae* measure the *true* solubility of phenols in proteins, and an explanation is offered for the abnormally low coefficients observed with colloidal solutions.

The interpretation of the observations that the germicidal powers of phenol, cresol, and chlorophenols run parallel with their partition coefficients with *protein coagulae,* whilst the coefficients with protein sols are all of the same order of magnitude (about 3) is however not so clear. If the solubility of phenols in coagulae is regarded as their normal solubility in proteins, then germicidal power in the case of phenols is proportional to the *true* partition coefficients, and the formation of a *solution* of the disinfectant in the bacterial proteins may be considered the first stage in the process of disinfection. No explanation is then given, however, of the absence of proportionality between germicidal power and the partition coefficients measured with proteins in the natural state, in which they occur in the cell (sols and gels). At the present time it can only be suggested that the *bound* water diminishes the solubility of cresol and chlorophenol in proteins to a *greater* extent than it does that of phenol itself, thus tending to maintain the partition coefficients at approximately the same value in all cases. When, however, the protein becomes coagulated through the dehydrating effect of the phenols, the associated water is expelled and transferred to the continuous phase, and the *true* partition coefficient specific and characteristic of each individual phenol reveals itself. The first phase in the process of disinfection by phenols is thus the formation of a solution in the bacterial proteins followed by coagulation, and cresol and chlorophenol are superior to ordinary phenol in germicidal power, because they induce coagulation, i.e., expulsion of *bound* water, at a lower concentration (Cooper, 1913, 1923).

SUMMARY

1. Coagulated proteins possess a much higher solvent power for phenols than proteins in a natural condition, e.g., sols and gels. This is true also

of picric acid, but to a lesser degree. Chloral hydrate, however, is exceptional, the uptake of which by proteins is not materially affected by the physical state of the protein.

2. Proteins precipitated from colloidal solution by the addition of a colloid of opposite electric charge or by formation of an insoluble salt do not exhibit this increased solvent power for phenol.

3. By means of experiments with red cells and egg white, in which due allowance has been made for the proportion of water bound to the protein phase, it has been found that the increased partition coefficients observed at coagulation are realities, and not due to calculation errors introduced by movement of water from one phase to another. The imbibed water may however diminish the solubility of phenol in proteins, thus accounting in the case of sols and gels for the low partition coefficients, which rise to the normal figure when the water is expelled at coagulation.

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THE RATE OF SOLUTION OF MAGNESIUM IN ACIDS[1]

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In a preliminary paper (16) the authors have treated the problem of the rate of solution of magnesium in acids from the point of view of the extended theory of acids and bases (5, 18). The present paper is a continuation of that study with an attempt to consider the problem from the point of view of the diffusion rate theory as well as from that of the Brönsted-Kilpatrick theory. It will be demonstrated that in either case it is necessary to consider the extended theory of acids as an important factor.

Consider first the reactions which take place when magnesium reacts with a strong acid such as hydrogen chloride. When hydrogen chloride dissolves in water, we have

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$

and the reaction goes practically to completion to the right. The reaction can, therefore, involve the water, the hydrogen ion (H_3O^+), or the chloride ion. The metal itself is composed of magnesium ions (Mg^{++}) and free electrons (10).

Equation 1 gives one possible primary reaction.

$$H_3O^+ + e \rightarrow H_2O + H \tag{1}$$

This might be followed by the reactions

$$\underset{\text{(solid)}}{Mg^{++}} \rightleftarrows \underset{\text{(dissolved)}}{Mg^{++}} \tag{1a}$$

$$2H \rightarrow H_2 \tag{1b}$$

the hydrogen escaping in the gaseous state. It is also possible for the primary reaction (3) to be

$$\underset{\text{(solid)}}{Mg^{++}} + Cl^- \rightarrow MgCl^+ \text{ or } MgCl_2 \tag{2}$$

which would be followed by reactions 1 and 1b.

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[1] Abstracted from the thesis of John Henry Rushton presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, April, 1933.

Centnerszwer (8) considers the reaction to be between the metal and the molecular acid, but his computations are based upon the application of the classical law of mass action to solutions of strong electrolytes and cannot be accepted (14).

If equation 1 is accepted as more probable, then in accordance with the extended theory of acids, any proton carrier should react with the metal, and for weak acids there should be a reaction with the molecules, as well as with the hydrogen ions. For example, in the case of acetic acid,

$$CH_3COOH + H_2O \rightleftarrows H_3O^+ + CH_3COO^-$$

and since this reaction does not go to completion to the right, in addition to the water reaction, two reactions are possible

$$H_3O^+ + e \rightarrow H_2O + H \qquad (1)$$

$$CH_3COOH + e \rightarrow CH_3COO^- + H \qquad (3)$$

In fact, in accordance with the formal definition of an acid,

$$\begin{matrix} \text{Acid} \leftrightarrows \text{Base} + \text{Proton} \\ A \rightleftarrows B + H^+ \end{matrix} \qquad (4)$$

Where A represents an acid and B its conjugate base, we have the general double acid-base reaction (6),

$$\underset{\text{Acid 1}}{A} + \underset{\text{Base 2}}{e} \longrightarrow \underset{\text{Base 1}}{B} + \underset{\text{Acid 2}}{A} \qquad (5)$$

where A can be H_3O^+, CH_3COOH, $CH_2ClCOOH$, $C_5H_5NH^+$, H_2O, etc. The water reaction is readily detectable at higher temperature as will be shown later.

The question of which is the rate-controlling process has been discussed recently by Hammett (11) in connection with the work of Brönsted and Kane on sodium amalgams. Hammett concludes that if it could be proved that diffusion was not a factor in the determination of the reaction velocity in the experiments of Brönsted and Kane and of Kilpatrick and Rushton, these experiments would be strong evidence for reaction 1 as the rate-determining step. King and Braverman (17) conclude that while the "old diffusion theory" is not satisfactory without modification, certain results are definitely contradictory to the Brönsted-Kilpatrick theory. King and Braverman are vague as to the modification. In explanation of the dissolution of metals, Palmaer (20) accepts the theory of local elements of de la Rive (9), and definitely rejects the diffusion theory. The theory of local elements seems to be well founded for impure metals, but does not apply to pure magnesium.

In the first experimental section the dissolving of magnesium in strong acids will be described. The temperature coefficient of the reaction, the relation of the rate to the concentration and volume of the solution and to the surface of the metal, the effect of stirring, and the effect of viscosity will be discussed.

EXPERIMENTAL PART

Four separate methods were used to follow the reaction. The amount reacted was determined at definite intervals of time by first, weighing the metal, second, measuring the volume of hydrogen evolved, third, titrating the solution, or fourth, measuring the amount of acid required to maintain a definite hydrogen-ion concentration as shown by an indicator. The last method was used in the study of the water reaction.

The apparatus used differed for the several methods mentioned above for following the reaction. The majority of the experiments were followed by measurement of the volume of hydrogen evolved. Samples of gas given off in reactions with hydrochloric, acetic, chloroacetic, and formic acids were analyzed for gases other than hydrogen. Hydrogen was found to be the only gas evolved. Two types of apparatus were employed, one for experiments at 0° and 25°C., and another for experiments at higher temperatures. Figure 1 illustrates the apparatus used in the 25°C. thermostat. Figure 2 shows the apparatus used for work at temperatures higher than 25°C.

The reaction chamber of these two pieces of apparatus differed both in size and shape. The 25°C. reaction flask was either a 300-cc. Florence flask or a special cylindrical flask as shown in the diagram. This special flask was used so that the level of the solution could be adjusted to various sizes of metal bars. The reaction vessel in the vapor thermostat was cylindrical and of very much smaller capacity. Several runs were made in the vapor thermostat by passing water at 25°C. through the vapor chamber of the thermostat. In this way parallel experiments were made in the two distinctly different reaction vessels and the results checked with each other. In each of the two pieces of apparatus the gas given off during the reaction was led to a water-jacketed gas buret, where the volume could be read at atmospheric pressure.

In the vapor thermostat the metal bar was first placed in the reaction vessel and allowed to come to temperature while a solution was placed in the delivery tube. Upon reaching thermal equilibrium, stopcock A was set so that when stopcocks B and C were opened the solution drained into the reaction vessel and the total volume of the system remained unchanged. Stopcock A was then turned so that the gas was delivered to the buret. As soon as the pressure in the gas buret could be made equal to atmospheric pressure, stopcock C was closed. By this method no gas was lost at any part of the reaction. Various liquids were used for work at the different temperatures.

Any part of the cylindrical bar of magnesium above the solution, or where reaction was not desired, was covered with collodion. No special methods were used to make the metallic surface active. It was found unnecessary to do this in the case of magnesium. The surface of the metal exposed varied from 7 to 35 cm.^{2} The metal cylinder was held in

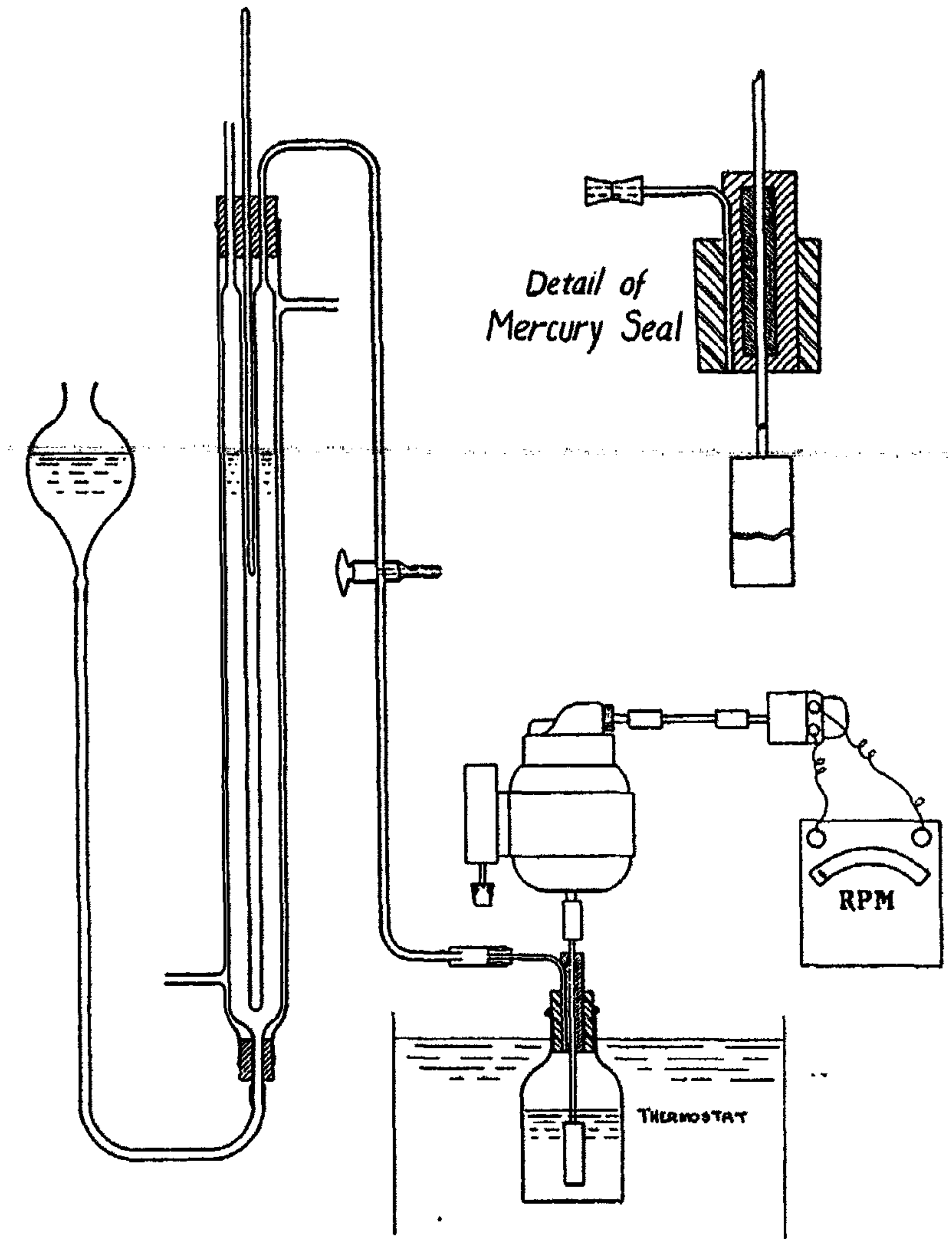

FIG. 1. APPARATUS FOR EXPERIMENTS AT 25°C. AND AT 0°C.

solution by a small steel rod threaded into one end of the bar. The steel rod was passed through a steel cap containing mercury, forming a seal (see detail in figure 1) (13). The end of the steel rod was attached directly to an electric motor whose speed could be controlled by a small resistance.

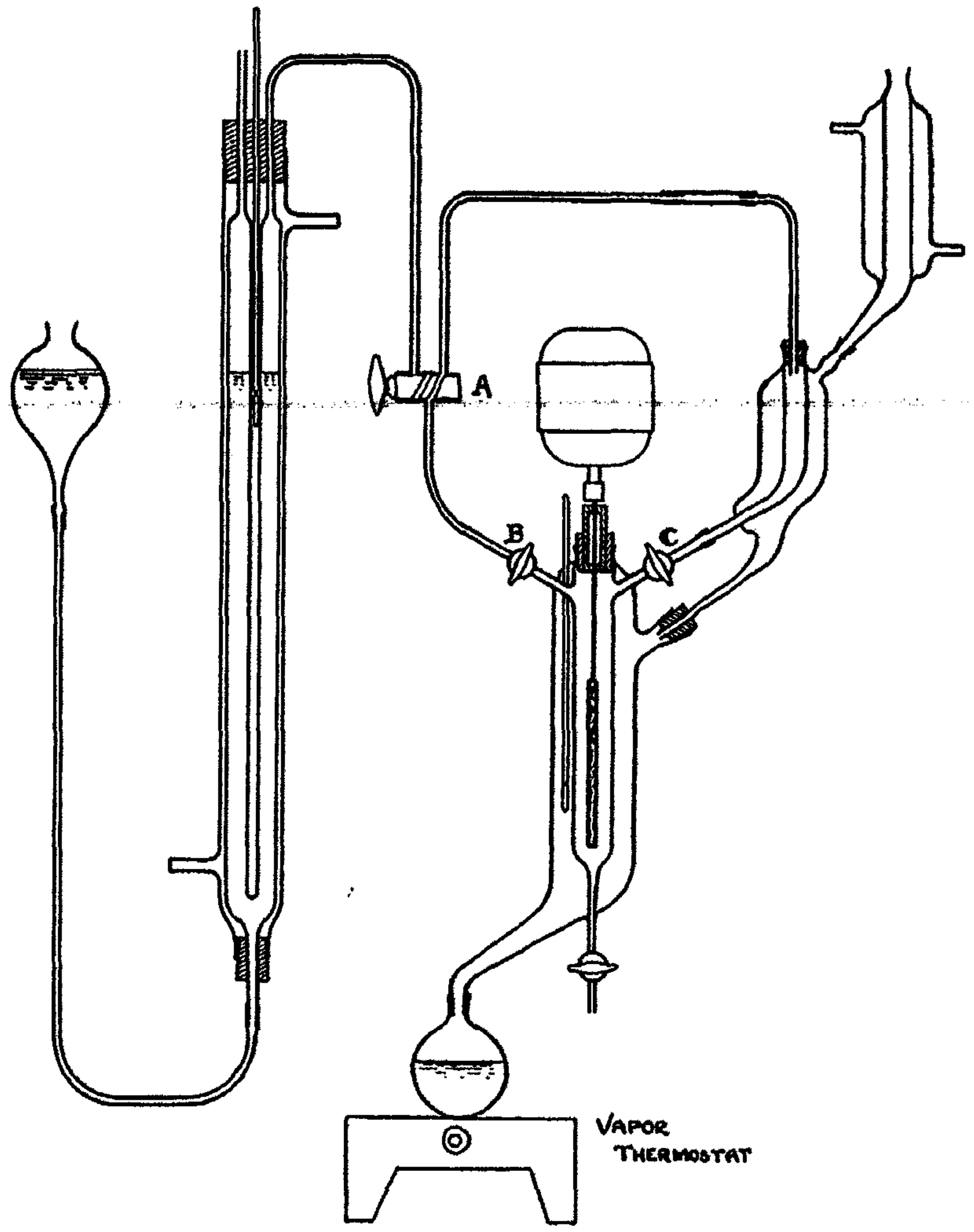

FIG. 2. APPARATUS FOR EXPERIMENTS AT ELEVATED TEMPERATURES

The opposite end of the motor shaft was connected to an electric tachometer with a scale reading directly in revolutions per minute.

To measure the rate of reaction by weight determinations, a set of stirrers was built. Six shafts were run simultaneously from a main shaft driven by an electric motor whose speed was controlled by a rheostat. Bars of metal were threaded onto the Bakelite shafts coupled to the main shaft. Six experiments were run simultaneously, the bars washed, dried, and weighed. Other weight determinations were made using the apparatus shown in figure 1.

TABLE 1

Data for two hydrochloric acid experiments

TIME	NUMBER 5*			NUMBER 22†		
	Hydrogen evolved H_t	$H_0 - H_t$	$\text{Log} \frac{H_0}{H_0 - H_t}$	Hydrogen evolved H_t	$H_0 - H_t$	$\text{Log} \frac{H_0}{H_0 - H_t}$
minutes	*cc.*			*cc.*		
1	6.0	132.2	0.0200	4.35	63.65	0.0285
2	11.4	126.8	0.0380	8.50	59.50	0.0570
3	16.8	121.4	0.0565	12.20	55.80	0.0855
4	22.0	116.2	0.0755	15.75	52.25	0.1140
5	26.6	111.6	0.9038	19.05	48.95	0.1425
6	31.5	106.7	0.1130	22.05	45.95	0.1710
7	36.0	102.2	0.1313	25.10	42.90	0.1995
8	40.3	97.9	0.1500	27.80	40.20	0.2280
9	44.4	93.8	0.1532	30.35	37.65	0.2565
10	48.4	89.8	0.1875	32 75	35.25	0.2850
11	52.2	86.0	0.2062	35.00	33.00	0.3135
12	55.8	82.4	0.2250	37.10	30 90	0.3320
13	59.2	79.0	0.2435	39.05	28.95	0.3705
14	62.6	75.6	0.2622	40.90	27.1	0.3990
15	65.7	72.5	0.2808	42.60	25.4	0.4275
16	68.8	69.4	0.2995	44.25	23.75	0.4570
17	71.7	66.5	0.3180	45.75	22.25	0.4850
18	74.5	63.7	0.3370	47.175	20.825	0.5125
19	77.2	61.0	0.3558	48.48	19.52	0.542
20	79.8	58.4	0.3743	49.70	18.3	0.570

* Experiment No. 5. Temperature = 25°C.; initial concentration of acid = 0.050 M; volume of acid = 225 cc.; H_0 = 138.2 cc.; surface speed = 2150 cm. per minute; metal area = 7.01 cm.^{2}; 57.8 per cent of reaction followed; no sodium chloride present; k at 2000 cm. per minute = 1.36.

† Experiment No. 22. Temperature = 25°C.; initial concentration of acid = 0.025 M; volume of acid = 225 cc.; H_0 = 68.0 cc.; surface speed = 2670 cm. per minute; metal area = 10.39 cm.^{2}; 65.3 per cent of reaction followed; 0.025 M sodium chloride present; k at 2000 cm. per minute = 1.34.

Experiments in the various reaction vessels showed that the rate of reaction as measured by the volume of hydrogen evolved, by the weight of metal dissolved, and by the decrease in acid concentration were in agreement. The shape of the reaction vessel and the length and diameter of the metal cylinder had no effect. The magnesium[2] itself was for most experiments

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[2] For this magnesium, the authors wish to thank The Aluminum Company of America.

of very high purity. The analysis showed no copper, zinc, lead, or free iron, 0.18 per cent of magnesium oxide, 0.02 per cent of silicon, and 0.02 per cent of iron and aluminum. A few experiments made with ordinary C.P. magnesium sticks gave no appreciable difference in rate.

METHODS OF EXPRESSING RESULTS

The kinetic equation, based on the hypothesis that the rate depends on the collisions of the acid with the metal and is consequently proportional to the acid concentration and to the surface of the metal, yields for the velocity constant of the reaction

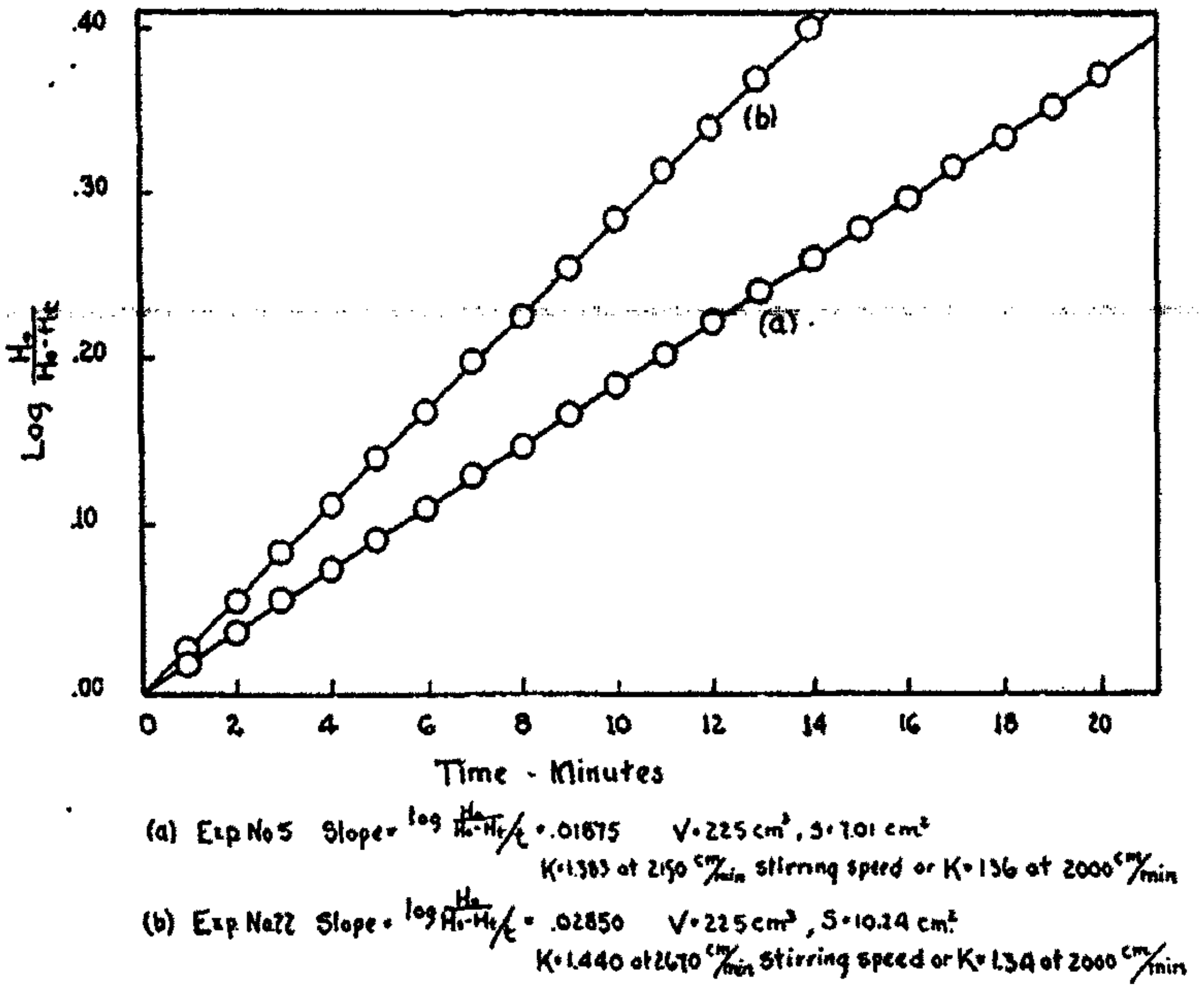


FIG. 3. RELATION BETWEEN $\log \frac{H_0}{H_0 - H_t}$ AND TIME FOR HYDROCHLORIC ACID EXPERIMENTS NOS. 5 AND 22

$$k = \frac{2.3V}{St} \log \frac{C_0}{C_t} \tag{6}$$

where V is the volume of the solution, S the surface, t the time, C_0 the initial acid concentration, and C_t the concentration at time t.

The same expression can be derived by assuming that the rate is controlled by a process of diffusion, and employing Fick's law. Consequently the fact that equation 6 fits the data does not distinguish between a chemical process and a process controlled by diffusion. Throughout the paper

V is expressed in cm.^{3}, S in cm.^{2}, and t in minutes, so that k has the dimension cm. × min.$^{-1}$.

Table 1 gives the necessary data for two typical experiments with hydrochloric acid. Figure 3, in which $\log \frac{H_0}{H_0 - H_t}$ is plotted as ordinate and time as abscissa, shows that the reaction follows the pseudo monomolecular law. The slope of the line is $\frac{k_1}{2.3}$, where

TABLE 2

Experiments at 25°C.

Stirring speed = 2000 cm. per minute. Volume of solution = 225 cc.

EXPERIMENT NO.	AREA OF METAL SURFACE S	k_1
5	7.01	0.04235
4	7.38	0.0403
23	10.38	0.0604
22	10.39	0.0618
3	7.71	0.0456
18	13.64	0.0807
17	13.65	0.0813
13	13.81	0.0786
14	13.78	0.0815
20	10.42	0.0635
19	10.43	0.0635
59	25.38	0.1530
25	32.42	0.1917
26	32.35	0.1925
24	32.40	0.193

TABLE 3

Experiments at 25°C.

Stirring speed = 2000 cm. per minute. Unit surface area

NUMBER OF DUPLICATE EXPERIMENTS	VOLUME OF ACID V	$\frac{1}{V}$	AVERAGE VALUE OF k_1	DEVIATION OF k_1
	cc.			per cent
5	37.5	0.02665	0.03575	4.2
3	180.0	0.05550	0.00745	1.9
5	215.0	0.00465	0.00624	0.5
5	225.0	0.00445	0.00595	2.1

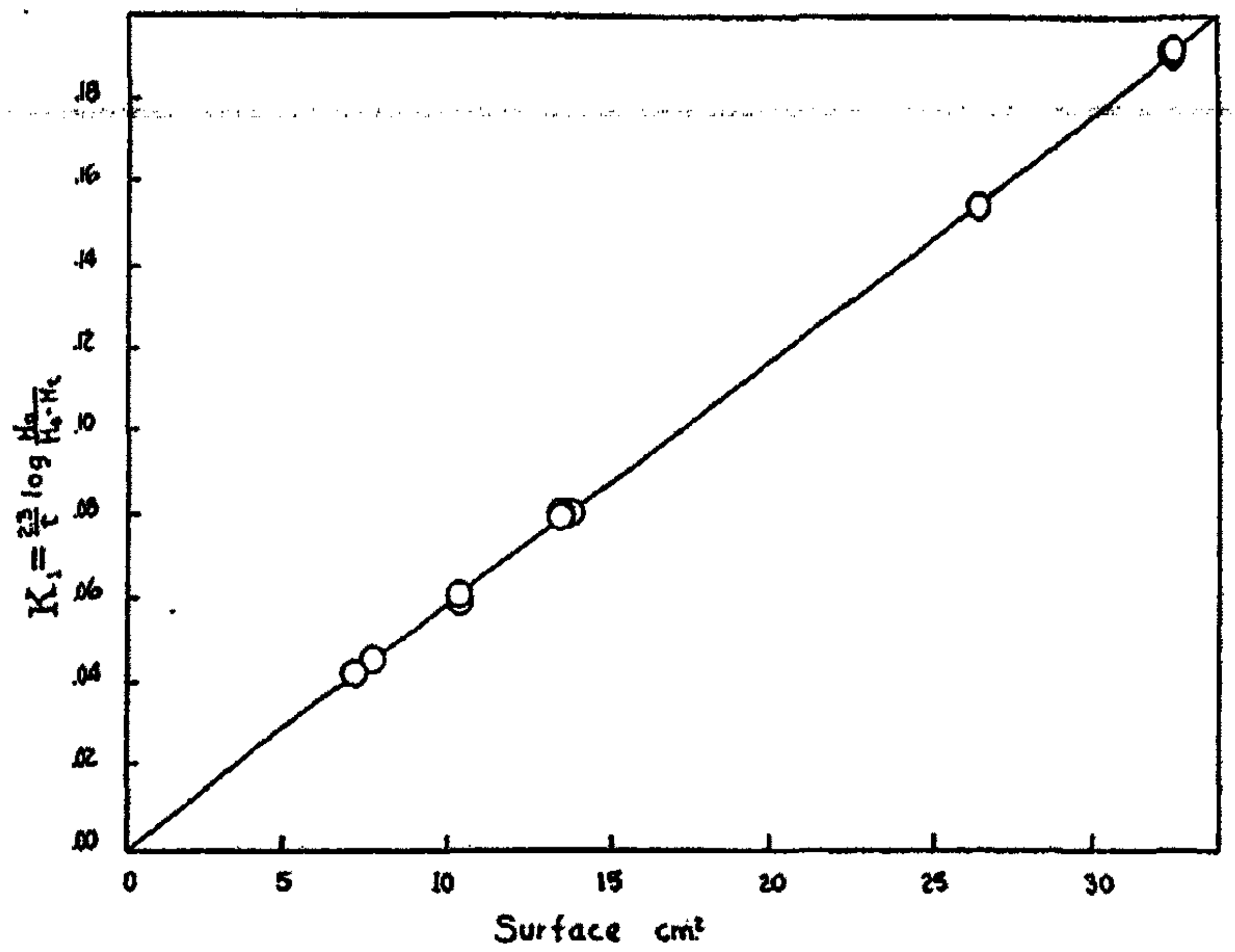
$$k_1 = \frac{2.3}{t}\log\frac{H_0}{H_0 - H_t} \qquad (7)$$

k_1 may be calculated for a series of solutions, using different volumes of solution and different areas of surface.

EFFECT OF SURFACE

Table 2 gives the k_1 values for a number of experiments in which the same volume of solution was used and the area of the surface of the metal was varied. The values of k_1 are shown in relation to the surface in figure 4. Over a wide range of surface k_1 is inversely proportional to the surface. A constant k_2 may now be defined

$$k_2 = \frac{k_1}{S} \quad \text{or} \quad k_2 = \frac{2.3}{St} \log \frac{H_0}{H_0 - H_t} \tag{8}$$



Volume Constant 225 cm³; Temperature 25°C.

FIG. 4. RELATION BETWEEN k_1 AND SURFACE

The values of k_2 are given for varying volumes of solution in table 3 and show that

$$k = k_2 V \quad \text{or} \quad k = \frac{2.3V}{St} \log \frac{H_0}{H_0 - H_t} \tag{6}$$

These relations have been determined for solutions having the same constant stirring. Table 4 gives the data used to relate k to the stirring of the solution. It was found that different amounts of stirring resulted with cylinders of metal of different diameters, and in order to measure stirring

TABLE 4

Hydrochloric acid experiments at 25°C.

EXPERIMENT NO.	SPEED OF METAL BAR	SURFACE STIRRING SPEED	k AT EXPERIMENT SPEED	k AT 2000 CM. PER MINUTE STIRRING SPEED	PER CENT OF REACTION FOLLOWED	INITIAL CONCENTRATION OF ACID
	r.p.m.	*cm. per min.*				*moles per liter*
33	0	0	0.235		10.7	0.050
34	0	0	0.232		27.0	0.050
35	0	0	0.231		30.8	0.050
36	0	0	0.225		41.2	0.050
37	0	0	0.229		56.0	0.050
7	600	1550	1.418	1.51	62.4	0.050
6	600	1590	1.504	1.61	59.8	0.025
8	800	2000	1.46	1.46	62.3	0.051
5	800	2150	1.38	1.36	57.8	0.050
4	800	2170	1.245	1.23	41.1	0.075
9	900	2200	1.495	1.46	62.3	0.050
23	800	2650	1.403	1.31	12.0	0.1235
22	800	2670	1.442	1.34	65.3	0.025
21	800	2700	1.31	1.20	12.5	0.075
3	1000	2730	1.44	1.33	39.0	0.1235
1	1000	2940	0.932	0.83	82.5	0.012
2	1000	2940	0.932	0.83	82.5	0.012
18	800	3060	1.485	1.33	66.5	0.050
17	800	3080	1.502	1.34	66.7	0.050
10	850	3090	1.268	1.08	61.2	0.050
13	1200	4700	1.695	1.28	61.8	0.050
14	1200	4500	1.690	1.33	64.4	0.050
38	2210	5570	1.30	0.97	99.2	0.010
59	2250	5840	1.68	1.22	99.5	0.050
53	2550	6240	1.87	1.34	100.	0.050
51	2550	6270	1.87	1.35	100.	0.050
52	2550	6240	1.70	1.22	99.3	0.025
50	2550	6270	1.78	1.28	98.0	0.025
49	2550	6300	1.78	1.34	98.0	0.025
48	2550	6300	1.94	1.38	98.5	0.050
47	2550	6300	1.99	1.42	98.7	0.050
46	2550	6320	1.78	1.28	100.	0.050
45	2550	6320	2.00	1.41	98.7	0.050
11	1850	7330	1.99	1.37	11.6	0.050
16	1850	7350	1.98	1.37	11.4	0.050
20	2800	9520	2.15	1.37	9.5	0.050
25	2000	9550	2.080	1.33	100.	0.050
19	2800	9580	2.162	1.37	1.0	0.050
26	2000	9670	2.125	1.34	100.	0.050
24	2000	9740	2.100	1.34	100.	0.050
15	3100	11800	2.472	1.47	1.5	0.050
12	3100	12200	2.460	1.46	1.5	0.050
				Av. = 1.33		

the surface velocity R was employed by multiplying the circumference of the cylinder by the revolutions per minute.

When the logarithm of the surface speed was plotted against the corresponding logarithm of k, it was found that the following relation held over a wide range of surface speeds,

$$k = aR^n \tag{9}$$

where a and n are constants, n being the slope of the line in figure 5 and a the value of k when $R = 1$. The values of a and n for magnesium and hydrochloric acid are 0.139 and 0.362, respectively.

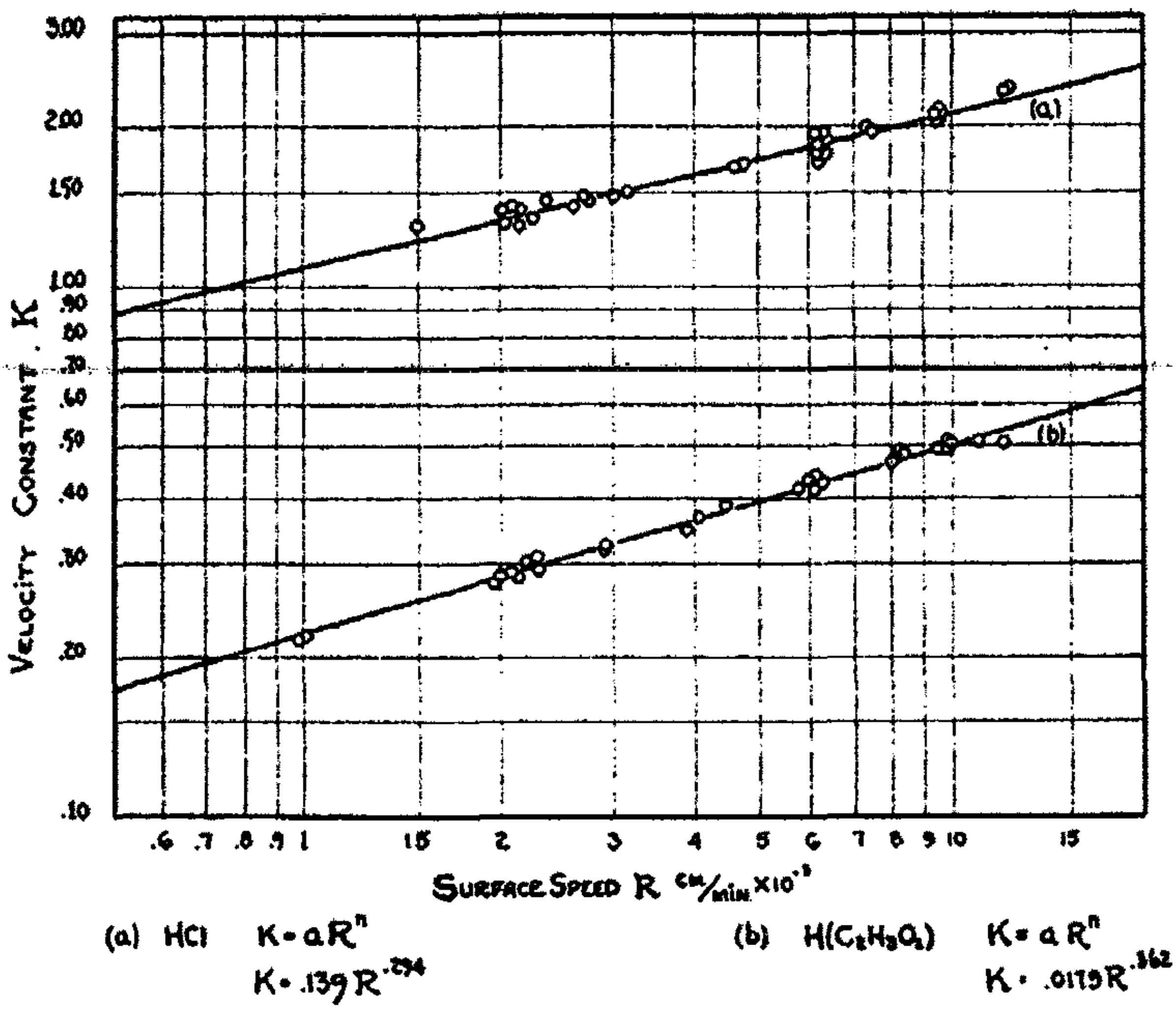


FIG. 5. LOGARITHMIC RELATION BETWEEN k AND STIRRING SPEED

TABLE 5

Hydrochloric acid experiments at 25°C.

NUMBER OF DUPLICATE EXPERIMENTS	METHOD	AVERAGE VALUES OF k AT 2000 CM. PER MINUTE STIRRING	AVERAGE DEVIATION
			per cent
8	Weight	1.309	8.5
35	Volume	1.335	6.0
8	Titration	1.312	7.2

Acetic acid behaves in a similar way, the essential difference being the value of a in equation 9. Many experiments were performed at surface speeds in the neighborhood of 2000 cm. per minute. To make all experiments comparable, the values of k have been calculated to 2000 cm. per minute by equation 9 and are given in table 5. The maximum deviation

TABLE 6

Values for hydrochloric acid experiments at 25°C.

All rate data at stirring speed of 2000 cm. per minute

NUMBER OF DUPLICATE EXPERIMENTS	CONCENTRATION OF ACID	AVERAGE MILLIEQUIVALENTS REACTED PER LITER PER CM.^{2} PER MINUTE OVER 1/10 REACTION	AVERAGE DEVIATION
	M		*per cent*
4	0.010	0.01062	7.2
2	0.012	0.00966	9.4
10	0.025	0.03246	5.7
25	0.050	0.06405	6.5
6	0.075	0.08605	6.6
4	0.1235	0.15440	7.3

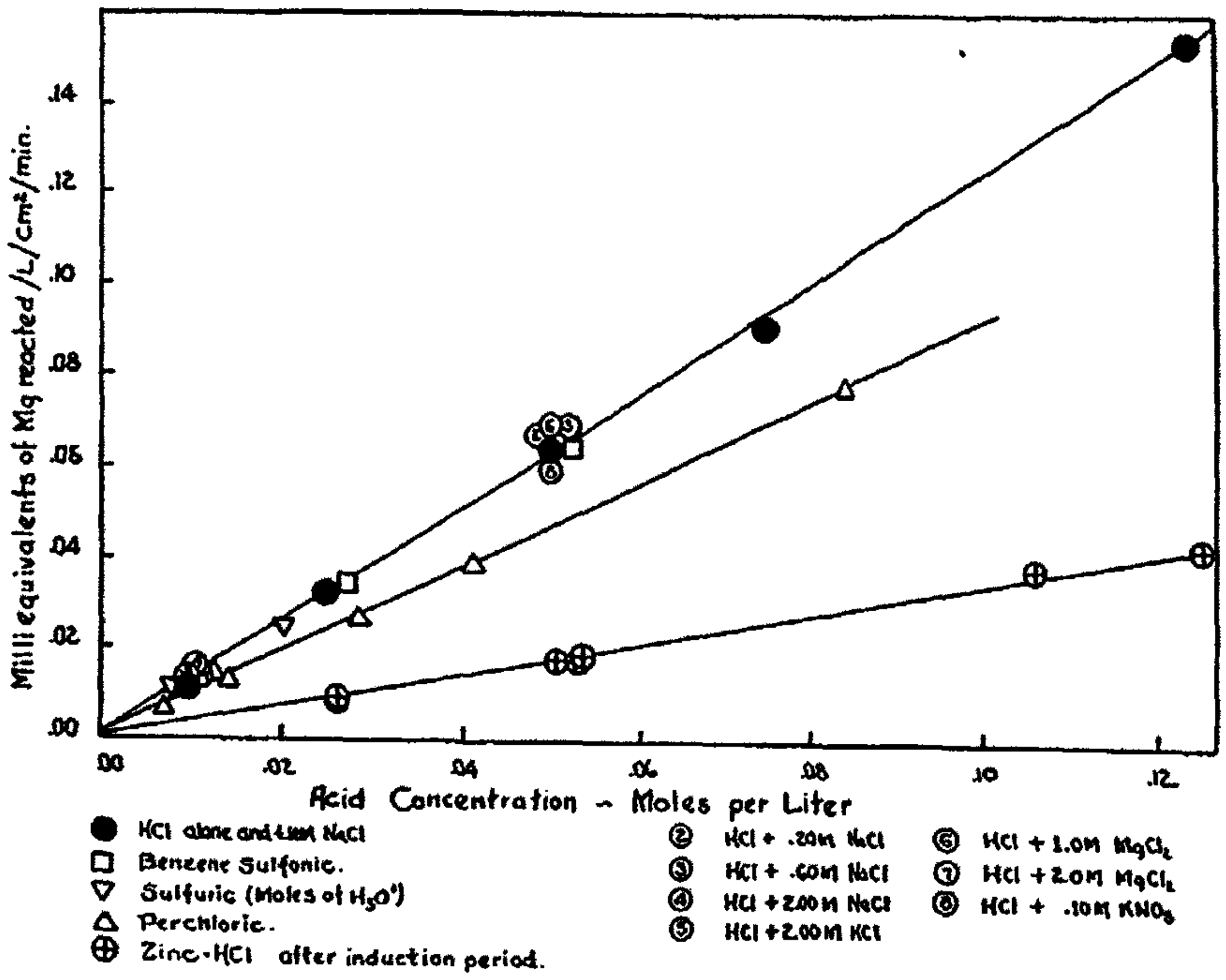


FIG. 6. REACTION WITH THE ACID H_3O^+

in k_{2000} is 17.5 per cent, and the average deviation is 6.1 per cent. These values include the earlier experiments where the rate of stirring was not determined accurately. Table 5 gives the values of k obtained by gas volume, by measurements of loss in weight of magnesium, and by titration of the solution. All the methods agree with the experimental error.

RELATION TO HYDROGEN-ION CONCENTRATION FOR STRONG ACIDS

In order to show the proportionality between the rate of reaction and the hydrogen-ion (H_3O^+) concentration, the one-tenth time of reaction was calculated from k and the average milliequivalents of magnesium reacted per minute, per square centimeter of surface, per liter of solution, at a stirring speed of 2000 cm. per minute. Table 6 gives these results and figure 6 shows the proportionality of the rate to the hydrogen-ion concentration. The intercept on the milliequivalent axis represents the water reaction, which will be discussed in a later section.

TABLE 7

Values for hydrochloric acid experiments at 25°C.

NUMBER OF DUPLICATE EXPERIMENTS	SALT ADDED	RATIO OF SALT TO ACID	VISCOSITY RELATIVE TO WATER	k_{2000}	DEVIATION FROM THE AVERAGE k_{2000}
					per cent
8	None	0	1.004	1.30	2.3
11	0.1 *M* NaCl	1 to 1	1.008	1.32	0.7
19	0.1 *M* NaCl	2 to 1	1.009	1.35	1.5
1	0.1 *M* NaCl	4 to 1	1.020	1.51	13.5
1	0.6 *M* NaCl	12 to 1	1.050	1.46	9.8
2	2.0 *M* NaCl	20 to 1	1.205	1.49	12.0
2	0.1 *M* KCl	2 to 1	0.999	1.365	2.6
2	2.0 *M* KCl	20 to 1	1.002	1.47	10.5
1	1.0 *M* $MgCl_2$	20 to 1	1.468	1.45	9.0
2	2.0 *M* $MgCl_2$	20 to 1	2.233	1.01	24.0
2	0.1 *M* KNO_3	2 to 1	0.995	1.22	8.3

EFFECT OF ADDED SALTS AND NON-ELECTROLYTES

In table 7 data are presented showing the change in k upon the addition of salts. In the fourth column is given the viscosity relative to water and in the sixth column is given the percentage change from k_{2000} for hydrochloric acid alone. In the case of 2 *M* sodium chloride the viscosity is 19.4 per cent higher than for 0.1 *M* sodium chloride, whereas k is 9.0 per cent higher. A 2 *M* potassium chloride solution has the same viscosity as a 0.1 *M* sodium chloride solution, but k is 9 per cent higher. Furthermore a 2 *M* magnesium chloride solution has a viscosity 200 per cent higher than a 0.1 *M* sodium chloride solution, but k is 25.2 per cent lower. From this it would appear that for these salts there is no general relation between rate of solution and viscosity.

In the case of non-electrolytes there seems to be a qualitative relationship, as shown in table 8.

TABLE 8

Values for viscosity experiments

NUMBER OF DUPLICATE EXPERIMENTS	SUGAR	GLYCERINE	VISCOSITY	RELATIVE VISCOSITY WATER TO SOLUTION	k_{2500}	DECREASE FROM AVERAGE k_{2500}	VISCOSITY INCREASE
(a) Values for 0.05 *M* hydrochloric acid experiments with sugar at 25°C.							
	moles per liter	*moles per liter*	*millipoises*			*per cent*	*per cent*
25	0		9.0	0.993	1.33	0	0
4	0.137		9.5	0.942	0.988	25.6	5.6
2	0.257		11.1	0.805	0.674	49.6	23.4
4	0.439		14.3	0.625	0.205	84.3	59.0
(b) Values for 0.05 *M* acetic acid experiments with sugar at 25°C.							
25	0		9.0	0.993	0.284	0	0
4	0.137		9.5	0.942	0.260	8.5	5.6
2	0.257		11.1	0.805	0.167	41.2	23.4
2	0.439		14.3	0.625	0.0546	80.6	59.0
(c) Values for 0.05 *M* acetic acid experiments with glycerine at 25°C.							
25		0	9.0	0.993	0.284	0	0
2		0.608	10.9	0.820	0.234	17.6	21.1
2		1.087	12.0	0.745	0.154	45.8	33.2
3		1.900	15.0	0.596	0.049	82.7	66.6

TABLE 9

Summary of variations of k with temperature

NUMBER OF DUPLICATE EXPERIMENTS	TEMPERATURE	$\frac{1}{T} \times 10^4$	AVERAGE k_{2500}	LOG k_{2500}	HEAT OF ACTIVATION	
	degrees C.					
2	0	36.6	0.444	−0.3526	k_{25}/k_0	7,120
38	25.0	33.5	1.338	+0.1260		
2	56.5	30.3	8.55	0.9320	$k_{56.5}/k_{25}$	11,500
2	76.0	28.65	22.20	1.3464	k_{76}/k_{25}	11,380
11	80.2	28.3	21.25	1.3274	k_{80}/k_{25}	10,520

EFFECT OF TEMPERATURE

The results of the determinations at different temperatures are given in table 9, and for the dissolution of magnesium in hydrochloric acid the logarithm of k is plotted against $1/T$ in figure 7. According to the Arrhenius equation, the slope of the line in figure 7 is $-\frac{A}{4.574}$, which gives a heat of activation of 10,200 calories. This corresponds to a temperature coefficient $k_{35}/k_{25} = 1.75$. A discussion of this value in relation to the diffusion theory will be given later.

EXPERIMENTS WITH OTHER STRONG ACIDS

Since in the case of strong acids H_3O^+ is the only acid present besides water, one would expect that all strong acids would give the same velocity constant except for changes due to primary salt effect if the rate is a chemical one, or changes due to viscosity if the rate is controlled by a diffusion process. Table 10 gives the results for perchloric acid and benzenesulfonic acid, and the proportionality to the hydrogen-ion concentration is shown in figure 6.

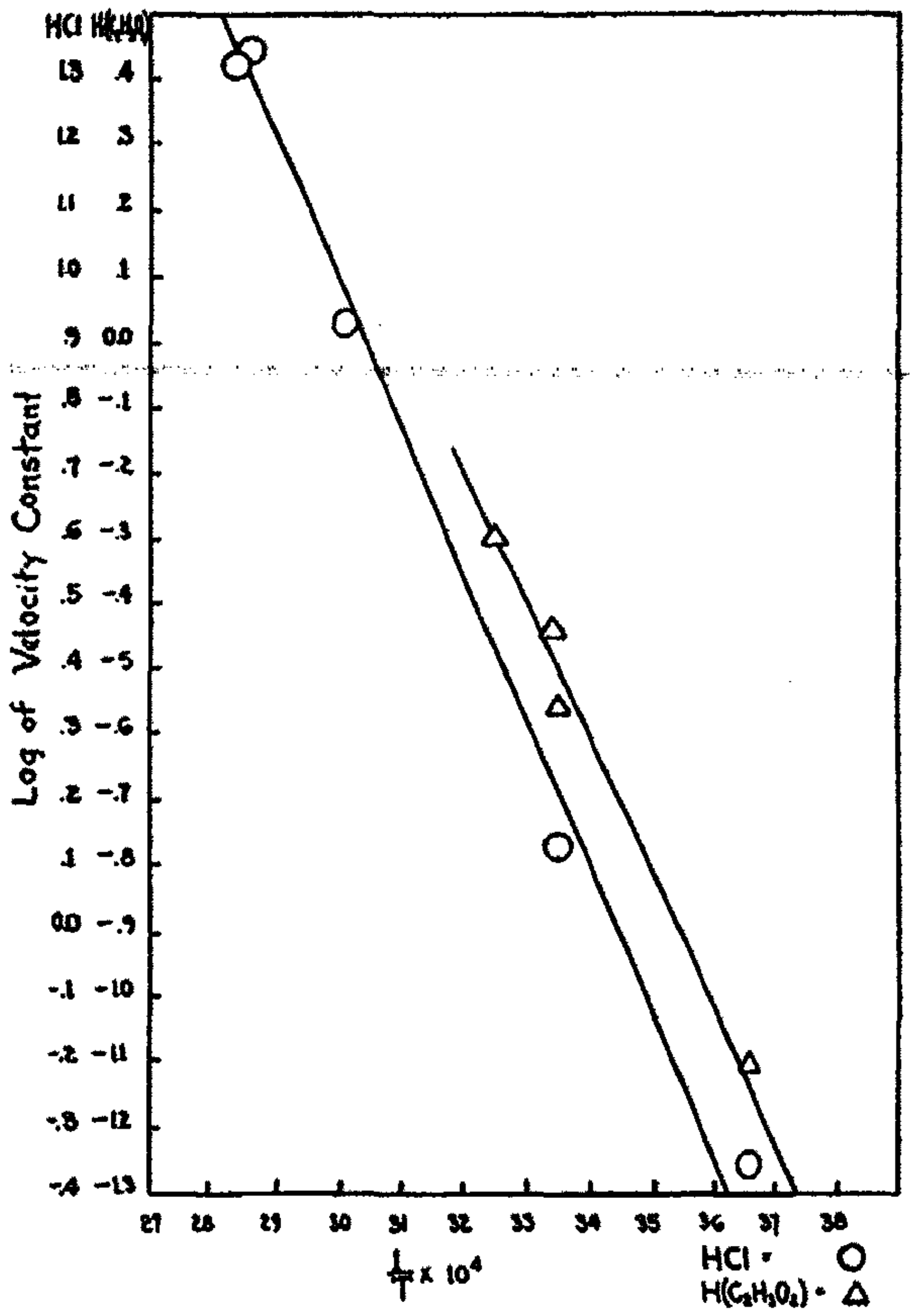


FIG. 7. RELATION BETWEEN VELOCITY CONSTANT AND TEMPERATURE

Perchloric acid gives lower values of k than benzenesulfonic or hydrochloric acids. In the case of sulfuric acid the concentrations of the hydrogen ion and the HSO_4^- ion were calculated from known values of the classical dissociation constant at the proper ionic strengths, and $k_{H_3O^+}$

TABLE 10

Data for perchloric acid and benzenesulfonic acid at 25°C.

CONCENTRATION OF ACID	SODIUM CHLORIDE CONCENTRATION	k_{1000}	DEVIATION FROM AVERAGE k_{1000}	MILLIEQUIVALENTS PER LITER PER CM.³ PER MINUTE	PER CENT OF REACTION FOLLOWED
(a) Perchloric acid					
moles per liter	*moles per liter*		*per cent*		
0.0073	0	0.919	14.0	0.00635	63
0.0141	0	1.016	6.1	0.01355	63
0.0293	0	0.980	8.4	0.0272	39
0.0417	0	1.003	6.2	0.0397	59
0.0835	0	0.997	6.8	0.0790	78
0.0123	0.10	1.215	13.0	0.0142	95
(b) Benzenesulfonic acid					
0.025	0.10	1.320	0.7	0.0313	56
0.050	0.10	1.340	0.7	0.0634	46

TABLE 11

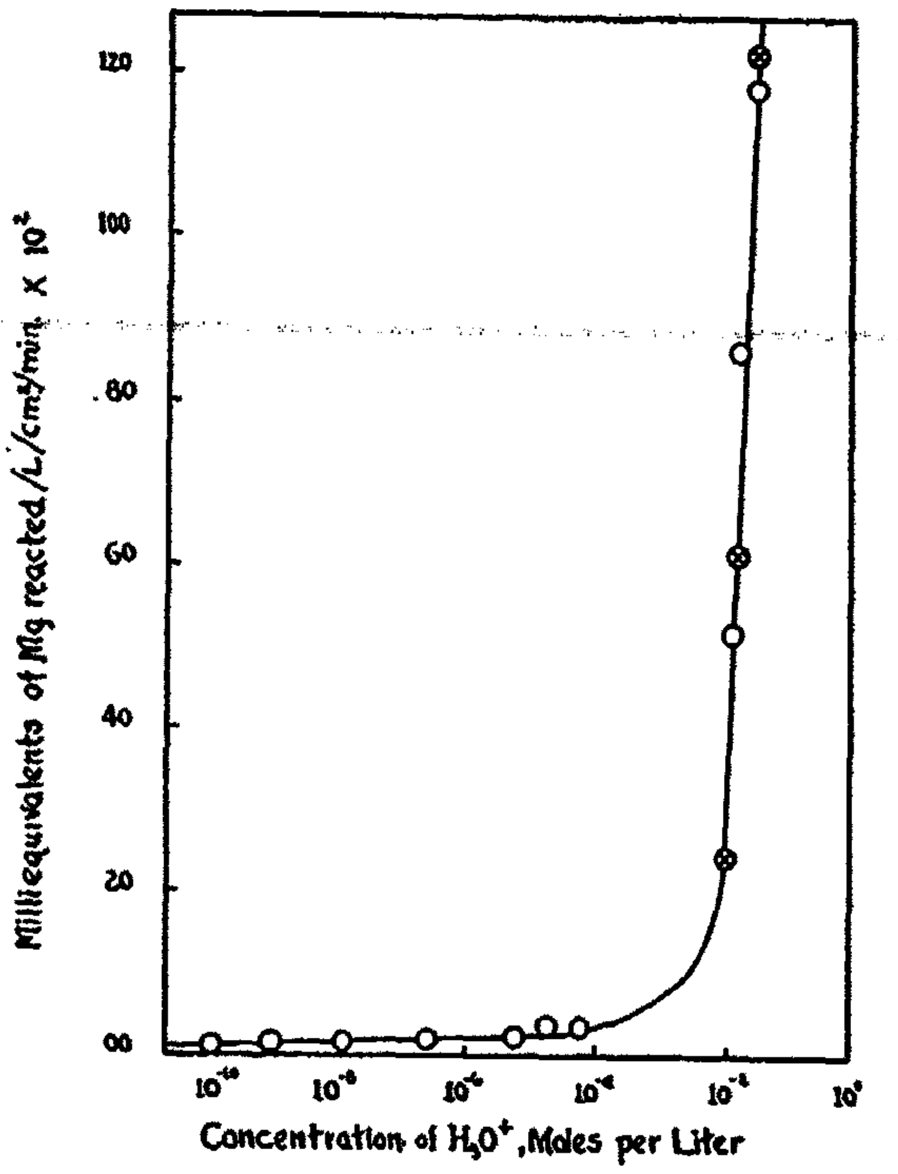
Summary of data for sulfuric acid and bisulfate ion at 25°C.

CONCENTRATION OF ACID	CONCENTRATION OF NaCl	k_{1000}	DEVIATION FROM AVERAGE k_{1000}	MILLIEQUIVALENTS PER LITER PER CM.³ PER MINUTE	PER CENT OF REACTION FOLLOWED
(a) Sulfuric acid					
M	*M*		*per cent*		
0.00926	0.10	1.407	9.5	0.0124	88.3
0.00926	0.10	1.322	2.9	0.0116	86.7
0.0184	0.10	1.182	7.9	0.0207	93.2
0.0184	0.10	1.227	4.5	0.0215	93.9
(b) Bisulfate ion (1 HSO_4^- to 1 Na_2SO_4)					
0.00139	0.0875	0.534	2.7	0.00071	82.6
0.00139	0.0875	0.534	2.7	0.00071	96.3
0.0040	0.075	0.525	1.1	0.00195	95.7
0.0040	0.075	0.525	1.1	0.00195	90.2
0.00761	0.0625	0.494	5.0	0.00358	89.5
0.00761	0.0625	0.508	2.2	0.00367	94.4
0.0109	0	0.535	3.0	0.00555	96.5
0.0109	0	0.500	3.8	0.00518	94.8

and $k_{HSO_4^-}$ calculated from the kinetic measurements. The results are given in table 11. It is seen that $k_{H_3O^+}$ is the same as that from hydrochloric and benzenesulfonic acids, while $k_{HSO_4^-}$ is decidedly less. The results for sulfuric acid are presented in figure 6, while those for the HSO_4^- ion are given graphically in figure 14. In reducing all experiments to 2000 cm. per minute in surface speed, it has been assumed that the relation for all strong acids is the same as that found for aqueous hydrogen chloride.

THE WATER REACTION

Magnesium reacts readily with water at higher temperatures and, as will be shown, this reaction is independent of the hydrogen-ion concentration.



Temperature 80°C.
Stirring speed 4880 cm/min.

○ Experimental value
⊗ Calc. from avg. values of K at 25°C.

FIG. 8. MILLIEQUIVALENTS VERSUS CONCENTRATION H_3O^+

As the concentration of the water is constant, the velocity can be expressed by the equation

$$v = k_w + k_{H_3O^+}C_{H_3O^+} \tag{10}$$

when there are no other acids present. k_w represents the water reaction.

That k_w is independent of the hydrogen-ion concentration was demonstrated experimentally by using the fourth method. The method consisted in maintaining a constant hydrogen-ion concentration by adding small amounts of strong acid from a microburet in the presence of an indicator. The amount of acid required was recorded at suitable intervals of time. It was found that acid was consumed at a constant rate.

The apparatus shown in figure 2 was used, without the gas buret. Experiments were carried out at the boiling point of benzene and of acetone. In table 12 are presented the results with and without added salt.

TABLE 12

Data for the water reaction

Stirring surface speed = 4880 cm. per minute

(a) Water at 80° and 56.5°C.

INDICATOR	CONCENTRATION OF H_3O^+	MILLI-EQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ AT 80°C.	MILLI-EQUIVALENTS $\times 10^{-2}$ AT 56.5°C.	HEAT OF ACTIVATION A	TEMPERATURE COEFFICIENT $\frac{k_{66.5}}{k_{56.5}}$
				calories	
Phenolphthalein	2×10^{-10}	1.088	0.991	930	1.04
Thymol blue	1.3×10^{-9}	1.288	0.688	6130	1.30
Phenol red	1.6×10^{-8}	1.672	0.799	7250	1.36
Bromcresol purple	5×10^{-7}	1.782	0.881	7030	1.34
Methyl red	8×10^{-6}	2.365	1.232	6420	1.31
Bromcresol green	3×10^{-5}	3.775	1.859	6990	1.34
Bromphenol blue	8×10^{-5}	3.560	1.628	7670	1.38
Thymol blue	2×10^{-2}	51.50	26.8	6550	1.32

(b) Solutions of magnesium chloride at 80°C.

CONCENTRATION OF H_3O^+	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ FOR 0.1 M $MgCl_2$	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ FOR 0.05 M $MgCl_2$	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ FOR 0.05 M KNO_3	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ FOR 0.10 M KNO_3
2×10^{-10}	3.74	2.32	2.30	
1.3×10^{-9}	3.24			
1.6×10^{-8}	3.63			
5×10^{-7}	3.52	2.22	2.36	3.64
8×10^{-6}	4.64			
3×10^{-5}	6.69			
8×10^{-5}	7.95	5.54	3.50	7.82

The results without added salt are presented graphically in figure 8. Included in this figure are points obtained by the second method for experiments at low concentrations of acid, the milliequivalents reacted per minute being corrected to the same surface speed. These points are in excellent agreement with those obtained by the fourth method. Figure 8 shows that below a hydrogen-ion concentration of $1 \times 10^{-5}M$ the reaction due to the hydrogen ion is negligible, and the rate is independent of the hydrogen-ion concentration. The curve of figure 8 is quite similar to certain cases observed in homogeneous catalysis (23). It is to be noted that the temperature coefficient $\frac{k_{68.5}}{k_{56.5}}$ is 1.34, which corresponds to a heat of activation of 7000 calories as against 10,000 for the H_3O^+ reaction.

The effect of salts was also studied; these results are given in table 12 and figure 9. In the experiments with added salt no allowance was made for the change in the dissociation constant of the indicator with change in electrolyte concentration, since this would not alter the general relationship appreciably.

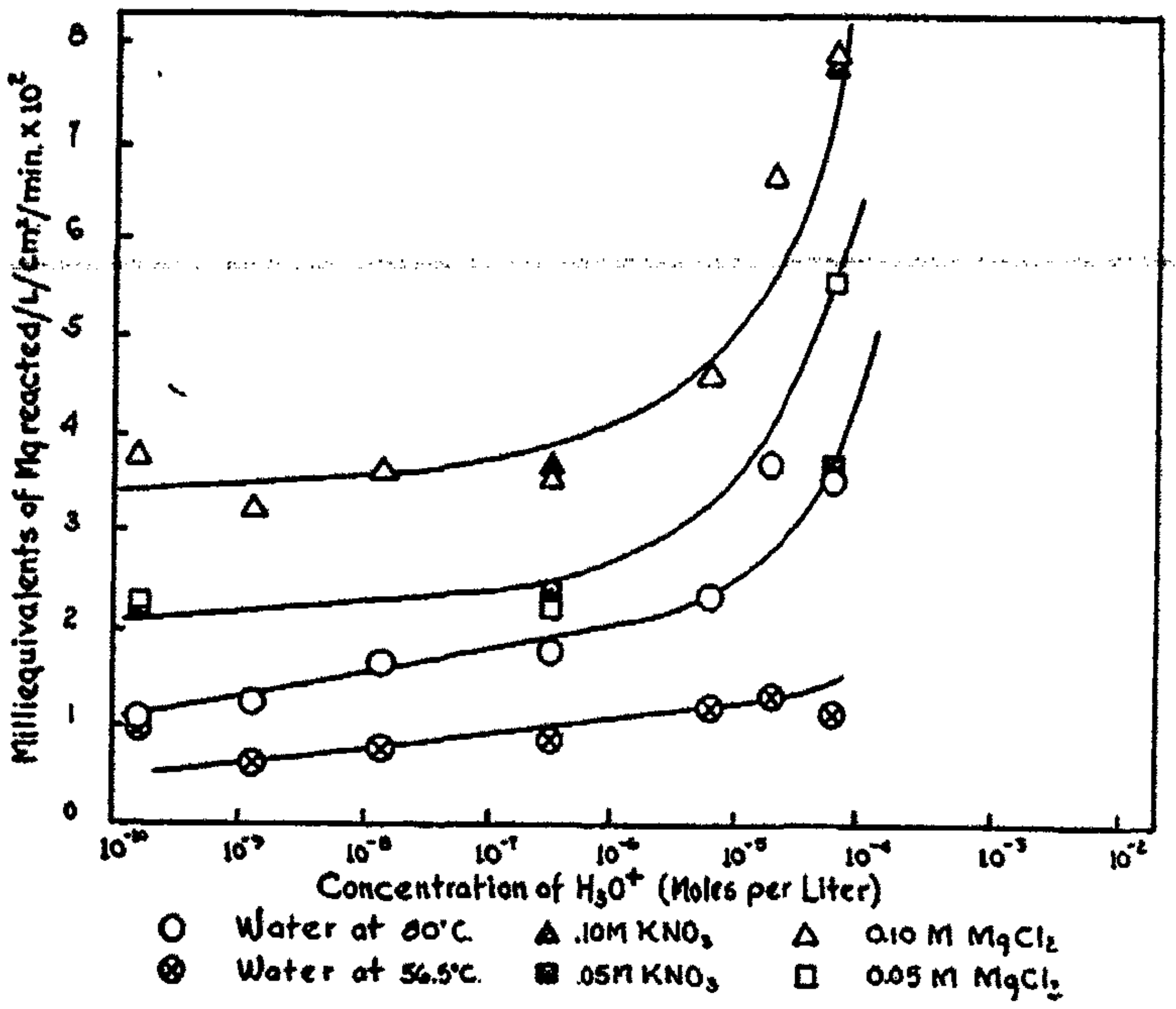


FIG. 9. WATER REACTION

In earlier experiments on the water reaction the gas evolution method was employed. In these experiments the evolution of gas did not start immediately and its subsequent evolution was not uniform. The metal became covered with an adherent film, and an insoluble compound was dispersed through the solution. In the presence of magnesium chloride or magnesium acetate, constant evolution of gas was obtained over a short interval. The results were similar to those in figure 9. See also reference 12.

TABLE 13

Acetic acid experiments at 25°C.

Acid base ratio = 1 to 1

EXPERIMENT NO.	R.P.M.	CM. PER MINUTE	k AT EXPERIMENT SPEED	k AT 2000	PER CENT REACTION	INITIAL ACID CONCENTRATION
84	0	0	0.0873		26.2	0.0485
45	0	0	0.0912		28.0	0.050
38	0	0	0.1047		45.0	0.050
39	0	0	0.1047		76.0	0.050
40	0	0	0.1047		15.1	0.050
41	0	0	0.1047		21.6	0.050
42	0	0	0.1047		31.8	0.050
85	425	1000	0.215	0.276	52.7	0.0485
46	425	1000	0.210	0.270	52.9	0.050
82	850	2000	0.281	0.281	62.6	0.0485
83	850	2000	0.274	0.274	61.6	0.0485
5	860	2180	0.289	0.282	19.8	0.0705
4	860	2190	0.295	0.285	20.7	0.0236
3	860	2210	0.310	0.297	21.7	0.0472
2	860	2230	0.302	0.290	21.4	0.0943
1	860	2250	0.290	0.277	10.0	0.382
25	800	2870	0.335	0.294	56.8	0.049
24	800	3790	0.357	0.284	62.5	0.098
81	1700	4010	0.403	0.313	75.7	0.0485
26	800	4660	0.395	0.292	73.4	0.0245
18	1200	5825	0.424	0.288	69.8	0.0980
74	2550	6040	0.426	0.287	77.9	0.051
75	2550	6040	0.437	0.294	78.5	0.0485
76	2550	6040	0.437	0.294	78.5	0.0485
20	1200	6240	0.430	0.286	73.1	0.0245
19	1200	6320	0.424	0.282	76.9	0.0490
15	2000	7240	0.438	0.277	79.4	0.0989
12	2000	7390	0.453	0.284	81.2	0.0989
6	2000	7430	0.468	0.292	82.2	0.0989
78	3400	8020	0.465	0.283	80.4	0.0485
79	3400	8020	0.473	0.287	81.0	0.0485
77	3400	8060	0.479	0.291	81.5	0.0485
23	2000	9550	0.496	0.284	74.5	0.0245
21	2000	9620	0.471	0.267	76.3	0.0989
9	2000	9740	0.490	0.277	90.5	0.0989
16	2000	9740	0.896	0.280	91.1	0.0495
14	2000	9780	0.503	0.284	91.2	0.0247
7	2000	9810	0.505	0.285	91.3	0.0495
11	2000	9810	0.487	0.276	90.5	0.0247
13	2000	9840	0.510	0.288	91.7	0.0495
17	2000	9840	0.496	0.280	91.4	0.0247
8	2000	9940	0.505	0.284	91.5	0.0247
22	2000	10350	0.504	0.287	78.4	0.0490
10	2000	11760	0.498	0.268	94.2	0.0490
				Av. = 0.284		

EXPERIMENTS WITH WEAK ACIDS

When a weak acid such as acetic acid is dissolved in water, there exists the usual double acid–base equilibrium.

$$\begin{array}{cccc} CH_3COOH + & H_2O \rightleftarrows & H_3O^+ + & CH_3COO^- \\ \text{Acid 1} & \text{Base 2} & \text{Acid 2} & \text{Base 1} \end{array} \qquad (11)$$

TABLE 14

Summary of acetic acid experiments at 25°C. and 2000 cm. per minute stirring speed

Acid base ratio = 1 to 1. Total ionic strength kept constant at 0.1 *M* with sodium chloride

NUMBER OF DUPLICATE EXPERIMENTS	INITIAL ACETIC ACID CONCENTRATION	CONCENTRATION OF ACETATE	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE
	M	*M*	
8	0.0246	0.0246	0.0066
1	0.0472	0.0472	0.0132
18	0.0495	0.0495	0.0132
2	0.0705	0.0705	0.0188
1	0.0943	0.0943	0.0258
8	0.0985	0.0985	0.0262
2	0.200	0.200	0.0478
1	0.382	0.382	0.1000

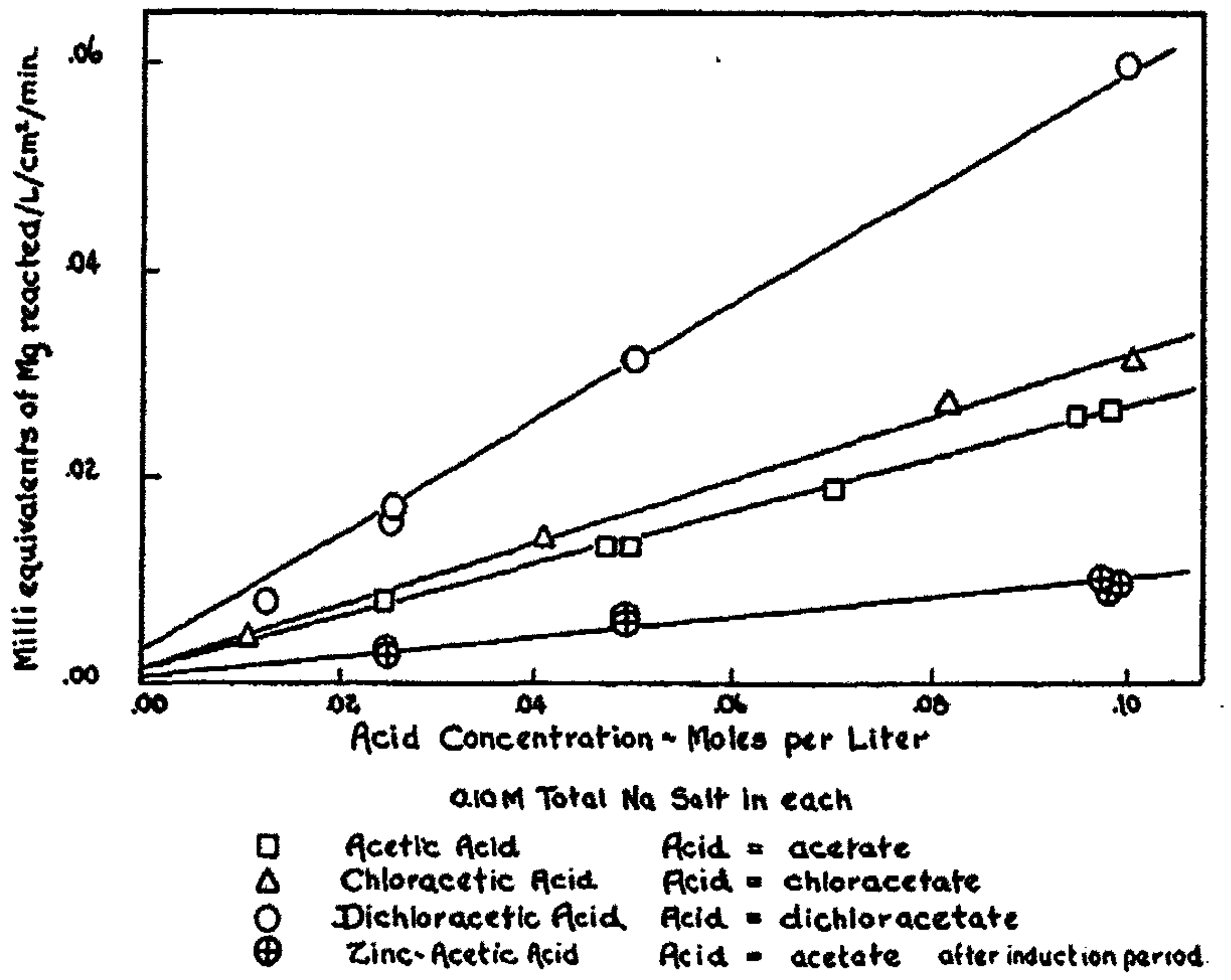


FIG. 10. REACTION WITH ACETIC ACID, CHLOROACETIC ACID, DICHLOROACETIC ACID

Since the reaction does not go completely to the right as in the case of a strong acid, there are, besides water, two acids, H_3O^+ and CH_3COOH. The problem, quite apart from the consideration of whether the reaction rate is controlled by diffusion or a chemical process, is whether the proton is brought to the metal by the H_3O^+ ion or the CH_3COOH molecule, or both. If it were brought by the H_3O^+ ion alone, then the rate would be given by equation 10 and the function of the acetic acid would be to supply more hydrogen ion. If both the H_3O^+ ion and the CH_3COOH molecule bring protons, the velocity should be represented by the equation

$$v = k_w + k_{H_3O^+}C_{H_3O^+} + k_{HAc}C_{HAc} \qquad (12)$$

Of course, there might exist a medium effect of acetic acid which would alter $k_{H_3O^+}$ in equation 10.

To test equation 12 it is necessary to carry out a series of experiments at constant hydrogen-ion concentration and varying acetic acid concentration. Actually at 25°C. k_w is negligible, and at hydrogen-ion concentrations around $1 \times 10^{-5}M$ the term $k_{H_3O^+}C_{H_3O^+}$ becomes almost negligible, so that $v = k_{HAc}C_{HAc}$ if our hypothesis is correct. To minimize the change in Kc, the classical dissociation constant of the acid, the experiments were carried out at constant ionic strength. In order to put the experiments on a comparable basis, the effect of stirring was determined (see table 13 and figure 5).

TABLE 15

Summary of experiments with acetic acid at elevated temperature

NUMBER OF DUPLICATE EXPERIMENTS	TEMPERATURE	$\frac{1}{T} \times 10^4$	AVERAGE k_{2000}	LOG k_{1000}	HEAT OF ACTIVATION A	
	degrees C.					
2	0	36.6	0.0794	−1.100	k_{25}/k_0	8,250
35	25	33.5	0.284	−0.546		
13	27	33.35	0.306	−0.436	k_{27}/k_0	9,750
9	35	32.5	0.506	−0.296	k_{35}/k_{25}	10,700
5	56.5	30.0	0.611	−0.214	$k_{56.5}/k_{25}$	5,000
3	76	38.65	0.698	−0.156	k_{76}/k_{25}	4,000
5	80.2	28.3	1.100	+0.042	$k_{80.2}/k_{25}$	5,200

Table 14 summarizes the results with acetate buffers, and figure 10 shows the proportionality between the increase in the reaction rate and the concentration of acetic acid. Table 14 and figure 10 prove the validity of equation 12. The intercept in figure 10 represents the amount reacting by way of the hydrogen ion and the water. The effect of viscosity has already been given in table 8. Table 15 gives the results at higher temperatures.

In figure 7 the logarithm of k is plotted against $1/T$; the slope of the line corresponds to a heat of activation of 9500 calories, or a temperature

TABLE 16

Data for hydrochloric acid–acetic acid experiment 3

H_0 for 0.025 M acetic acid = 70.2 cc.

TIME	HYDROGEN H_t	HYDROGEN DUE TO 0.01 M HCl	HYDROGEN DUE TO $HC_2H_3O_2$ PRESENT	$H_0 - H_t$	LOG $\frac{H_0}{H_0 - H_t}$
minutes	*cc.*	*cc.*	*cc.*		
1	8.0	6.0	2.0	68.2	0.0130
2	18.7	10.8	7.9	62.3	0.0520
3	25.0	14.5	10.5	59.7	0.0700
4	31.3	17.5	13.8	56.4	0.0950
5	36.9	19.8	17.1	53.1	0.1218
6	41.0	21.6	19.4	50.8	0.1405
7	45.3	23.0	22.3	47.9	0.1660
8	49.0	24.1	24.9	45.3	0.1905
9	52.0	24.9	27.1	43.1	0.2120
10	55.6	25.7	29.9	40.3	0.2412

TABLE 17

Summary of mixed acid experiments at 25°C.

EXPERIMENT NO.	HYDROCHLORIC ACID CONCENTRATION	ACETIC ACID CONCENTRATION	k_{1000} FOR THE ACETIC ACID	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE DUE TO 0.01 M H_3O^+	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE DUE TO $HC_2H_3O_2$	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE TOTAL	PER CENT DECREASE OF $HC_2H_3O_2$ DUE TO H_3O^+	PER CENT INCREASE OF H_3O^+ DUE TO $HC_2H_3O_2$
	M	M						
1	0.01	0.005	0.276	0.01263	0.00131	0.01394	0.223	1.6
2	0.01	0.010	0.281	0.01263	0.00267	0.01530	0.219	1.0
3	0.01	0.025	0.274	0.01263	0.00651	0.01914	0.218	0.5
4	0.01	0.050	0.285	0.01263	0.01353	0.02616	0.216	0.2
5	0.01	0.075	0.280	0.01263	0.01998	0.03261	0.214	0.1

coefficient k_{35}/k_{25} of 1.69. It should be pointed out that a few experiments at 80°C. and 76°C. gave lower values.

EXPERIMENTS WITH MIXTURES OF HYDROCHLORIC AND ACETIC ACIDS

In order to test further the idea that the proton is brought to the metal by the molecular acid, a series of experiments were carried out in mixtures of hydrochloric and acetic acids. The addition of acetic acid increased the

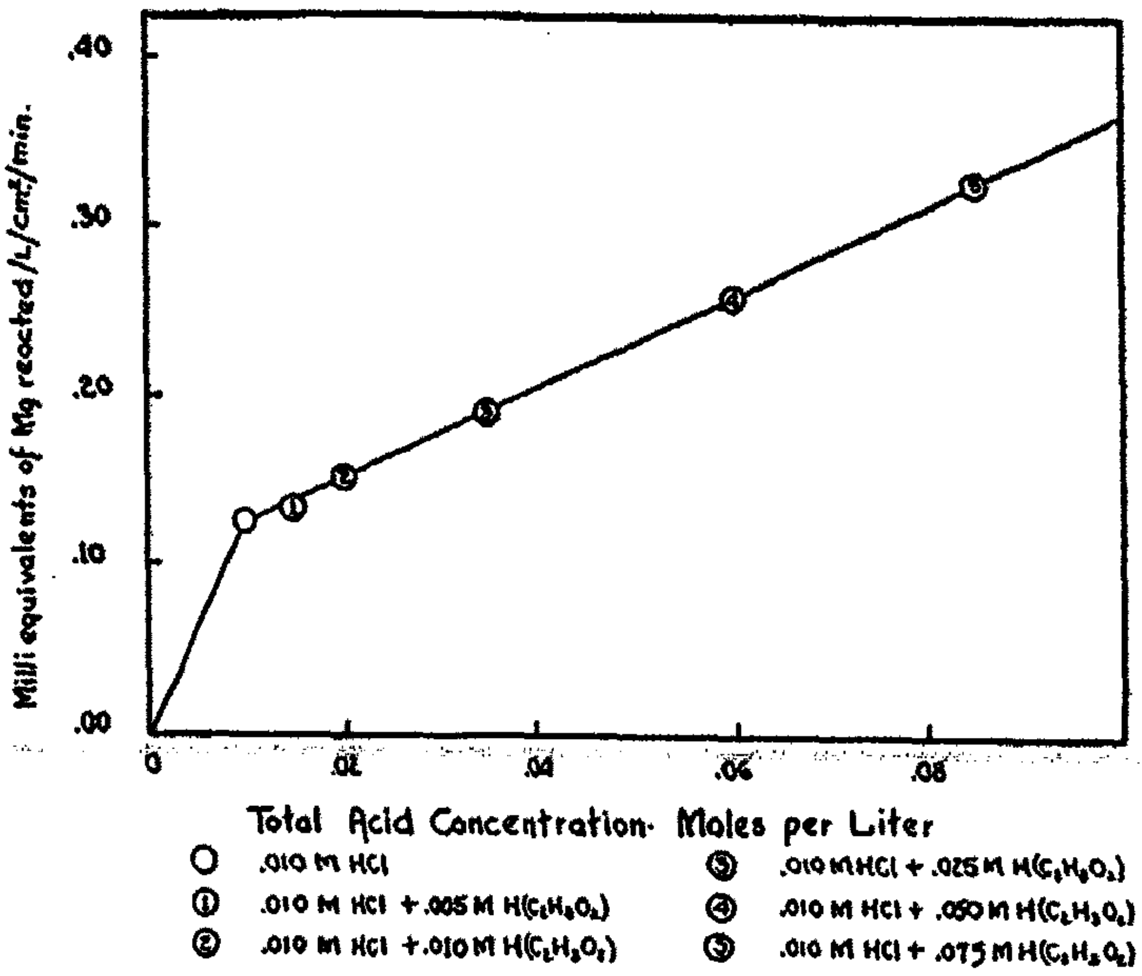


FIG. 11. REACTION WITH MIXED HYDROCHLORIC AND ACETIC ACIDS

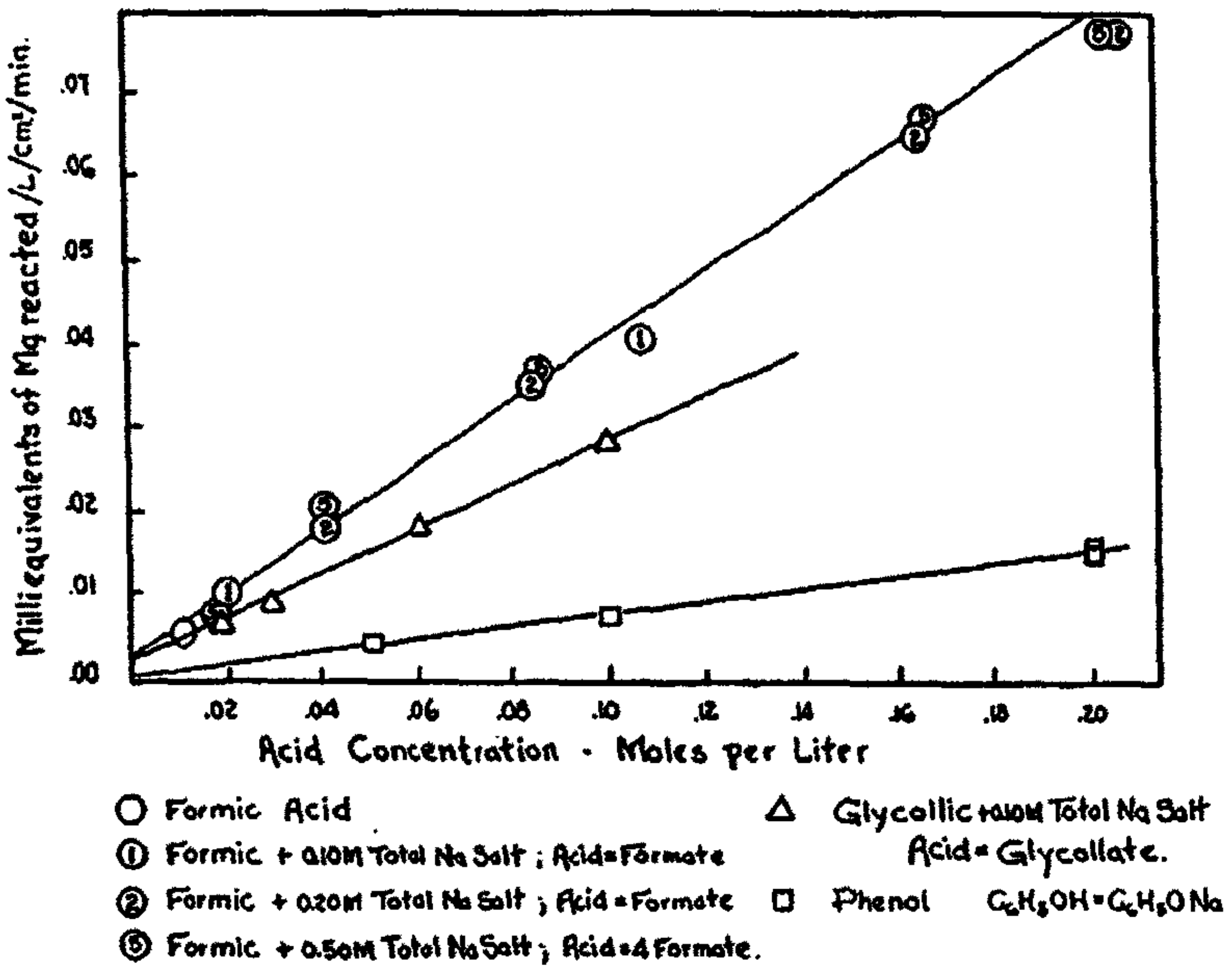


FIG. 12. REACTION WITH FORMIC ACID, GLYCOLLIC ACID, PHENOL

hydrogen-ion concentration slightly. If equation 12 holds, there should be a noticeable increase in rate upon the addition of acetic acid; if the hydrogen ion is the sole carrier, there should be very little change in rate. The method of calculation is indicated in table 16. Column 2 gives the total gas evolved, column 3 the gas evolved in 0.01 M hydrochloric acid solutions,

TABLE 18

Experiments with chloroacetic and dichloroacetic acids

Acid base ratio 1 to 1. 0.1 M total ionic strength

ACID CONCENTRATION	k_{1000}	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE	PER CENT REACTION FOLLOWED
(a) Experiments with chloroacetic acid at 25°C.			
M			
0.0106	0.384	0.0037	44.2
0.0412	0.363	0.0142	23.8
0.0815	0.352	0.0271	63.5
0.1016	0.320	0.0309	21.5
(b) Experiments with dichloroacetic acid at 25°C.			
0.0125	0.662	0.00786	45.6
0.0250	0.645	0.0153	80.8
0.0252	0.675	0.0170	63.4
0.050	0.658	0.0312	91.8
0.100	0.622	0.0591	91.8

TABLE 19

Experiments with formic acid at 25°C.

ACID CONCENTRATION	ACID BASE RATIO	IONIC STRENGTH	k_{1000}	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE	PER CENT REACTION FOLLOWED
M		M			
0.0103	Acid alone	—	0.438	0.00426	27
0.0205	1 to 1	0.2	0.436	0.00842	42
0.0214	1 to 1	0.1	0.400	0.00813	28
0.041	1 to 1	0.2	0.465	0.0181	54
0.041	4 to 1	0.05	0.512	0.0199	34
0.082	1 to 1	0.2	0.455	0.0352	48
0.082	4 to 1	0.05	0.492	0.0380	44
0.107	1 to 1	0.1	0.398	0.0402	23
0.164	1 to 1	0.2	0.430	0.0659	63
0.164	4 to 1	0.05	0.482	0.0750	40
0.205	1 to 1	0.2	0.410	0.0795	58
0.205	4 to 1	0.05	0.402	0.0785	15
2.068	Acid alone	—	0.430	0.8400	9

and column 4 the difference. A plot similar to figure 3 shows that the part of the reaction due to the acetic acid follows a first order law. Table 17 summarizes these results and shows the change in the hydrogen-ion concentration in each experiment. The average value of k_{HA_0} for the experiments is 0.280, as compared with 0.284 from the results in solution buffered with respect to the hydrogen ion. This is good evidence that whether the rate is controlled by a chemical process or one of diffusion the metal reacts with the molecular acid. This result is represented graphically in figure 11. The milliequivalents of magnesium reacted are plotted against the total acid concentration.

TABLE 20

Experiments with glycollic acid at 25°C.

Acid base ratio = 1

ACID CONCENTRATION	k_{2000}	MILLIEQUIVALENTS PER PER LITER PER CM.^{2} PER MINUTE	PER CENT REACTION FOLLOWED
M			
0.0175	0.357	0.00592	41
0.0298	0.306	0.00863	43
0.0595	0.354	0.0195	44
0.0993	0.303	0.0284	46

TABLE 21

Experiments with phenol

1 C_6H_5OH to 1 C_6H_5ONa

NUMBER OF DUPLICATE EXPERIMENTS	PHENOL CONCENTRATION	k_{2000}	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE
	M		
2	0.200	0.0778	0.01488
2	0.100	0.0815	0.00775
2	0.050	0.0764	0.00415

The slope of the first part of the line represents $k_{H_3O^+}$ and corresponds to the slope in figure 6. The slope of the second part of the line corresponds to that of the line for acetic acid in figure 10. It should be emphasized that the hydrogen-ion concentration has been increased less than two per cent by the addition of acetic acid, yet the rate is increased twofold.

Table 18 summarizes the experiments with monochloroacetic and dichloroacetic acids.

Figure 10 shows good proportionality between the increase in reaction rate and the acid concentration. The order is that of the acid strength. The intercept for dichloroacetic acid is lower than would be expected.

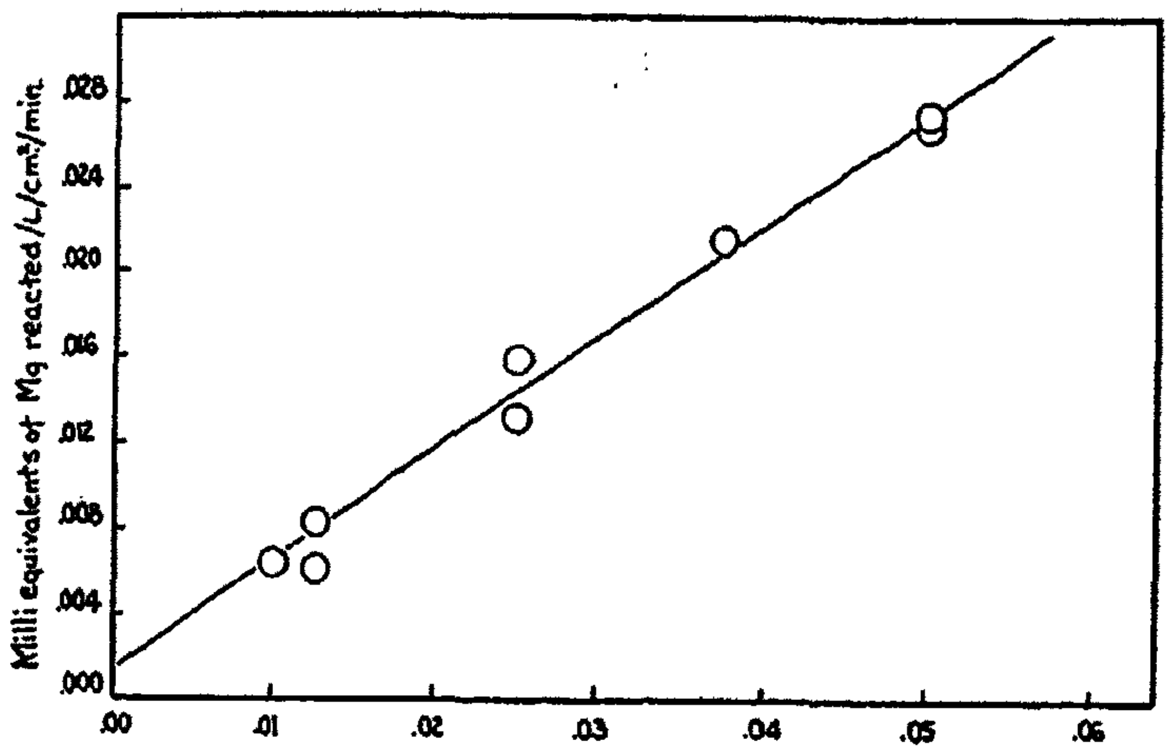
Table 19 and figure 12 give the results for formic acid. All experiments are calculated to a surface speed of 2000 cm. per minute using equation 9, using the same values for a and n as for acetic acid.

The results for glycollic acid are also represented in figure 12, the data being given in table 20. Again there is good proportionality between the increase in rate and the concentration of the molecular acid.

TABLE 22

Experiments with pyridinium ion

CONCENTRATION OF PYRIDINIUM	k_{1000}	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE
M		
0.05	0.586	0.0278
0.05	0.581	0.0275
0.0375	0.559	0.01988
0.025	0.522	0.01238
0.025	0.516	0.01222
0.0125	0.432	0.00512
0.0125	0.438	0.0052
0.01	0.424	0.00402



$1\ C_5H_5N$ to $1\ C_5H_5NHCl$

FIG. 13. REACTION WITH PYRIDINIUM ION

In order to show that in general molecular acids react with magnesium, a few experiments were carried out in phenol-phenylate buffers. Table 21 and figure 12 summarize the results.

Table 22 and figure 13 give the results with pyridinium-pyridine buffers.

In both cases equation 12 applies and the velocity constants are in accord with the lower strength of the acids.

TABLE 23

Experiments with citric and tartaric acids

NUMBER OF DUPLICATE EXPERIMENTS	ACID CONCENTRATION	k_{1000}	MILLIEQUIVALENTS PER LITER PER CM.^{3} PER MINUTE	PER CENT AVERAGE OF REACTION FOLLOWED
(a) Experiments with citric acid				
	M			
2	0.0473	1.13	0.0508	52.4
2	0.0310	1.08	0.0318	72.5
1	0.0236	1.07	0.0240	31.4
1	0.0118	1.16	0.0130	66.5
2	0.0104	1.14	0.0113	41.4
2	0.0081	1.13	0.0087	60.6
2	0.0039	1.10	0.0041	62.9
(b) Experiments with dihydrogen citrate ion				
2	0.05	0.494	0.0235	74.0
1	0.025	0.498	0.0119	57.8
1	0.0125	0.492	0.0058	82.0
2	0.0059	0.500	0.0028	30.0
(c) Experiments with monohydrogen citrate ion				
2	0.05	0.182	0.00866	82.0
1	0.025	0.185	0.00440	34.0
2	0.0125	0.187	0.00222	45.0
(d) Experiments with tartaric acid				
2	0.0243	0.730	0.0169	93.6
2	0.0180	0.710	0.0121	96.9
2	0.01205	0.702	0.0080	94.6
2	0.00578	0.710	0.0039	95.6
(e) Experiments with bitartrate ion				
2	0.0502	0.220	0.0105	82.3
2	0.0442	0.216	0.0091	84.5
2	0.0380	0.230	0.0083	84.5
1	0.0250	0.225	0.0054	87.5
2	0.0067	0.218	0.0014	84.5

In the case of dibasic and tribasic acids such as tartaric and citric acids, it was necessary to determine the velocity constants for the several acids present. In order to do this it was necessary to obtain the classical dissociation constants at suitable ionic strengths and to calculate the concentrations of the various acids present. The necessary values for tartaric and citric acid were obtained from the literature (2, and especially 21). The method of calculating the velocity constants was similar to that used for the mixtures of acetic and hydrochloric acids. The results are summarized in table 23, and the proportionality of the increase in rate due to each acid is shown in figure 14.

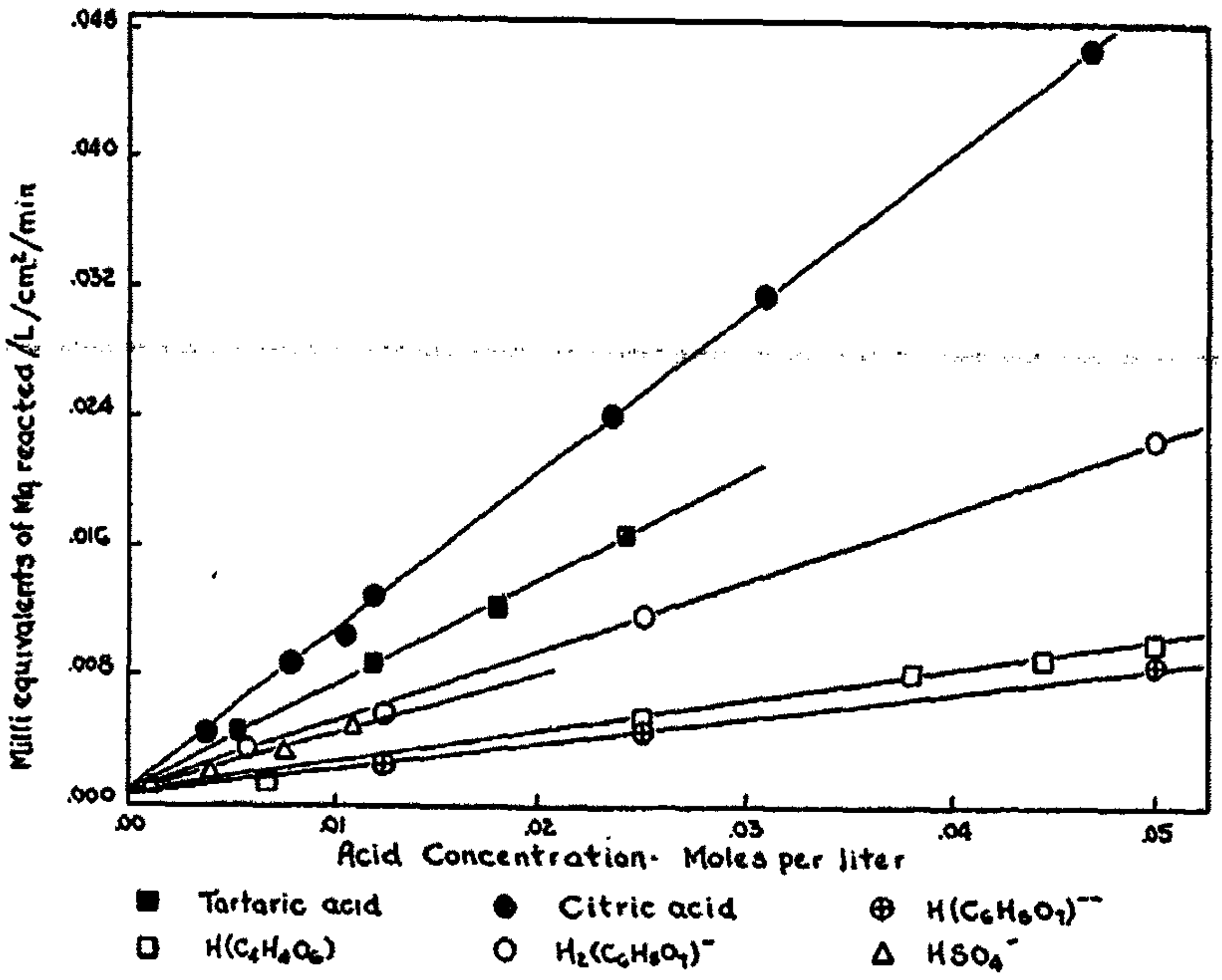


FIG. 14. REACTION WITH TARTARIC ACID, CITRIC ACID, $H(C_4H_4O_6)^-$, $H_2(C_6H_5O_7)^-$, $H(C_6H_5O_7)^{--}$, AND HSO_4^-

EXPERIMENTS WITH ZINC

Experiments on the dissolution of zinc in hydrochloric acid and in acetic acid were carried out under the same experimental conditions as those prevailing in the experiments with magnesium. With zinc an induction period of twenty to twenty-five minutes was noticed, after which the evolution of hydrogen followed the same law as in the case of magnesium. Beginning at the end of the induction period, k_{2000} and the milliequivalents reacted were calculated in the same way as in the experiments with magnesium.

Table 24 gives the data for hydrochloric acid and figure 6 shows the proportionality between the rate and the hydrogen-ion concentration, after the induction period.

TABLE 24

Experiments with zinc and hydrochloric acid at 25°C.

Weight determinations

ACID CONCENTRATION	CONCENTRATION OF ADDED SALT	k_{1000}	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE
M	*M*		
0.1063	0.10 NaCl	0.375	0.03775
0.0530	0.10 NaCl	0.359	0.01805
0.0530	0.10 NaCl	0.361	0.01815
0.0265	0.10 NaCl	0.375	0.00944
0.0265	0.10 NaCl	0.365	0.00919
0.0133	0.10 NaCl	0.359	0.00454
0.050	0.10 NaCl	0.375	0.00178
0.050	0.10 KNO_3	5.18	0.0245
0.050	0.10 KNO_3	5.23	0.0248
0.100	0.10 KNO_3	6.63	0.0628

TABLE 25

Experiments with zinc and buffered acetic acid solutions at 25°C.

Weight determinations

ACID CONCENTRATION	CONCENTRATION OF ADDED SALT	CONCENTRATION OF SODIUM ACETATE	k_{1000}	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE
M	*M*	*M*		
0.0980		0.100	0.107	0.00997
0.0980		0.100	0.097	0.00902
0.0490	0.050 NaCl	0.050	0.124	0.00577
0.0490	0.050 NaCl	0.050	0.130	0.00605
0.0245	0.025 NaCl	0.025	0.114	0.00265
0.0245	0.025 NaCl	0.025	0.118	0.00275
0.100	0.100 NaCl		0.105	0.00991
0.100	0.100 KNO_3		4.10	0.389
0.100	0.100 KNO_3		4.20	0.399

TABLE 26

Comparison of reaction rates of magnesium and zinc at 25°C.

METAL	k_{1000} FOR HCl	k_{1000} FOR HCl + 0.05 *M* KNO_3	k_{1000} FOR $HC_2H_3O_2$	k_{1000} FOR $HC_2H_3O_2$ + 0.1 *M* KNO_3
Mg	1.33	1.20	0.284	0.280
Zn	0.367	5.20	0.113	4.10

Table 25 and figure 10 present the results obtained in acetate-acetic acid buffer solutions and show the proportionality between the rate and the concentration of molecular acid, after the induction period. In both cases the addition of potassium nitrate has a marked effect on the rate. It was found, as King and Braverman found (17), that potassium nitrate has very little, if any, effect on the rate of solution of magnesium. The results obtained with the two metals are given in table 26.

There is evidence that at high concentrations of potassium nitrate, zinc undergoes other reactions. In regard to the absence of the effect of potassium nitrate upon the dissolution of magnesium, attention is called to the recent results of Whitby (26), who found that when magnesium reacts with acids, in the presence of air, no oxygen is consumed.

DISCUSSION OF THE RESULTS

In table 2 the relation between the velocity and the surface was clearly shown. Whether the measured surface represents the actual surface reacting or is proportional to it cannot be determined by these experiments. It may be that active areas of the surface are being used and that the chemical process involves adsorption and activation (25) at the surface, but reproducibility of the results would indicate that this is not the case.

In the water reaction sodium chloride and magnesium salts caused an increase in the rate of reaction. One explanation of the effect is that the salt dissolves the magnesium oxide or forms a soluble complex salt (19). This prevents the formation of insoluble coatings which might impede the reaction. Another explanation favored by Bancroft (1) is that the added salts peptize the magnesium oxide coating.

As has been indicated throughout the paper, the most difficult problem connected with a reaction at a metal-liquid interface is to decide whether the rate-controlling process is the chemical reaction or diffusion. King and Braverman (17), after a study of the reaction of zinc with acids following along the lines of the preliminary publication by Kilpatrick and Rushton (16), concluded, "It is impossible to decide at present whether other acids than H_3O^+ react directly with magnesium, zinc, cadmium, and marble, since previous experiments have measured rates controlled largely by diffusion rates." They reached this conclusion on the basis of certain observed facts which, in general, have been accepted as criteria of the validity of the diffusion rate theory. These are:

(1) Different solids dissolve at nearly the same rate.
(2) Stirring has a marked effect on the rate.
(3) The rate of solution is inversely proportional to the viscosity.
(4) The rates observed follow diffusion coefficients for comparable experimental conditions.
(5) The temperature coefficients are small compared to those of chemical reactions.

Consider the first point outlined above. Table 27 gives the only comparable results on a milliequivalent basis. These results are to be compared with table 26 in the experimental part of this paper. The results do not bear out a diffusion controlled process.

In regard to the second point, the effect of stirring has been thoroughly studied and the relationship $k = aR^n$ is difficult to explain on the basis of any chemical rate theory. However, owing to temperature effects it is not practicable to extend the study to such surface speeds that the thickness of the so-called diffusion layer would be such that the rate of the chemical reaction would be measured.

The results of experiments to test the effect of change in viscosity are definitely contradictory to the diffusion theory in the case of salts, and for non-electrolytes the inverse proportionality is at best qualitative.

If one attempts to compare the velocity constants for the different acids with the meager data on diffusion coefficients existing in the literature, one finds that the order for decreasing velocity constants is as follows: the acid H_3O^+, formic acid, acetic acid, citric acid, tartaric acid, and phenol. On the other hand, the diffusion coefficients are in the following order: hydrochloric acid, formic acid, acetic acid, phenol, tartaric acid, and citric acid. Of course, the exponents of the idea that the H_3O^+ ion is the only acid present might not consider that it was necessary for acids other than the H_3O^+ to diffuse to the metal. It has been shown that this conclusion is not in accord with the experimental results. It may be stated that the indefiniteness of the diffusion theory makes it especially difficult to distinguish between diffusion and any other rate-controlling process. This vagueness is particularly evident when one considers the reaction of magnesium with acids at temperatures above 50°C. It has been experimentally demonstrated that there are at least two reactions in aqueous solutions of strong acids. First, a water reaction independent of the hydrogen-ion concentration, and second, a reaction dependent on the hydrogen-ion concentration. If one assumes that the diffusion process consists of a diffusion of a hydrogen ion through a layer poorer in hydrogen ions up to the metal surface, and that this is the rate-controlling process, with subsequent diffusion of magnesium ion away from the metal surface, then what is the diffusion layer involved in the reaction of magnesium with water, which is independent of the hydrogen-ion concentration? It may be pointed out that this layer cannot be a film of hydrogen because the rate is unchanged by the addition of a depolarizer.

TABLE 27

Results of King and Braverman at 25°C.

Surface speed = 24,000 cm. per minute

METAL	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE FOR 0.007 M HCl + 0.05 M KNO_3	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE FOR 0.03 M $HC_2H_3O_2$ + 0.05 M KNO_3
Mg	0.0235	0.031
Zn	0.0215	0.032

The temperature coefficient for the reaction with the hydrogen ion is 1.7 for a 10-degree interval. Centnerszwer (8) reports 1.2 for unstirred and stirred solutions. Bonsdorff (4) obtains a value which decreases markedly with increasing temperature. The temperature coefficient for the water reaction is 1.34. Still it is difficult to picture a diffusion mechanism for the water reaction. A general criterion of the statement that chemical reactions usually have temperature coefficients greater than 2 for a 10-degree interval is that these temperature coefficients usually apply to reactions taking place in one phase and not to reactions at an interface.

In those cases where an induction period exists, i.e., where the initial rate is slower than that in a later part of the reaction, the rate during the induction period is probably governed by chemical reactions. This must be the case even though conditions favor a diffusion controlled reaction, irrespective of the induction period. If chemical reactions have high temperature coefficients, the temperature coefficient for the induction period should be greater than that of the subsequent reaction, if the latter is controlled by diffusion. There are no data in the literature sufficiently consistent to test this point.

The arguments in favor of a chemical process controlling the rate are:

(1) High temperature coefficient.

(2) Proportionality of rate to the concentration of acid present or, in general, for a number of acids

$$v = k_1C_{A_1} + k_2C_{A_2} + k_3C_{A_3} + \dots$$

(3) Independence of the rate of the H_3O^+ ion concentration in the case of weak acids.

(4) A linear relationship between the logarithm of the velocity constant and the logarithm of the acid strength.

The temperature coefficient has been discussed. It has been shown experimentally that at constant H_3O^+ concentration the rate of reaction is proportional to the concentration of the other acids present. This has been clearly demonstrated throughout the experimental work. With the phenol-phenylate buffers the H_3O^+ concentration was of the order of 1×10^{-10} *M*, and at 25°C. neither the reaction with the H_3O^+ ion nor the water reaction is more than detectable. From the experiments at 80°C. one calculates that at 25°C. by the water reaction 0.0001 milliequivalent of magnesium reacts per cm.^{2} per minute per liter. Yet in the presence of 0.1 *M* phenol 0.00775 milliequivalent reacts. It should also be remembered that the rate is proportional to the concentration of phenol.

That the rate of reaction, in the case of weak acids, is independent of the hydrogen-ion concentration is shown by the data in the tables referring to the acids in question. The rate is practically independent of the acid–base ratio in the buffer solutions. For the water reaction the point is illustrated by table 12 and figure 8.

Arguments two and three, which were given in favor of a chemical process controlling the rate, might also be advanced in favor of a modified diffusion explanation if one considers the problem from the standpoint of the extended theory of acids. In other words, if it is postulated that diffusion governs the rate, it must be admitted that in the case of an acid like acetic acid the diffusion of the molecular acid to the metal must be considered, as well as the diffusion of the hydrogen ion. Subsequently, two reactions take place at the surface of the metal. The reactions formulated by equation 1

$$\begin{aligned} &H_3O^+ + e \rightarrow H + H_2O \\ &HAc + e \rightarrow H + Ac^- \end{aligned}$$

would apply in principle to any acid. However, it is difficult to picture a diffusion mechanism for the water reaction. Whatever the rate-controlling process in these reactions, the principle that they must be considered from the viewpoint of the extended theory of acids is the thesis of this work.

Although King and Braverman conclude that it has not been proven that acids other than the H_3O^+ react with metals, they are forced to fall back on the extended theory of acids to explain their results. This is particularly true in their experiments with sodium acetate and acetic acid, and with citric and tartaric acids. In this connection the experiments in mixtures of hydrochloric and acetic acids recorded in table 16 should be noted. It is again emphasized that there are two reactions present, that due to H_3O^+ and that due to molecular acetic acid. k (acetic acid) calculated from these experiments is in agreement with k (acetic acid) calculated from experiments at low hydrogen-ion concentrations. In other words, the hydrogen-ion concentration has been changed from 1×10^{-5} *M* to 1×10^{-2} *M* and yet k (acetic acid) is unchanged.

In the preliminary paper the velocity constant was related to the acid strength of the reacting acid by an equation of the type

$$k_a = G_1 K_A{}^x \tag{13}$$

where k_a is the velocity constant and K_A the dissociation constant of the reacting acid. This equation cannot be expected to hold exactly even in homogeneous catalysis for different types of acid. By different types is meant different charge types such as H_3O^+, HSO_4^- and uncharged acids like acetic acid and water. In fact the relationship seems to hold exactly only for an homologous series (15). The effect of the charge of the base in a reaction showing basic catalysis has been demonstrated by Brönsted and Volquartz (7), and more recently by Pedersen (22).

Furthermore, in addition to the difference in type, the statistical factor must be taken into account. When this is done, the general equation becomes

$$k_a = G_1 K_A^{\,x} q^x p^{1-x} \tag{14}$$

where k_a is the velocity constant for the acid considered, G_1 is a constant, K_A is the acid strength constant, q the number of positions at which a proton can be attached to the molecule of the conjugate base, p the number of ionizable hydrogen atoms in the molecule, and x has a value greater than zero and less than one. To test this relationship the equation can be put in the form

TABLE 28

Data necessary for testing relationship between velocity constant and acid strength

ACID	q	p	K_A	LOG $\frac{q}{p} K_A$	k_{2000}	LOG $\frac{k}{p}$
H_3O^+	1	1	55.6	1.745	1.33	0.124
Bisulfate	4	1	5.1×10^{-2}	−0.690	0.519	−0.285
Dichloroacetic	2	1	5×10^{-2}	−1.000	0.592	−0.228
Tartaric	2	2	1.45×10^{-3}	−2.838	0.712	−0.448
Chloroacetic	2	1	1.41×10^{-3}	−2.550	0.355	−0.450
Citric	2	3	1.3×10^{-3}	−3.160	1.119	−0.428
Formic	2	1	1.8×10^{-4}	−3.444	0.443	−0.354
Glycollic	2	1	1.36×10^{-4}	−3.566	0.327	−0.485
Dihydrogen citrate	4	2	4.7×10^{-5}	−4.027	0.496	−0.605
Acetic	2	1	1.8×10^{-5}	−4.444	0.284	−0.547
Bitartrate	4	1	1.27×10^{-5}	−4.294	0.223	−0.652
Pyridinium	1	1	7.4×10^{-6}	−5.131	0.507	−0.295
Monohydrogen citrate	6	1	2.2×10^{-6}	−4.879	0.185	−0.733
Phenol	1	1	1.1×10^{-10}	−9.959	0.0809	−1.092
Water	1	1	1.1×10^{-16}	−15.959	2.28×10^{-4}	−3.432
Results of Tarle						
H_3O^+	1	1	55.6	1.745	1.33	0.090
1,2,5-Dioxybenzoic	2	1	1.8×10^{-3}	−2.666	0.774	−0.111
β-Resorcylic	2	1	5.15×10^{-4}	−2.987	0.511	−0.292
Tricarballylic	2	3	2.2×10^{-4}	−3.839	0.489	−0.788
Acetic	2	1	1.8×10^{-5}	−4.444	0.390	−0.409

$$\frac{k_a}{p} = G_1 \left(K_A \frac{q}{p} \right)^x$$

If $\log \frac{k_a}{p}$ is plotted against $\log \frac{q}{p} K_A$, the points for each charge type should fall in a straight line with slope x and intercept G_1. Table 28 summarizes

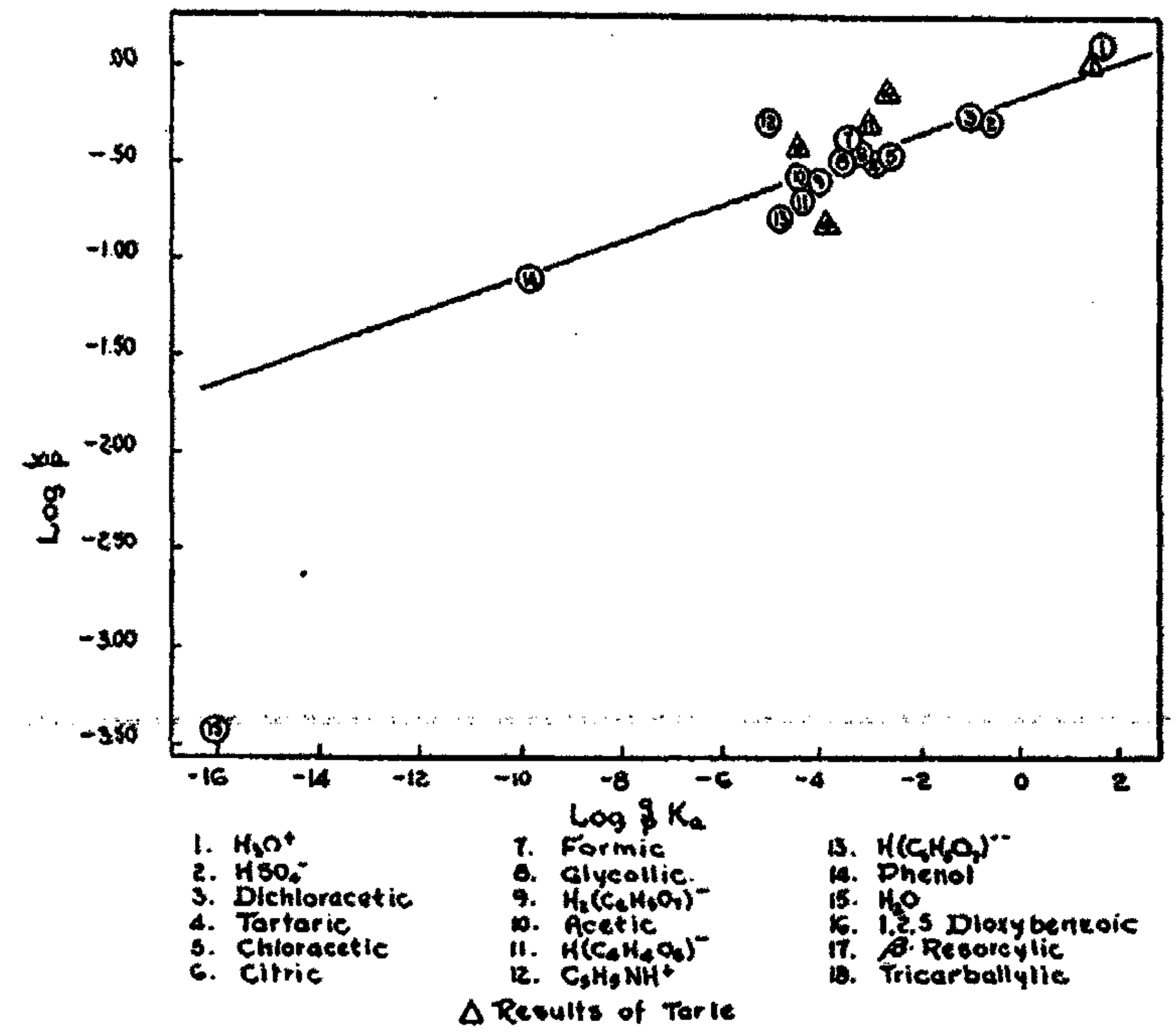


FIG. 15. RELATION BETWEEN VELOCITY CONSTANT k AND ACID STRENGTH

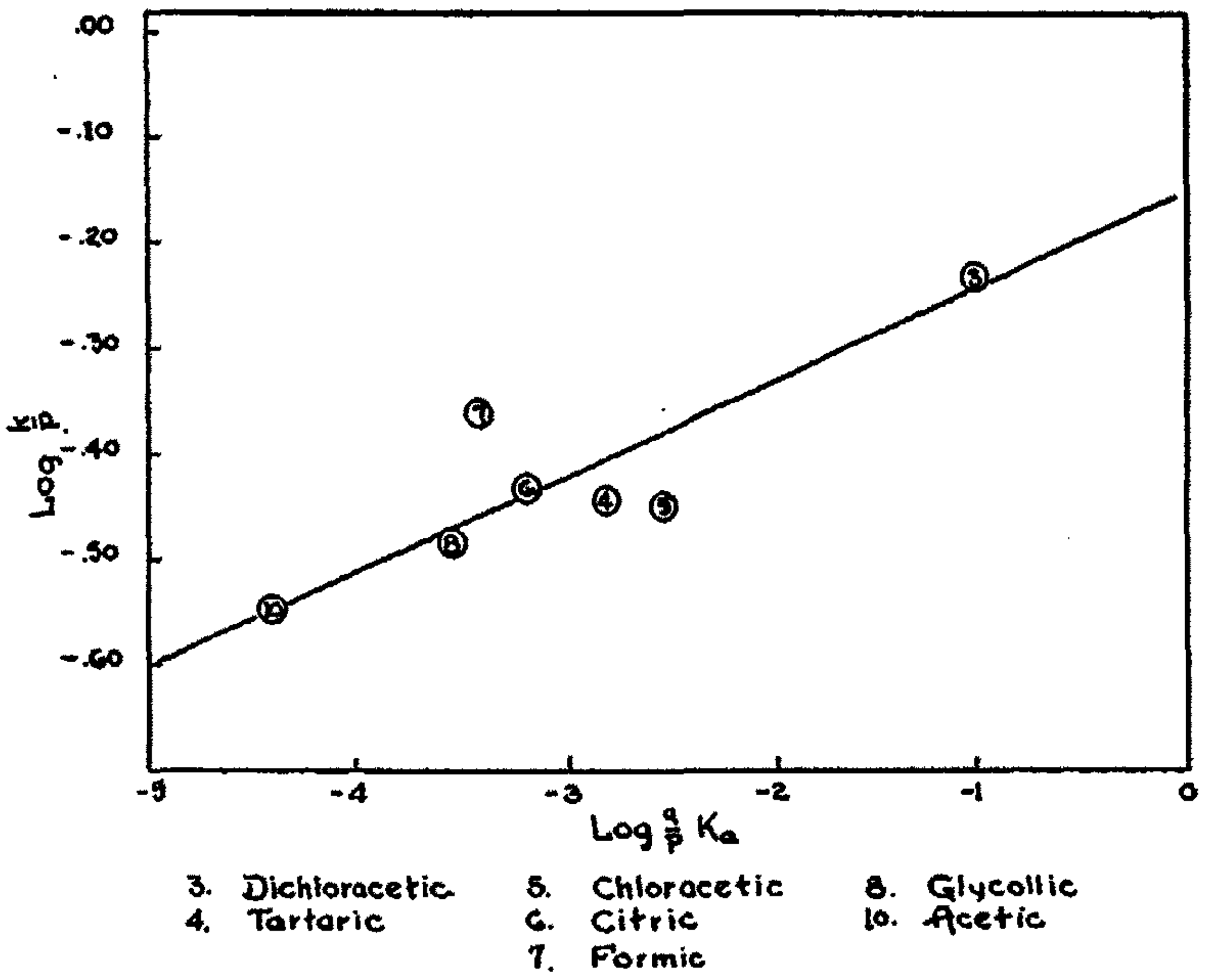


FIG. 16. RELATION BETWEEN VELOCITY CONSTANT k AND ACID STRENGTH

the data necessary for testing the general relationship between the velocity constant and the acid strength of the different acids.

Figure 15 shows the relationship for all acids studied and in addition includes the results of Tarle (24). Tarle's results are not strictly comparable with those in this work, since his data are not complete enough to determine surface speed.

Figure 16 shows on a larger scale the small section of figure 15 which covers the carboxylic acids. While the agreement with the theory is not exceptional, it is to be noted that there is a general relationship between the velocity constant and the acid strength. From theoretical considerations it is to be expected that for equal strength the positively charged acids will show greater velocity constants. This is borne out by the position of hydrogen ion and pyridinium ion in the plot. From the same considerations it is to be expected that a negatively charged acid will fall below the line drawn through the uncharged acids. This is also evident from the plot. The value of x is 0.091.

SUMMARY

(1) Rates of solution of magnesium in aqueous solution of acids have been determined by four different experimental methods, and the results are found to be reproducible and in agreement for the different samples of magnesium.

(2) The kinetic law for the reaction has been derived and extensively tested over the whole course of the reaction. The general kinetic equation is

$$v = k_1 C_{\mathrm{H_2O}} + k_2 C_{\mathrm{H_3O^+}} + k_3 C_{\mathrm{A}} + \ldots\ldots \text{ etc.}$$

where A represents an acid other than the H_3O^+ or water.

(3) For strong acids the primary reaction is with the H_3O^+ ion.

(4) For weak acids the rate of reaction is not proportional to the hydrogen-ion concentration, but rather the increase in rate is proportional to the concentration of the acid present.

(5) A relation has been found between the surface speed of the metal and the rate of its reaction.

(6) The effect of viscosity has been investigated.

(7) The temperature coefficient has been determined for the water reaction, the H_3O^+ reaction, and the molecular acetic acid reaction.

(8) The results have been discussed from the standpoint of the diffusion theory and the Brönsted-Kilpatrick theory. The results are definitely not in agreement with the "old diffusion theory," but may be thought of in terms of a modified diffusion theory based on the extended theory of acids. However, any modification must account for the water reaction.

(9) On the basis of the Brönsted-Kilpatrick theory the velocity constants have been related to the acid strength.

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THE CALCULATION OF PARTIAL MOLAL SOLUTE QUANTITIES AS FUNCTIONS OF THE VOLUME CONCENTRATION, WITH SPECIAL REFERENCE TO THE APPARENT MOLAL VOLUME[1]

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The partial molal solute quantity $\bar{G}_2$ is important and frequently used in thermodynamic calculations. Many methods have been developed for calculating $\bar{G}_2$ from a particular extensive property, usually through the intermediate apparent molal quantity Φ (G_2), but most of these are based upon the weight concentration. Lewis and Randall (7) outlined various methods, both analytical and graphical. To mention only a few of the other methods most recently used: La Mer and Gronwall (6) analytically derived a fourth order equation for the partial molal volume as a function of the molality. Adams and Gibson (1) calculated the partial specific volume from the apparent specific volume plotted against the square root of the weight fraction. Randall and Rossini (9) developed an equation for calculating the partial from the apparent molal heat capacity as a function of the square root of the molality. Young and Vogel (14) discussed at length methods of calculating partial molal quantities in general, but dealt only with equations based on weight concentration.

Within recent years, however, experimental evidence has shown, in the case of most electrolytes, a linear relationship between many apparent molal properties and the square root of the volume concentration, which holds even in concentrated solutions. This relationship in the case of $\Phi(V_2)$, discovered by Masson (8), has been checked by the very careful measurements of Geffcken (2, 3) and also by Scott (13). Moreover, Redlich and Rosenfeld (10) derived from the Debye-Hückel theory an equation showing that $\bar{V}_2$, and hence also $\Phi(V_2)$, should be linear functions of $c^{\frac{1}{2}}$ at very *low* concentrations. The same relationship was found in the case of the apparent molal compressibility by the present author, who discussed the experimental and theoretical aspects of this problem in a recent article (4). Such a simple and general relationship seems an ideal starting

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[1] Some conclusions in this article were briefly discussed in the Symposium on Electrolytes held at the Washington meeting of the American Chemical Society, March, 1933.

point in calculating partial molal quantities. This paper indicates how such calculations may be made.

DEFINITIONS

G is any extensive property of a solution containing n_1 and n_2 moles of solvent and solute of molecular weights M_1 and M_2, respectively. The corresponding *apparent* molal solute property is defined thus:

$$\Phi\,(G_2) = (G - n_1\overline{G}_1{}^0)/n_2 \qquad (1)$$

and the *partial* molal properties of solute and solvent are given by the equations

$$\overline{G}_2 = \left(\frac{\partial G}{\partial n_2}\right)_{n_1} \qquad (2)$$

and

$$\overline{G}_1 = \left(\frac{\partial G}{\partial n_1}\right)_{n_2} \qquad (2')$$

The superscript ^{0} is used at zero concentration. d and d_1 are the densities of solution and of solvent, c is the concentration (moles of solute per liter of solution), and m is the molality (moles of solute per 1000 g. of water).

The apparent molal volume is defined by any of the following equations:

$$\Phi\,(V_2) = \frac{V - n_1\overline{V}_1{}^0}{n_2} \qquad (3)$$

$$\Phi\,(V_2) = \frac{1000}{c} - \frac{1}{d_1}\left[\frac{1000d}{c} - M_2\right] \qquad (4)$$

$$\Phi\,(V_2) = \frac{1000}{c} - \frac{1000}{md_1} \qquad (5)$$

CALCULATION OF THE APPARENT MOLAL VOLUME

The usual method is to calculate $\Phi(V_2)$ directly from density measurements, using equation 4. These values are then plotted against $c^{\frac{1}{2}}$ and the best curve fitted to them. The following method is, however, much simpler. Rearrange equation 4 as follows:

$$1000\left(\frac{d_1 - d}{c}\right) = d_1\,\Phi\,(V_2) - M_2 \qquad (6)$$

If we now plot $F \equiv 1000\left(\dfrac{d_1 - d}{c}\right)$ against $c^{\frac{1}{2}}$ we can calculate Φ as a function of $c^{\frac{1}{2}}$, for the intercept

$$F^0 = d_1\Phi^0 - M_2$$

and the slope

$$\frac{\partial F}{\partial c^{\frac{1}{2}}} = d_1 \frac{\partial \Phi}{\partial c^{\frac{1}{2}}}$$

hence

$$\Phi^0 = \frac{F^0 + M_2}{d_1} \tag{7}$$

and

$$\frac{\partial \Phi}{\partial c^{\frac{1}{2}}} = \frac{1}{d_1} \frac{\partial F}{\partial c^{\frac{1}{2}}} \tag{8}$$

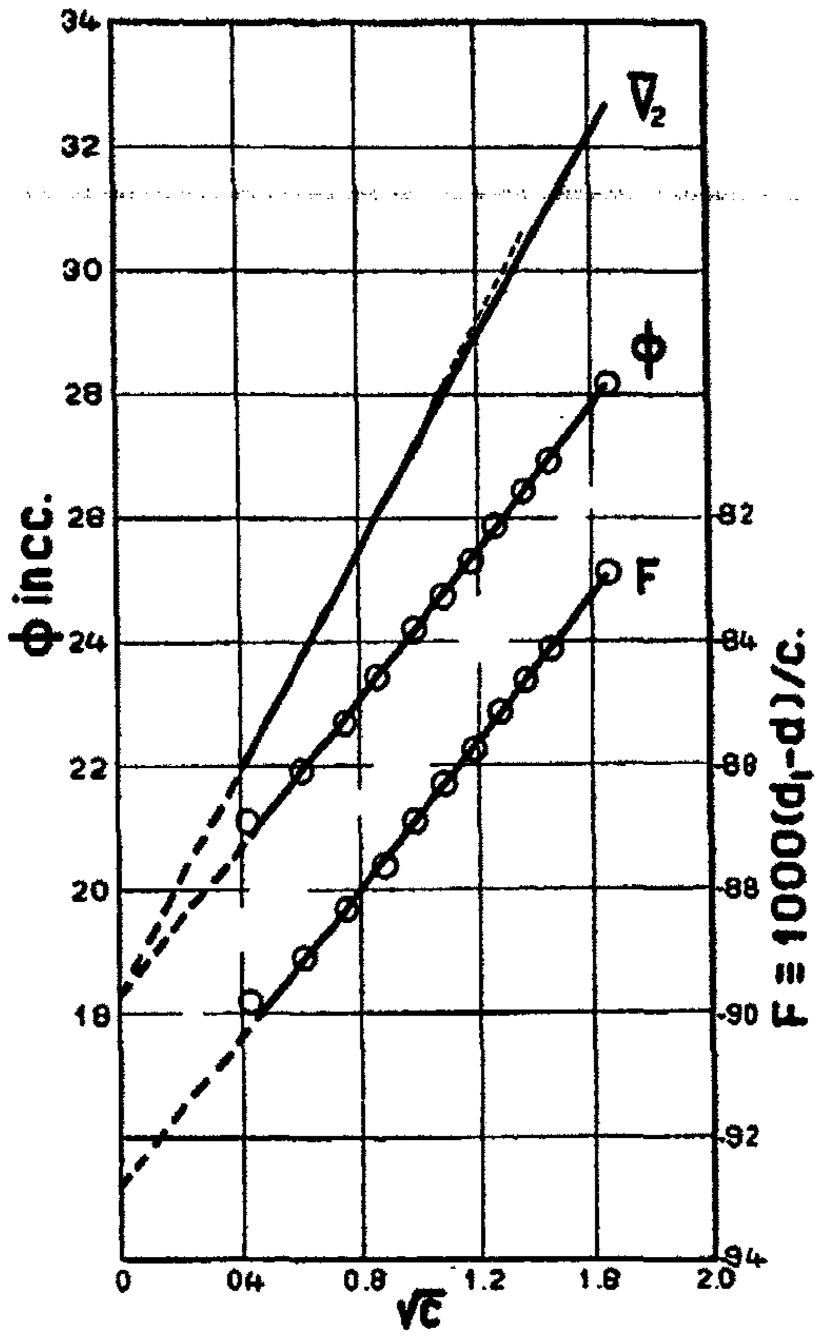

FIG. 1. Φ AND F FOR CALCIUM CHLORIDE AT 25°C.

The experimental points are thus smoothed by the F plot, and the extra calculations, involving the d_1 and M_2 terms, are required only *once*, to obtain the final values of the coefficients.

In order to illustrate the method, the density data for calcium chloride at 25°C., taken from the International Critical Tables (5), have been used to calculate F and Φ. Both are linear functions[2] of $c^{\frac{1}{2}}$ up to 3 c as may be seen in figure 1. The equation for F was found to be

$$F = -92.81 + 5.97c^{\frac{1}{2}}$$

whence,

$$\Phi = 18.24 + 5.99c^{\frac{1}{2}}$$

A direct plot of Φ values gives the almost identical result,

$$\Phi = 18.26 + 5.99c^{\frac{1}{2}}$$

The method of calculating Φ from F is not limited to the special case in which each is a linear function of $c^{\frac{1}{2}}$. If F is *any* known function of $c^{\frac{1}{2}}$, the corresponding equation for Φ can easily be calculated. Thus, if

$$F = F^0 + F\ (c^{\frac{1}{2}})$$

$$\Phi = \frac{F^0 + M_2}{d_1} + \frac{1}{d_1} F\ (c^{\frac{1}{2}}) \tag{9}$$

W. C. Root (12) has derived a useful equation for the density of a solution obeying Masson's law. Using molal concentration this becomes

$$d = d_1 + Ac + Bc^{\frac{3}{2}}$$

This equation may be generalized as follows:

$$d = d_1 - \frac{F^0c}{1000} - \frac{c}{1000} F\ (c^{\frac{1}{2}}) \tag{10}$$

or,

$$d = d_1 + \left[\frac{M_2 - d_1\Phi^0}{1000}\right] c - \frac{d_1c}{1000} \Phi\ (c^{\frac{1}{2}}) \tag{11}$$

In particular, if Φ can be expressed as a power series in terms of $c^{\frac{1}{2}}$, the corresponding equation for the density will be

$$d = d_1 + Ac + Bc^{\frac{3}{2}} + Cc^2 + \text{— —} \tag{11'}$$

where the coefficients A, B, C are calculable from those of the Φ equation.

THE CALCULATION OF $\overline{G}_2$ FROM $\Phi(G_2)$

The equation connecting these two functions is derived as follows: Differentiating equation 1 gives

$$\overline{G}_2 = \left(\frac{\partial G}{\partial n_2}\right)_{n_1} = \Phi(G_2) + \frac{\partial \Phi(G)}{\partial \ln\ n_2} = \Phi(G_2) + \frac{\partial \Phi(G_2)}{\partial c} \cdot \frac{\partial c}{\partial \ln\ n_2} \tag{12}$$

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[2] The relationship does not hold at higher concentrations.

Now

$$c = \frac{1000\, d}{M_2 + \left[\frac{n_1}{n_2} M_1\right]} \tag{13}$$

Eliminating d between equations 4 and 13 and rearranging terms gives

$$\Phi(V_2) = \frac{1000}{c} - \frac{M_1}{d_1} \cdot \frac{n_1}{n_2} \tag{14}$$

Differentiating equation 14 with respect to $\ln n_2$ and rearranging terms gives

$$\left(\frac{\partial c}{\partial \ln n_2}\right)_{n_1} = c \left[\frac{1000 - c\Phi(V_2)}{1000 + c^2 \dfrac{\partial \Phi(V_2)}{\partial c}}\right] \tag{15}$$

Combining equations 12 and 15 gives the desired result:

$$\overline{G}_2 = \Phi(G_2) + c \left[\frac{1000 - c\Phi(V_2)}{1000 + c^2 \dfrac{\partial \Phi(V_2)}{\partial c}}\right] \frac{\partial \Phi(G_2)}{\partial c} \tag{16}$$

Whence,[3]

$$\overline{V}_2 = \Phi(V_2) + c \left[\frac{1000 - c\Phi(V_2)}{1000 + c^2 \dfrac{\partial \Phi(V_2)}{\partial c}}\right] \frac{\partial \Phi(V_2)}{\partial c} \tag{16'}$$

If Φ is expressed as a function of $c^{1/2}$ instead of c, equation 16 becomes

$$\overline{G}_2 = \Phi(G_2) + c^{1/2} \left[\frac{1000 - c\Phi(V_2)}{2000 + c^{3/2} \dfrac{\partial \Phi(V_2)}{\partial c^{1/2}}}\right] \frac{\partial \Phi(G_2)}{\partial c^{1/2}} \tag{17}$$

and

$$\overline{V}_2 = \Phi(V_2) + c^{1/2} \left[\frac{1000 - c\Phi(V_2)}{2000 + c^{3/2} \dfrac{\partial \Phi(V_2)}{\partial c^{1/2}}}\right] \frac{\partial \Phi(V_2)}{\partial c^{1/2}} \tag{17'}$$

This equation is perfectly general, and does not impose any particular functional relation on Φ and $c^{1/2}$. In the particular case where, as with most

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[3] This equation was given by Geffcken (reference 2, equation 4). He discussed the relationship between Φ (V_2) and $\overline{V}_2$ in the dilute solution, but did not use this equation in actual calculation of values of $\overline{V}_2$.

electrolytes, $\Phi(G_2)$ and $\Phi(V_2)$ are linear functions of $c^{1/2}$, equation 17 can be further simplified to

$$\bar{G}_2 = \Phi^0(G_2) + \left[\frac{3000 - c\Phi^0(V_2)}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}}\right]\frac{\partial\Phi(G_2)}{\partial c^{1/2}}\,c^{1/2} \tag{18}$$

If we are concerned with V_2, this equation becomes

$$\bar{V}_2 = \Phi^0(V_2) + \left[\frac{3000 - c\Phi^0(V_2)}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}}\right]\frac{\partial\Phi(V_2)}{\partial c^{1/2}}\,c^{1/2} \tag{18'}$$

At infinite dilution,

$$\bar{G}_2^0 = \Phi^0(G_2)$$

At low concentrations, $c\Phi^0(V_2)$ and $c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}$ are small compared with 3000 and 2000, respectively, and, as Geffcken pointed out,

$$\bar{V}_2 = \Phi^0(V_2) + 3/2\,\frac{\partial\Phi(V_2)}{\partial c^{1/2}}\,c^{1/2} \tag{19}$$

The limiting form of the equation at low concentration is similar to that developed by Randall and Rossini (9) for calculating the partial from the apparent molal heat capacity expressed as a function of the square root of the molality, namely,

$$\bar{C}_{p_2} = \Phi^0(C_{p_2}) + 3/2\,\frac{\partial\Phi(C_{p_2})}{\partial m^{1/2}}\,m^{1/2}$$

WEIGHT AND VOLUME CONCENTRATION

Plots against $c^{1/2}$ do not differ very much from those against $m^{1/2}$ at very low concentrations, since at the limit m is proportional to c. However, the difference may become appreciable at higher concentration. In general, rearranging equation 5 gives the relationship between c and m, namely[4]

$$\frac{c}{m} = d_1\left[1 - \frac{c\Phi(V_2)}{1000}\right] \tag{20}$$

c and m may be almost identical if $\Phi(V_2)$ is small or negative; or very different, if Φ is large. To illustrate this strikingly specific character of c/m we have chosen two univalent electrolytes as different as possible,

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[4] The ratio is given by Geffcken (2) without the d_1. c and m are proportional and *not* equal, although the difference is small.

namely, lithium hydroxide and cesium iodide. The corresponding equations for $\Phi(V_2)$ are[5]

$$\Phi(V_2) = -6.00 + 3.00c^{1/2}$$

$$\Phi(V_2) = 47.9 + 1.47c^{1/2}$$

The values of c/m and $c^{1/2}/m^{1/2}$ calculated from equation 20 are given in table 1 at several values of $c^{1/2}$ and are plotted in figure 2.

TABLE 1

Values of c/m and $c^{1/2}/m^{1/2}$ calculated from equation 20

$c^{1/2}$	LiOH		CsI	
	c/m	$c^{1/2}/m^{1/2}$	c/m	$c^{1/2}/m^{1/2}$
0.0	0.9971	0.9985	0.9971	0.9985
0.5	0.9982	0.9991	0.9849	0.9924
1.0	1.0001	1.0000	0.9478	0.9736
1.5	1.0005	1.0002	0.8847	0.9406
2.0	0.9971	0.9985	0.7943	0.8800

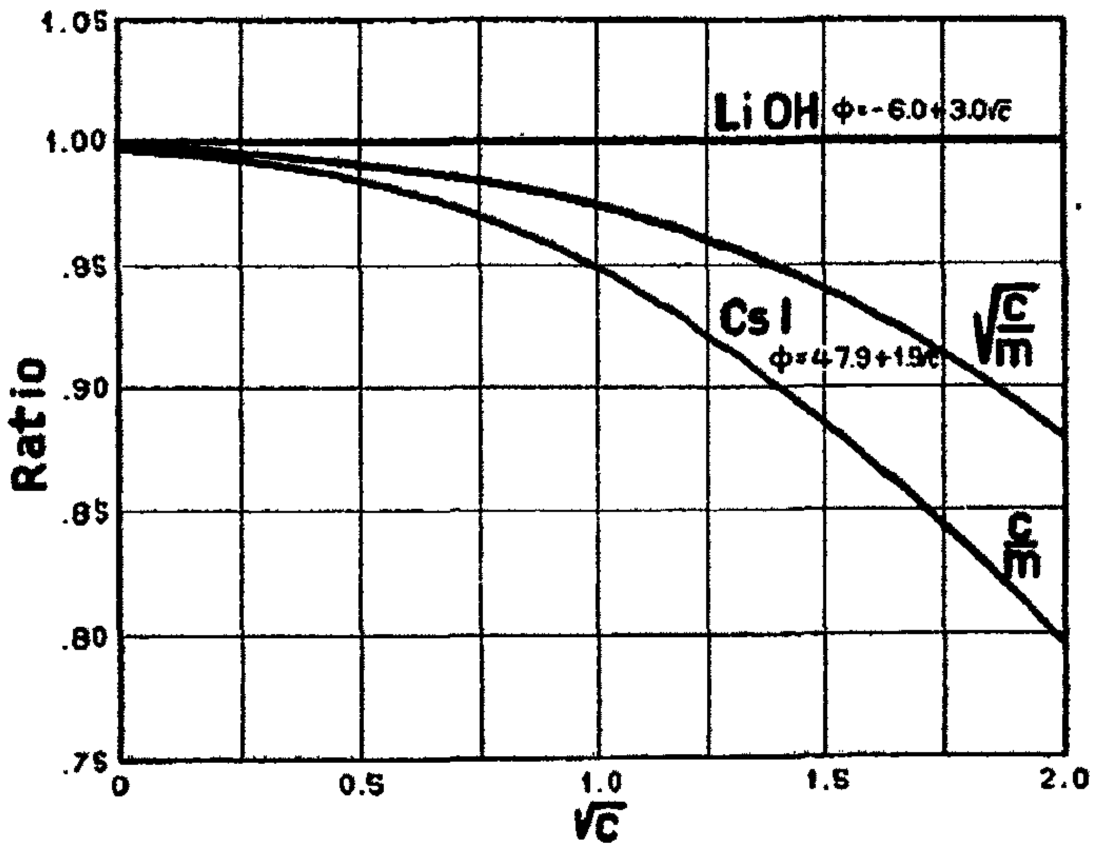

FIG. 2. DEPENDENCE OF c/m RATIO ON $\Phi(V_2)$

CALCULATION OF $\overline{V}_2$

As an application of equation 18′ we have taken the case of calcium chloride which was previously mentioned. The equation for the partial molal volume is

$$\overline{V}_2 = 18.25 + \left[\frac{3000 - 18.25c}{333.89 + c^{3/2}}\right] c^{1/2}$$

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[5] The first was calculated from the density data of the International Critical Tables, 1st edition, Vol. III, p. 76; the second was taken from Geffcken (2).

The graph of this function is included in figure 1. Notice that $\overline{V}_2$ is nearly linear up to about 1 *c*. It is only above this concentration that the curve for $\overline{V}_2$ deviates appreciably from the dotted line which represents the limiting slope of the tangent.

In order to test the more general case to which equation 17′ is applicable we have studied the very precise specific volume data for ammonium nitrate solutions from 0.1 to 11 *c* at 25°C. which were obtained by Adams and Gibson (1). These particular data were chosen because the authors had made very careful computations on a *weight* basis with which we could compare the results obtained from our equation. Moreover, in this case $\Phi(V_2)$ is large, so that the weight and volume scales diverge sharply at high concentration. We calculated values of $\Phi(V_2)$ from their data at fourteen points and found that they could be represented fairly well by the linear equation

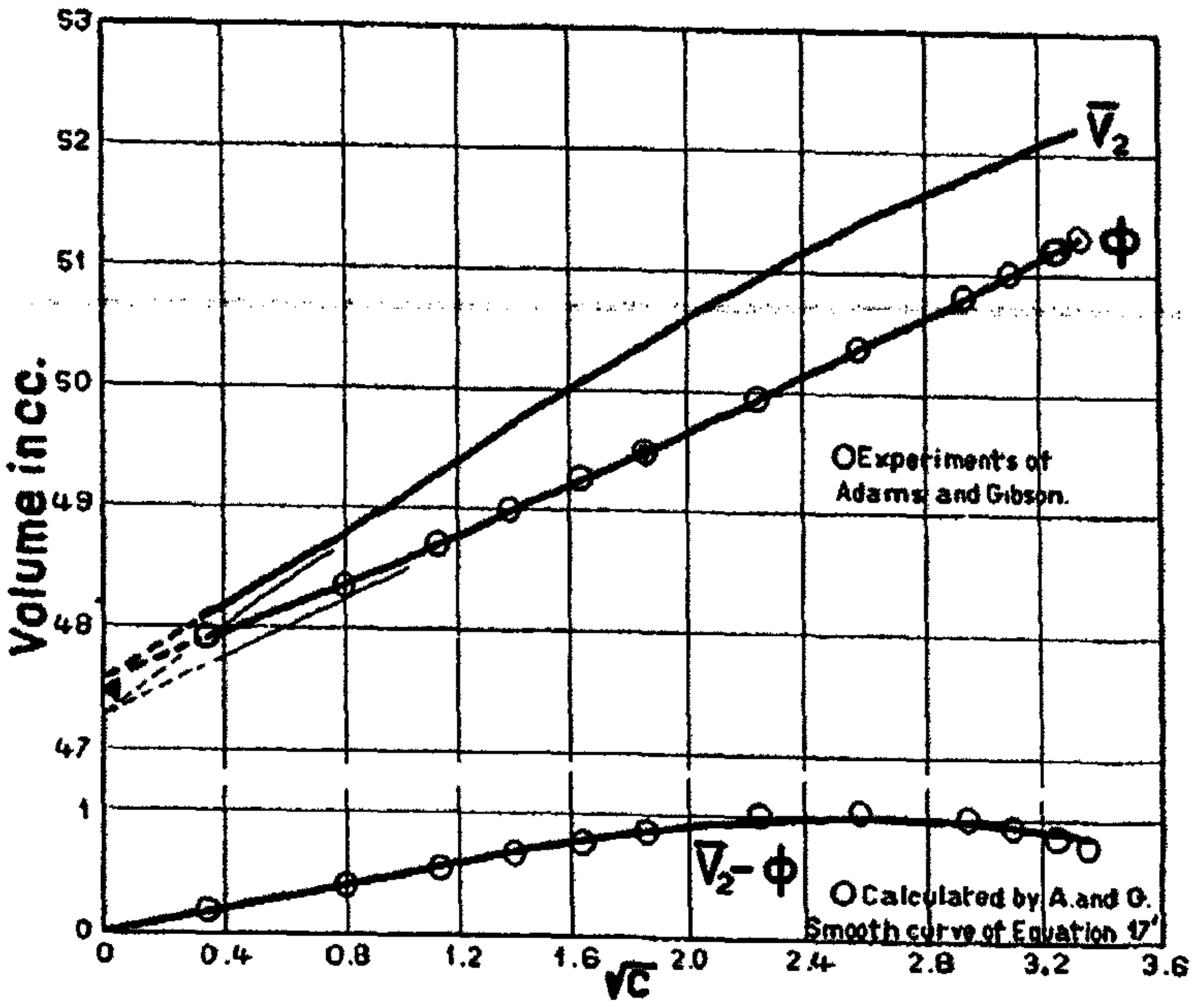

FIG. 3. AMMONIUM NITRATE AT 25°C.

$$\Phi = 47.280 + 1.2049c^{\frac{1}{2}}$$

However, appreciably better agreement was given by a second order equation in $c^{\frac{1}{2}}$, namely,

$$\Phi = 47.558 + 0.966c^{\frac{1}{2}} + 0.0474c$$

The average deviation in *d* calculated from the linear equation is 4.6 × 10^{-5} and from the quadratic curve 3.2 × 10^{-5}. The improved agreement was particularly noticeable in the lower concentrations, and for this reason the extrapolation to zero concentration is much better with the quadratic equation. This is shown by the heavy line in figure 3. The lighter line represents the linear equation which extrapolates to an appreciably lower point. The two curves are practically identical above about 0.25 *c*.

From the second order equation for Φ we calculated the corresponding equation for *d*, of the form indicated by equation 11′, namely:

$$d = 0.997077 + 0.032628c - 9.63 \times 10^{-4}\, c^{3/2} - 4.73 \times 10^{-5}\, c^{2}$$

In calculating the partial molal volume, equation 17′ is changed to the form

$$\overline{V}_2 - \Phi(V_2) = \left[\frac{1000 - c\Phi(V_2)}{2000 + \dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}\, c^{3/2}}\right] c^{1/2}$$

where

$$\frac{\partial\Phi(V_2)}{\partial c^{1/2}} = 0.966 + 0.948c^{1/2}$$

Our equation for $\overline{V}_2 - \Phi(V_2)$ is plotted at the bottom of figure 3. The equation for $\overline{V}_2$ is likewise included. Calculations from the linear and quadratic equations for Φ differ appreciably only below 0.25 *c*.

Adams and Gibson calculated φ (apparent volume per gram) and $\overline{V}_2$ (partial volume per gram). Plotting φ against the square root of the *weight fraction*, x_2, two equations were required to cover the whole range of concentration, namely:

$$\varphi = 0.59318 + 0.049161x_2^{1/2} \qquad (0 < x_2 < 0.10)$$
$$\varphi = 0.594118 + 0.043431x_2^{1/2} + 0.020524x_2^{3/2} \qquad (x_2 > 0.10)$$

They used the first equation in extrapolating to zero concentration. Our *molal* properties, $\Phi(V_2)$ and $\overline{V}_2$ are obtained by multiplying their values by the molecular weight (80.047). Their extrapolated value for $\Phi^0(V_2)$, indicated by the black triangle in figure 3, lies between our values extrapolated by the quadratic and linear equations. It is considerably nearer the former and agrees very well with our conclusions.

They calculated the partial volume by substituting in the equation

$$\bar{v}_2 = x_1x_2\frac{\partial\varphi}{\partial x_2} + \varphi$$

They evaluated the tangent $\dfrac{\partial\varphi}{\partial x_2}$ by tabular difference plots of φ and also checked the values of $2\bar{v}_2$ analytically from their interpolation equations.

A comparison of the results obtained by the weight and volume plots, given in table 2, illustrates the extremely good agreement in almost all cases. In figure 3, the values of Adams and Gibson for $\overline{V}_2 - \Phi(V_2)$ are indicated by circles on the plot of our equation. The only appreciable deviations are shown at the two highest concentrations.

In comparing the two different methods of calculation the volume concentration plot is simpler, since one equation will cover the whole range of concentration. The weight fraction method requires *two* equations with different values for φ^0 as well as for the coefficient of $x_2^{\frac{1}{2}}$. Moreover, the volume plot smoothes the $\overline{V}_2$ curve in accordance with our present knowledge of simple functional relationships. The advantage of using a function which has theoretical justification rather than an empirical equation is particularly evident in the extrapolation to zero concentration. Redlich and Rosenfeld (11) illustrate strikingly the difference between a linear plot of $\overline{V}_2$ against $c^{\frac{1}{2}}$ and the fourth order empirical equation of La Mer and Gronwall, which passes through the same points and yet extrapolates to a very different value.

TABLE 2

Ammonium nitrate at 25°C.—Comparison of methods

x_2	c	Φ (Gucker)	$10^3 \Delta \Phi =$ "obsd." − calcd.*	$\overline{V}_2 - \Phi$ (Gucker)	$\overline{V}_2 - \Phi$ (A.&G.)	$10^2 \Delta$ † (G − A.&G.)	$\overline{V}_2$ (Gucker)	$10^2 \Delta \overline{V}_2$ (G − A. & G.)
0.00	0.0	47.558	(−80)	0.00	0.00	0	47.56	8
0.01	0.125	47.906	−30	0.18	0.19	−1	48.08	1
0.05	0.635	48.358	−6	0.40	0.40	0	48.76	1
0.10	1.297	48.720	6	0.57	0.55	2	49.29	1
0.15	1.984	49.013	−7	0.70	0.68	2	49.71	2
0.20	2.700	49.273	−7	0.80	0.78	2	50.07	2
0.25	3.444	49.514	−13	0.88	0.87	1	50.39	2
0.35	5.024	49.961	−5	0.98	1.01	−3	50.94	−3
0.45	6.733	50.384	6	1.03	1.05	−2	51.41	−3
0.55	8.584	50.795	11	1.01	1.01	0	51.80	−1
0.60	9.567	50.999	10	0.98	0.95	3	51.98	2
0.65	10.590	51.204	−1	0.93	0.86	7	52.13	7
0.68	11.224	51.326	−11	0.89	0.79	10	52.22	11
						Av. = 3		Av. = 3

* "obsd." values were slightly corrected to even concentrations by Adams and Gibson. Calcd. values from our equation.

† $\Delta = (\overline{V}_2 - \Phi)\ (G) - (\overline{V}_2 - \Phi)\ (A.\&G.)$

SUMMARY

We have described a simple method of calculating the apparent molal volume, $\Phi(V_2)$, as a function of $c^{\frac{1}{2}}$, which is shown to give the same results as the usual more laborious method.

We have compared volume and weight concentration. The ratio c/m is a specific property of the individual solute which depends on $\Phi(V_2)$ and may vary from 1 to less than 0.8.

We have developed a general equation for calculating any partial molal solute quantity, $\bar{G}_2$, from the corresponding apparent property $\Phi(G_2)$ as a function of c, and a special equation applicable when Φ is a linear function of $c^{\frac{1}{2}}$. Since many apparent molal properties of most electrolytes and some non-electrolytes show such a linear relationship, this equation has a very wide applicability.

We have shown the application of these equations in calculating partial molal volumes. In the case of ammonium nitrate we have compared our values of $\bar{V}_2$ calculated from a single equation for $\Phi(V_2)$ with those which Adams and Gibson calculated from two weight fraction plots. Our results are in substantial agreement with theirs, but theory and numerical simplicity seem to favor the volume concentration method.

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A NOTE ON THE COMPUTATION OF THE PARTIAL VOLUMES OF THE COMPONENTS IN AQUEOUS SOLUTIONS

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Certain advantages in convenience and accuracy arising from the use of volume concentrations rather than weight concentrations in the computation of those properties of phases of variable composition which depend on slopes, such as the partial volumes of the components, have been emphasized by Gucker in a recent article (6). Indeed, it appears that the apparent volume of the solute is more closely a linear function of the square root of the volume concentration than of the square root of the weight concentration. The formula for calculating the partial or partial molal volumes of the solute from volume concentration data is, it must be admitted (4), rather clumsy. If, however, one computes the partial volume of the *solvent* directly from the density data, one finds that the formulas involved are extremely simple and seem to furnish perhaps one of the most elegant ways of calculating partial or partial molal volumes. The object of this note is to call attention to the equation for computing the partial volumes of the solvent from density–volume concentration data and to apply the equation to data on solutions of sodium chloride, sodium sulfate, potassium chloride, potassium iodide, and lithium nitrate.

The symbols used are as follows:

V = Total volume of phase containing m_1 grams of solvent and m_2 grams of solute.
v = Specific volume of the phase.
v_w = Specific volume of pure solvent.
v_1 = Partial volume (per gram) of solvent in a given phase.
v_2 = Partial volume (per gram) of solute in a given phase.
ϕ_2 = Apparent volume (per gram) of solute in a given phase.
x_1 and x_2 = Weight fractions of solvent and solute, respectively.
ρ_w = Density of pure solvent.
ρ = Density of phase.
$\rho_1 = \frac{1}{v_1}$ = Fictive density[1] of the solvent in a given phase.

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[1] The *fictive density* of a component in a solution may be defined as the reciprocal of its partial volume. The term *fictive volume* is frequently used for the quantity which is called the *partial volume* in this paper. The term *partial volume* is preferred as it emphasizes the definition and is closely allied to the partial molal volume.

c_2 = Concentration of solute in grams per cubic centimeter of solution $= \rho x_2$.

By definition

$$V = m_1 v_w + m_2 \phi_2 \tag{1}$$

and

$$v_1 = \left(\frac{dV}{dm_1}\right)_{P,T,m_2} \tag{2}$$

Hence

$$\left(\frac{d\phi_2}{dm_1}\right)_{P,T,m_2} = \frac{v_1 - v_w}{m_2} \tag{3}$$

As

$$c_2 = \frac{m_2}{V}$$

it follows that

$$v_1 = -\frac{m_2}{c_2}\frac{dc_2}{dm_1} \tag{4}$$

From equations 3 and 4 it may readily be shown that

$$v_1 = -\frac{1}{c_2^2}\frac{dc_2}{d\phi_2}(v_1 - v_w) \tag{5}$$

or

$$v_1 = \frac{v_w}{1 + c_2^2 \dfrac{d\phi_2}{dc_2}} \tag{6}$$

If the variable be changed from c_2 to $c_2^{\frac{1}{2}}$, we obtain equations 7 and 8:

$$v_1 = \frac{v_w}{1 + \frac{1}{2} c_2^{\frac{3}{2}} \dfrac{d\phi_2}{dc_2^{\frac{1}{2}}}} \tag{7}$$

or

$$\rho_1 = \rho_w + \frac{1}{2} c_2^{\frac{3}{2}} \frac{d\phi_2}{dc_2^{\frac{1}{2}}} \rho_w \tag{8}$$

Now Gucker has shown that if

$$f = \frac{\rho_w - \rho}{c_2} \tag{9}$$

then

$$\rho_w \phi_2 = f + 1 \tag{10}$$

and that

$$\rho_w \frac{d\phi_2}{dc_2^{1/2}} = \frac{df}{dc_2^{1/2}} \tag{11}$$

Thus, as a final expression for the fictive density of the solvent in a phase we have equation 12:

$$\rho_1 = \rho_w + \frac{1}{2} c_2^{3/2} \frac{df}{dc_2^{1/2}} \tag{12}$$

Equations 12 and 17′ are particularly applicable to gaseous solutions where the data are frequently expressed in tables with the density as entry and the concentration in mass per unit volume as argument.

As the chief value of equation 12 lies in the presumption that ϕ_2 or f is a linear function of the square root of the volume concentration, it was considered desirable to determine by the method of least squares how closely equation 13 represents good density data over the entire range.

$$-f = \frac{\rho - \rho_w}{c_2} = a + bc_2^{1/2} \tag{13}$$

$$\rho - \rho_w = ac_2 + bc_2^{3/2} \tag{14}$$

It is a relatively simple matter to determine the coefficients a and b in equation 13 by the method of least squares, as

$$a = -\frac{\begin{vmatrix} \sum f & \sum c_2^{1/2} \\ \sum fc_2^{1/2} & \sum c_2 \end{vmatrix}}{\begin{vmatrix} n & \sum c_2^{1/2} \\ \sum c_2^{1/2} & \sum c_2 \end{vmatrix}} \quad \text{and} \quad b = -\frac{\begin{vmatrix} n & \sum f \\ \sum c_2^{1/2} & \sum fc_2^{1/2} \end{vmatrix}}{\begin{vmatrix} n & \sum c_2^{1/2} \\ \sum c_2^{1/2} & \sum c_2 \end{vmatrix}} \tag{15}$$

where n is the number of terms in the table of density and concentration. However, at low concentrations f is the ratio of two very small quantities, and small errors in density produce large changes in f and too much weight may be given to these deviations, which are within the allowable error of experiment. Equation 14 avoids this difficulty but necessitates the summation of several more powers of the volume concentration. The least-square solution of equation 14 gives a and b as follows:

$$a = -\frac{\begin{vmatrix} \sum fc_2 & \sum c_2^{5/2} \\ \sum fc_2^{3/2} & \sum c_2^{3} \end{vmatrix}}{\begin{vmatrix} \sum c_2^{2} & \sum c_2^{5/2} \\ \sum c_2^{5/2} & \sum c_2^{3} \end{vmatrix}} \qquad b = -\frac{\begin{vmatrix} \sum c_2^{2} & \sum fc_2 \\ \sum c_2^{5/2} & \sum fc_2^{3/2} \end{vmatrix}}{\begin{vmatrix} \sum c_2^{2} & \sum c_2^{5/2} \\ \sum c_2^{5/2} & \sum c_2^{3} \end{vmatrix}} \tag{16}$$

In this paper *a* and *b* for the sodium sulfate solutions were evaluated by the application of equation 16 over the whole range of concentration, but for the solutions of the other salts *a* and *b* were computed from equation 15, applied over the range from $c_2 = 0.05$ (approximately) to the highest concentration.

The results of the computations are given in tables 1 to 5. At the head of each table equation 13 or 14, with the appropriate values of *a* and *b*, is given and the tables themselves show how well the equation fits the data and the values of the partial volumes of the components computed by the equations:

$$\frac{1}{v_1} = \rho_1 = \rho_w + \frac{b}{2} c_2^{3/2} \tag{12'}$$

and

$$v_2 = \frac{v}{x_2} - \frac{x_1 v_1}{x_2} \tag{17}$$

which may also be written in the convenient form,

$$v_2 = v_1 \left(1 - \frac{\rho - \rho_1}{c_2} \right) \tag{17'}$$

The partial molal volume of a component may be obtained by multiplying its partial volume by its molecular weight.

The data on which the results in table 1 are based are those of Hall (7) and are of a high order of accuracy.

The least-square residuals in column 4, however, show that equation 13 does not represent the results within the error of experiment. The fit is good and, as an interpolation formula, equation 14 leaves little to be desired, but as a means of determining slopes it leaves room for uncertainty. With sodium chloride solutions some idea of the uncertainty in the slopes may be had from a comparison of the partial volumes of the salt as calculated by equations 12′ and 17, and those computed very carefully by Adams (1) with the aid of an empirical cubic equation and a deviation curve. This comparison is made in the last two columns of table 1.

In the 5 per cent solution and in the 25 per cent solution the agreement is poor, but in the intermediate solutions the two methods give results which are in excellent accord.

Table 2 illustrates the result of fitting equation 14 by the method of least squares to Gibson's (5) results for the densities of solutions of sodium sulfate, which were measured with considerable care. The least-square residuals are small, but are outside the experimental error and show a distinct curvature.

TABLE 1

Computations for solutions of sodium chloride at 25°C.

$(\rho - \rho_w)/c_2 = 0.72122 - 0.15345c_2^{\frac{1}{2}}$

x_2	c_2	$(\rho - \rho_w)_{\text{calcd.}}$	$\rho_{\text{obsd.}} - \rho_{\text{calcd.}} \times 10^5$	v_2	v_2 (Adams)
0.0	0.0	0	0	0.2796	0.2914
0.02	0.02022	0.01414	−4	0.3145	—
0.03	0.03055	0.02121	−4	0.3213	—
0.05	0.05163	0.03544	−2	0.3318	0.3304
0.10	0.10688	0.07172	4	0.3537	0.3539
0.15	0.16596	0.10932	2	0.3716	0.3725
0.20	0.22909	0.14840	−4	0.3870	0.3873
0.25	0.29654	0.18909	−1	0.4002	0.3991

TABLE 2

Computations for solutions of sodium sulfate at 25°C.

$(\rho - \rho_w) = 0.92212c_2 - 0.23567c_2^{\frac{3}{2}}$

x_2	c_2	$(\rho - \rho_w)_{\text{calcd.}}$	$\rho_{\text{obsd.}} - \rho_{\text{calcd.}} \times 10^5$	v_1	v_2	v_2 (1926)
0.0				1.00293	0.0781	0.0860
0.01	0.01006	0.009039	$-1._4$	1.00281	0.1151	0.1144
0.02	0.02030	0.018039	$-2._2$	1.00259	0.1296	0.1288
0.03	0.03072	0.027061	$-2._1$	1.00229	0.1409	0.1394
0.05	0.05212	0.045254	$-0._1$	1.00152	0.1588	0.1578
0.10	0.10890	0.091954	$1._2$	0.99869	0.1942	0.1940
0.15	0.17068	0.140770	$3._1$	0.99464	0.2225	0.2226
0.20	0.23781	0.191957	$-0._2$	0.98937	0.2476	0.2478
0.25	0.31069	0.245681	$-0._4$	0.98282	0.2701	0.2698
0.28	0.35736	0.279181	$1._6$	0.97824	0.2829	0.2824

The partial volumes of the salt, as computed directly from equations 12′ and 17, the residuals being neglected, are compared with the values of the partial volumes as calculated by Gibson from several empirical equations and deviation curves. The agreement is good, except at zero concentration where, it is believed, all weight should be given to the formula involving the square root of the concentration. Sodium sulfate changes the density of water very markedly and the partial volumes of the salt increase rapidly with the concentration; it is remarkable, then, that a two-constant equation such as equation 14 should represent the density as a function of the concentration so precisely.

Apparently the best data on the densities of potassium chloride solutions are those of Baxter and Wallace (2) and of Geffcken (3). In the determination of the coefficients *a* and *b* in equation 13 all the points except the first three of Baxter and Wallace were used. In general the equation fits the data well, but there is a pronounced departure at the highest concentrations. The residual of 5×10^{-5} in Baxter and Wallace's data, and the residuals of 11×10^{-5} and 7×10^{-5} in Geffcken's results for the most concentrated solutions seem to indicate inconsistencies in the experimental work. The partial volumes of water and of potassium chloride in the various solutions were computed by equations 12 and 17′ and are given in the fourth and fifth columns of table 3. The residuals were neglected in these calculations, and indeed the experimental results hardly warrant the use of a deviation curve.

TABLE 3

Computations for solutions of potassium chloride at 25°C.

$(\rho - \rho_w)/c_2 = 0.64611 - 0.1159c_2^{\frac{1}{2}}$

c_2	$(\rho - \rho_w)_{\text{calcd.}}$	$\rho_{\text{obsd.}} - \rho_{\text{calcd.}} \times 10^5$	v_1	v_2	
0.01235	0.00782	0	1.00285	0.374_4	Baxter and Wallace
0.02023	0.01274	−2	1.00276	0.380_1	
0.02491	0.01564	−1	1.00270	0.382_8	
0.04988	0.03094	−5	1.00228	0.394_5	
0.06850	0.04218	1	1.00189	0.400_1	
0.12447	0.07533	2	1.00038	0.415_2	
0.17094	0.10226	1	0.99883	0.422_1	
0.24964	0.14684	−1	0.99571	0.438_9	
0.10633	0.06468	8	1.00091	0.410_3	Geffcken
0.15397	0.09248	0	0.99942	0.421_9	
0.20636	0.12247	−2	0.99750	0.431_8	
0.28836	0.16837	−11	0.99399	0.444_9	
0.28926	0.16887	−7	0.99395	0.444_9	

Being interested in the effect of pressure on the solubility of potassium iodide, we examined the partial volumes of this salt in aqueous solutions. The results are given in table 4. The data are those of Baxter and Wallace (2), and of Shibata and Hölemann (9), the latter's results being marked with an asterisk. The equation at the head of the table was obtained by the method of least squares using $c_2^{\frac{1}{2}}$ as argument (equation 13). It is obvious that the two sets of data are not consistent and the passing of linear equations through both sets separately indicated that those of Baxter and Wallace were smoother than those of Shibata and Hölemann. It is also obvious that the linear relationship does not hold over the whole concentration range for this salt—the highest points fall off the straight line. Unfortunately, the inconsistencies between the two sets of experimental results do not admit of an accurate estimate of this curvature.

TABLE 4

Computations for solutions of potassium iodide at 25°C.

$(\rho - \rho_w)/c_2 = 0.72825 - 0.02403c_2^{\frac{1}{2}}$

c_2	$(\rho - \rho_w)_{\text{calcd.}}$	$\rho_{\text{obsd.}} - \rho_{\text{calcd.}} \times 10^5$	v_1	v_2
0.04571	0.03305	−1	1.00281	0.280_7
0.09185	0.06622	−1	1.00259	0.283_7
0.16686*	0.11988	1*	1.00209	0.287_2
0.18466	0.13257	−2	1.00196	0.288_0
0.27000*	0.19326	6*	1.00121	0.290_8
0.35477*	0.25328	10*	1.00036	0.293_1
0.44465*	0.31669	15*	0.99932	0.295_4
0.46084	0.32809	0	0.99912	(0.296_0)
0.64032*	0.45400	8*	0.99670	(0.299_6)
0.92425	0.65173	−47	0.99268	(0.304_3)

* Data of Shibata and Hölemann.

TABLE 5

Computations for solutions of lithium nitrate at 25°C.

$(\rho - \rho_w)/c_2 = 0.58035 - 0.04534c_2^{\frac{1}{2}}$

m	c_2	$(\rho - \rho_w)_{\text{calcd.}}$	$\rho_{\text{obsd.}} - \rho_{\text{calcd.}} \times 10^5$
1.0339	0.06895	0.03919	−10
2.1115	0.13662	0.07700	100
3.3106	0.20685	0.11578	18
4.5706	0.27579	0.15349	38
5.9276	0.34474	0.19089	29
7.3940	0.41368	0.22802	6
8.9836	0.48262	0.26489	−13
10.7055	0.55157	0.30153	26
11.8331	0.59318	0.32354	−37
12.8639	0.62934	0.34260	−72

The partial volumes, v_1 and v_2, in table 4 were computed directly from the equation

$$\rho - \rho_w = 0.72818c_2 - 0.02429c_2^{\frac{3}{2}}$$

which, according to the least-square criterion, is the best straight line which may be passed through Baxter and Wallace's results. No attempt was made to take account of the deviations from the above equation and in consequence the results at the higher concentration are not to be taken as final.

Pearce and Nelson (8) published a very complete series of densities of solutions of lithium nitrate over the whole concentration range at 25°C. Equation 13 was fitted to these data by the method of least squares and the results are recorded in table 5. The least-square residuals are very large and indicate that $(\rho - \rho_w)/c_2$ is by no means a linear function of the square root of the volume concentration. An analysis also reveals that the results are somewhat erratic; indeed the density of the 2.115 molal solution was so far off that it was omitted from the least-square calculation. Unless the results of Pearce and Nelson are very much in error it appears that the linear equation is of little use in the computation of partial volumes in lithium nitrate solutions.

It seems significant that the greater the contraction in volume produced by a salt on forming an aqueous solution, the better does the linear function of $c_2^{\frac{1}{2}}$ represent the apparent volume of the salt.

SUMMARY

The computation of the partial or partial molal volumes of the components in a solution is always a laborious process if the best use is to be made of the experimental data. The use of the volume concentration and Gucker's function *f*, together with equations 12 and 17 or 17′ in this paper, furnishes a relatively simple method of calculation, which in the case of many aqueous salt solutions (four out of the five examined here) yields values of the partial volume of the salt which are trustworthy to within one per cent, and, if a deviation curve is used, even higher accuracy may be obtained. If, however, the plot of *f* against the square root of the volume concentration is so strongly curved that higher powers of $c_2^{\frac{1}{2}}$ are to be introduced into the analytical expression, or if the desired accuracy of the computation requires the introduction of higher powers of $c_2^{\frac{1}{2}}$, the virtue of the volume concentration as an argument is lost and either weight or volume concentrations may equally well be used. The method of least squares is particularly recommended in the fitting of the empirical equations 13 and 14 to the experimental data.

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THE TEMPERATURE COEFFICIENT OF THE RATE OF COMBINATION OF HYDROGEN AND OXYGEN UNDER ALPHA RADIATION

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Although this reaction has been extensively investigated under many conditions for various purposes (5), the temperature range of the alpha-ray reaction has never been extended above 130°C. nor below −80°C. The investigations of the thermal reaction by Hinshelwood and Thompson (2) and of the photochemical reaction by Kistiakowski (3), both at higher temperatures, make it appear desirable to extend the temperature limits of the alpha-ray reaction in both directions. Owing to the nature of the reactants and to the absence of the reverse reaction, the decomposition of water vapor by alpha rays, the reaction lends itself admirably to such a purpose.

The objects of the study are to contribute to the knowledge of the reaction mechanism, especially to the transition from a constant quantized reaction with no temperature coefficient at lower temperature to a chain reaction with about the same temperature coefficient as the photochemical reaction at higher temperatures.

Incidentally the sensitization or catalytic effect of ions of water vapor has been discovered and found to be 100 per cent efficient.

GENERAL PROCEDURE

The manometer method of following the course of the reaction has been used in all except one experiment. The two methods of using radon, (1) by mixing directly with the reactants, and (2) by confining it in a thin alpha-ray bulb at the center of the reaction sphere, have been employed. Reaction spheres of Pyrex glass were used. Both static and circulating systems were employed with various conditions as to extent and temperature of the dead arm kept at lower temperature for condensation of water vapor, since it was not feasible to employ an internal drying agent at high temperature. Electrolytic gas was generated from barium hydroxide solution between platinum electrodes and stored in a vessel without stop-

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cocks. Figure 1 shows the apparatus used in the circulation method, in which I is the reaction sphere containing an alpha-ray bulb at its center in the electrical furnace H at a controlled temperature, E is the all-glass magnetic circulating pump of simple design (8), and J is a heating coil to raise the temperature of a small platinum catalyst to produce initial saturation with water vapor. G is a liquid air trap sometimes used to remove the water vapor from the circulating mixture.

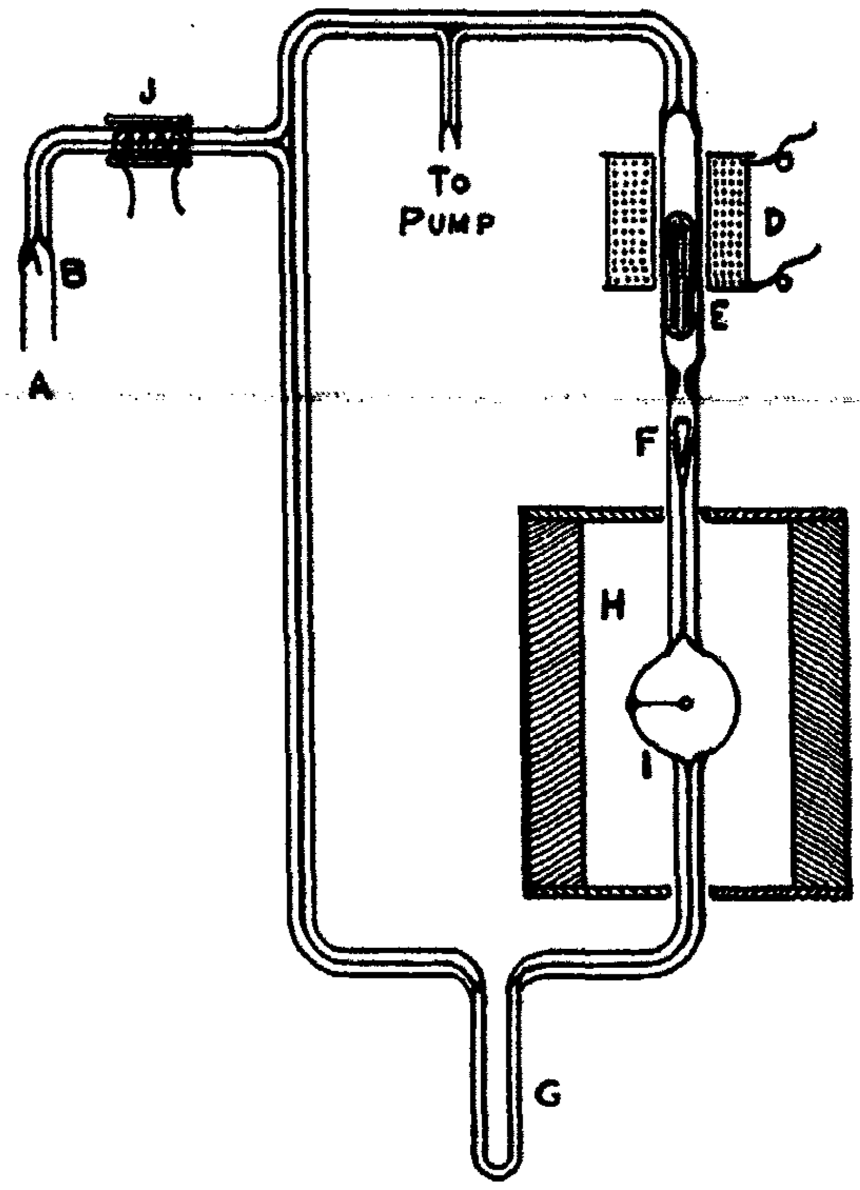

Fig. 1. Apparatus Used in the Circulation Method

Radon purified by the method of Livingston (7) is introduced either into the alpha-ray bulb of figure 1, the stem of which is then sealed and closed as far as the bulb (by a technique to be described later), or is introduced into the tube shown in the breaker M of figure 2, from which it is introduced into sphere G in the static method after breaking *in vacuo*.

TREATMENT OF DATA

The quantity of radon is initially measured by its gamma radiation and its decay is subsequently followed by the table of Kolowrat. The gas pressures (at constant volume) have all been corrected to 0°C. The kinetic constant is calculated in the usual way (reference 5, p. 116) from the equation

$$\left(\frac{k\mu}{\lambda}\right)' = \text{const.} = \frac{\text{nat log}\,\dfrac{P_1}{P_2}}{E_0\,(e^{-\lambda t_1} - e^{-\lambda t_2})}$$

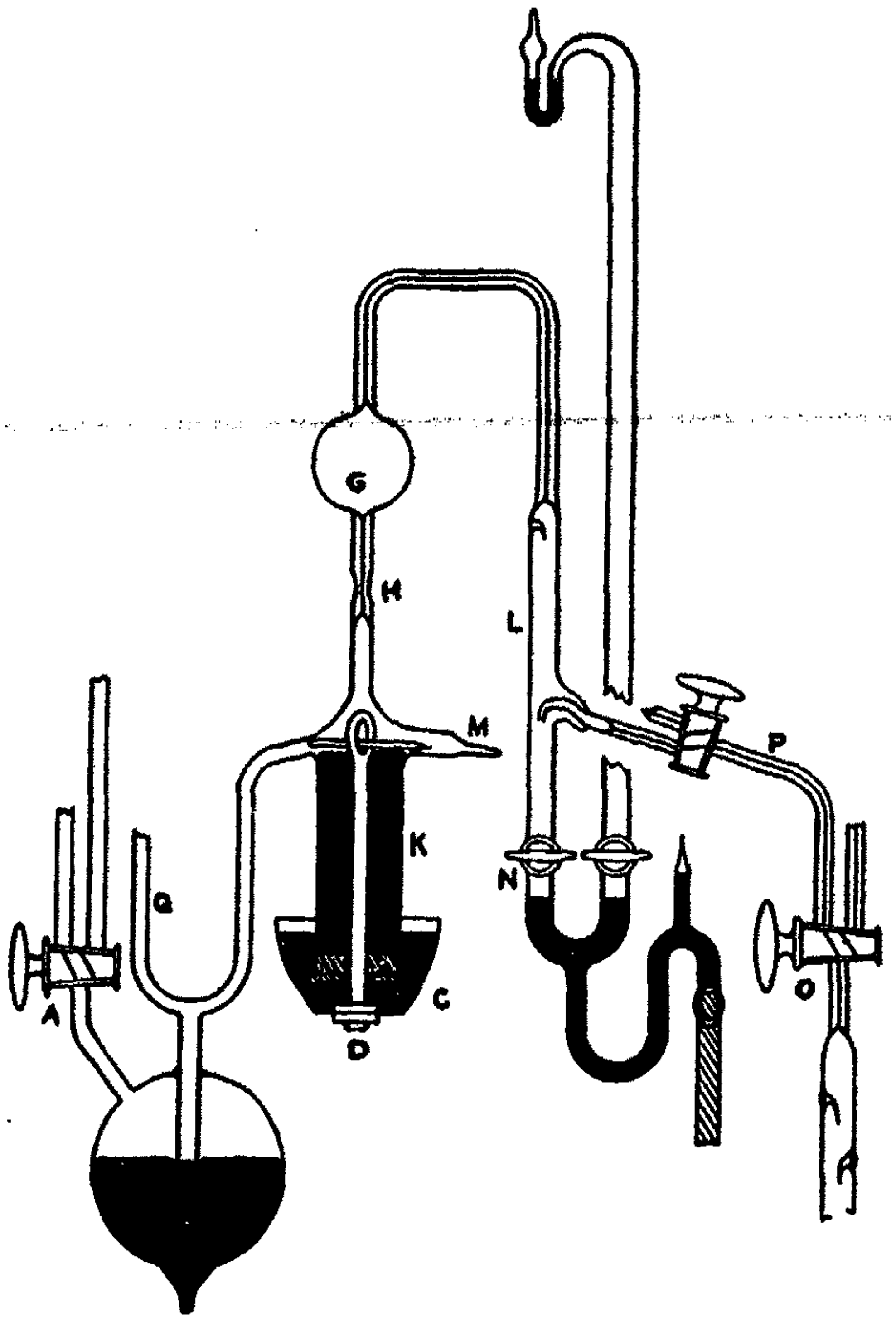

Fig. 2

From the values of $\left(\frac{k\mu}{\lambda}\right)'$ for each interval the number of molecules of hydrogen and oxygen reacting per ion pair is calculated and reported as $-M/N$, where N is the total number of ion pairs from O_2, H_2, or H_2O except in cases where ions of water vapor may be neglected. Comparison of yields under different conditions is therefore obtained by direct comparison of corresponding M/N values. It is assumed that the amount of ionization by alpha particles is unaffected by temperature at any temperature employed.

EFFECT OF WATER VAPOR

Duane and Scheuer (1) found that water vapor is not decomposed by alpha rays. On the other hand it is normally ionized and hence may possibly contribute to the forward reaction just as Lind and Bardwell (6) later found many foreign gas ions do in various reactions including the effects of ions of nitrogen, oxygen, and neon in water synthesis. Such an effect of water vapor in water synthesis would be "autocatalytic," increasing with increase of water vapor produced in the reaction itself. Such an effect has hitherto escaped observation because at ordinary temperature most of the water formed condenses out. An effect of H_2O^+ (or possibly H_2O^-) ions would be expected to become relatively more important at low pressures of electrolytic gas saturated with water vapor. But in the reactions at low pressure in the investigations of recoil atom effect (4) an internal drying agent was used so as to prevent any influence of water vapor on the recoil effect.

In the present experiments at higher temperatures, however, the water vapor concentration becomes sufficiently great to contribute materially to the ionization and also, as will be shown, to the reaction rate.

On going up in temperature a marked increase in $-M/N$ is observed, which may be due either to a true temperature effect or to the catalytic effect of water vapor ions or to both. The effect of water ions must be known or eliminated in order to evaluate the true temperature coefficient. Both methods have been used, to remove water vapor by the circulation method or to calculate the additional effect in the presence of water vapor and subtract it. Both lead to the same net result at a given temperature. Moreover the agreement confirms the 100 per cent efficiency of water vapor ions, which was assumed in making the subtractive correction.

Another accelerating effect, that of low pressure, which was first thought to exist, proved to be spurious upon more complete removal of water vapor and was due to the relatively enhanced effect of the latter at low pressures of reactants.

The practically complete elimination of water vapor (not extreme drying) leaves then only the true yield $-M/N$ which remains constant at 4.5[3] from −180°C. to ordinary temperature and then rises steadily to 20

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[3] Throughout this paper the results are expressed in terms of $-M/N$, i.e., the number of molecules of hydrogen and of oxygen reacting per ion pair produced both in hydrogen and in oxygen ($-M_{H_2+O_2}/N_{H_2+O_2}$). In terms of water molecules formed the value is $2/3 \times 4.5 = 3$. This is lower than the earlier value 4, because the values of the average intensity of ionization obtained from the Mund equation are higher and hence N is higher and M/N is lower.

at 400°C.; between 400°C. and 500°C. the values were not reproducible owing to the thermal reaction; above 500°C. the reaction becomes explosive.

EXPERIMENTS AND CALCULATIONS IN STATIC SYSTEM

In the following tables are reported the observations and calculations of experiments under various conditions of temperature and of water removal.

The experiments in static systems above 100°C. were found quite useless in attempting to find the true temperature coefficient of reaction rate, because the slow rate of diffusion of water vapor from the reaction sphere out to room temperature produces a higher partial pressure of water vapor in the reaction sphere than is allowed for by simply applying the water vapor correction for the outside (lower) temperature. The application of cooling baths outside is ineffective in speedy removal of water vapor, since it is the rate of diffusion outward, not the rate of condensation after arriving there, which is the controlling factor. The apparent yield in water synthesis per ion pair continues to rise even at a constant higher temperature, which may be due either to an actual increase of rate due to accumulation of more water vapor (which seems improbable, beyond a certain limit, over the long periods of time that prevail toward the end of the reaction) or to the increasing importance of water vapor relative to the diminishing pressure of electrolytic gas, since both are ionized in proportion to their amounts present.

Table 1 will illustrate such a false rise of $-M/N$ at 275°C. due to this cause. P_0 = the pressure of reactants corrected to 0°C., after subtracting aqueous tension at the outside temperature. P_{eq} = the pressure of reactants at 0°C. increased by the ion equivalence[4] of the water vapor pressure.

As already explained, the large rise in $-M/N$ is spurious and caused by accumulating water vapor above equilibrium with the outside temperature, but owing to the uncertainty of its amount, correction cannot be made until the water concentration is known or eliminated.

One method of procedure which was adopted with fair success was to make a rate measurement at each temperature so as to obtain a value of M/N before enough water vapor had been produced or the reactants sufficiently diminished to influence the value of M/N. Such measurements were made at 25°, 75°, 125°, 160°, 199°C. The details are not reported but the results are given in figure 3 and agree with the results where water vapor is rigidly removed.

A second method consisted in employing an alpha-ray bulb (with com-

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[4] It is P_{eq} which is substituted in the general kinetic equation to obtain the velocity constant $\left(\frac{k\mu}{\lambda}\right)'$ from which M/N is calculated in the usual way.

TABLE 1

Rate of combination at 275°C. with incomplete removal of water vapor

Volume of reaction sphere = 10.41 cm³. Diameter of reaction sphere = 2.708 cm. Initial radon = 0.1059 curie. Static system with radon mixed with $2H + O_2$

ELAPSED TIME		$e^{-\lambda t}$	P_0	P_{eq}	RECOIL ATOM CORRECTION	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE OF REACTION
days	*hours*							*degrees C.*
0	0	1.00000	367.8	400.8	—	—	—	—
0	22	0.8478	312.7	345.7	1.119	9.2	3.7	25
1	6.58	0.7955	289.5	322.5	1.137	12.5	4.9	25
1	20.42	0.7216	248.2	281.2	1.155	17.5	6.8	285
2	4.25	0.6758	215.3	248.3	1.180	25.7	9.8	275
2	20.92	0.5968	168.8	201.8	1.218	24.8	9.3	275
3	4.83	0.5620	142.4	175.4	1.268	38.1	13.9	275
3	10.25	0.5396	128.8	161.8	1.311	38.6	13.5	275
3	18.25	0.5082	112.0	145.0	1.351	32.5	11.2	275
4	4.92	0.4689	93.1	126.1	1.407	34.4	11.7	275
4	20.42	0.4174	62.7	100.2	1.520	42.2	13.7	275
5	2.92	0.3975	58.1	91.1	1.664	45.2	14.0	275
5	8.58	0.3814	46.5	79.5	1.797	79.9	23.8	275
5	21.83	0.3447	15.9	48.9	2.334	125.1	33.6	275
5	22.83	0.3421	11.1	44.1	4.019	375.1	87.5	275
5	23.83	0.3396	7.9	40.9	5.710	284.4	61.9	275

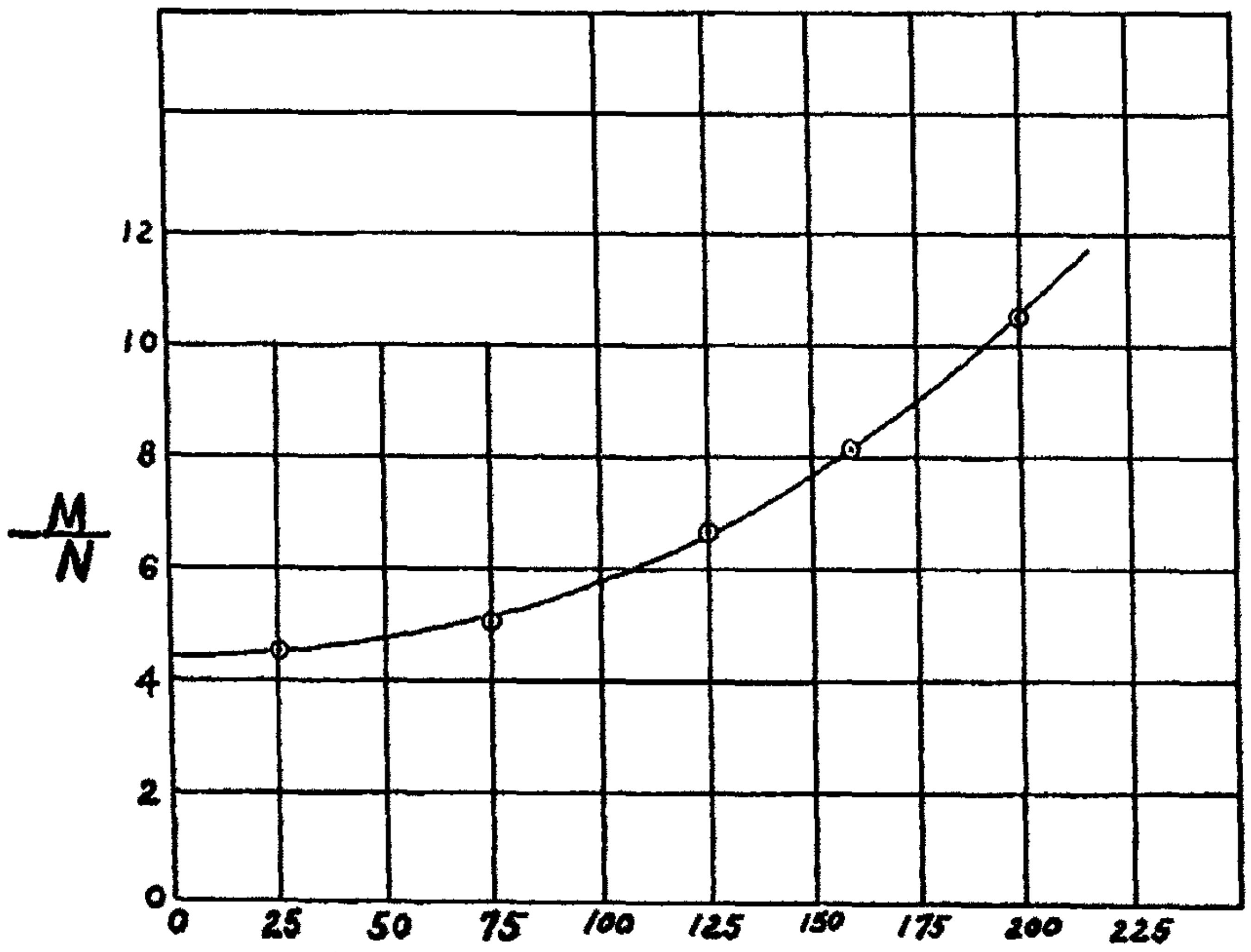

Fig. 3

pletely closed stem) mounted at the center of the reaction sphere. This permitted surrounding the entire sphere with liquid air or carbon dioxide mixture so as to freeze the water vapor on the walls as ice. This method is naturally limited to the low temperature measurements. When the bath is removed the water vapor produced at higher temperature causes an enhancement[5] in M/N as shown in table 2.

A special experiment was made to examine the value of M/N at −78°C. which was apparently higher than that either at 25° or −183°C. The results were: at 25°C., 4.4, 4.65; at −78°C., 5.1, 4.98, 4.61; at 25°C., 4.03. The results for −78°C. are lower than in table 2 but still somewhat higher than those for 25°C., for which no explanation has been offered.

TABLE 2

Rate of synthesis at low temperatures in absence of water vapor compared to that in its presence at higher temperatures

Volume of reaction sphere = 14 cc. Radon in alpha-ray bulb = 0.100 curie

TIME ELAPSED		e^-	P_0	P_{eq}	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE
days	*hours*						*degrees C.*
—	—	1.0000	446.0	482.0	—	—	—
	19.0	0.8672	415.0	451.0	5.00	4.42	25
1	19.5	0.7216	371.7	371.7*	7.58	6.56	−78
2	20.5	0.5982	340.4	340.4*	7.23	6.25	−78
3	19.5	0.5034	318.7	318.7*	6.95	6.00	−78
4	20.0	0.4190	304.6	340.6	4.81	—	—
5	19.5	0.3512	294.0	294.0*	5.22	4.52	−183
6	20.5	0.2912	285.8	285.8*	4.72	4.08	−183
7	19.5	0.2450	276.7	312.7	6.22	5.38	25
8	20.5	0.2039	241.9	277.9	35.0	30.3	353
9	20.5	0.1703	151.8	187.8	48.1	41.6	380
10	19.0	0.1439	141.6	177.6	21.2	18.4	290

* At these temperatures water froze on the sides of the vessel so that no water vapor is present in the path of the alpha particles.

EXPERIMENTS WITH CIRCULATING SYSTEM

It became evident that for the prompt and complete removal of water vapor the reactant gases should be circulated through an outside liquid air trap. This was accomplished by means of an all-glass pump and an alpha-ray bulb to prevent circulation of the radon. The results given in table 3 demonstrate the constancy of M/N at 175°C. under these conditions and

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[5] That these enhanced values are not due alone to the higher temperature is evident when they are compared with those of corresponding temperatures in the absence of water vapor, as shown in table 4.

are to be contrasted with those of table 1 where water vapor was allowed to accumulate.

TABLE 3

Synthesis of water at 175°C. in absence of water vapor

Volume of reaction sphere = 12.150 cc. Volume of system outside oven = 8.104 cc. E_0 = 0.100 curie, in alpha-ray bulb. Circulation with all-glass pump

TIME ELAPSED		$e^{-\lambda t}$	P_0	P_{eq}	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE
days	*hours*						*degrees C.*
—	—	1.0000	159.6	192.6	—	—	—
—	18.75	0.8686	134.8	167.8	10.48	—	25
2	16.25	0.6176	110.6	143.6	6.21	4.5	25
2	17.67	0.6111	109.4	109.4*	—	—	—
2	23.25	0.5860	106.2	108.2*	11.97	8.7	175
3	20.75	0.4987	95.1	128.1	12.65	9.2	175
4	13.25	0.4407	87.1	120.1	11.13	8.0	175
4	24.67	0.4045	81.9	114.9	12.21	9.1	175
5	21.25	0.3467	74.9	107.9	10.81	7.4	175
6	22 33	0.2873	67.6	100.6	11.86	8.6	175
7	22.00	0.2405	65.1	95.1	12.02	8.9	173

TABLE 4

Synthesis of water at various temperatures in absence of water vapor

Volume of sphere = 14 cc. E_0 = 0.100 curie in alpha-ray bulb. Circulation by all-glass pump

TIME ELAPSED		$e^{-\lambda t}$	P_t	P_{eq}	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE
days	*hours*						*degrees C.*
—	—	1.0000	595.7	543.7	—	—	—
—	20	0.8608	557.1	502.9	5.6	4.5	25
1	17.5	0.7325	510.8	464.5	6.15		25
2	6.25	0.6657	461.6	414.1	17.2	13.2	300
2	17.75	0.6106	446.9	400.4	6.1	4.65	25
3	4.00	0.5655	434.1	374.3	15.0	11.45	300
3	20.00	0.5016	184.1	162.7	130.6	99.8	500
4	19.25	0.4213	148.7	133.7	24.4	18.6	350
4	19.75	0.4196	445.9	398.0	(1)		
5	18.75	0.3532	393.4	353.5	17.8	13.6	358
6	18.5	0.2956	326.7	292.1	33.15	25.14	404
7	18.5	0.2469	92.7	82.1	260.4	198.4	500

(1) More reaction gas added.

Circulation by thermal convection was also tried, but was found to give results less satisfactory than the foregoing. It only remained then to apply the circulation method at various temperatures. In each case the alpha-

TABLE 5

Synthesis at higher temperature in absence of water vapor

Volume of sphere = 14 cc. E_0 = 0.105 curie in alpha-ray bulb. Circulation by means of all-glass pump

TIME ELAPSED		$e^{-\lambda t}$	P_{e_0}	P_{eq}	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE
days	*hours*						*degrees C.*
—	—	1.0000	288.4	315.4	—	—	—
—	17.75	0.8751	276.8	301.8	3.0	4.6	25
1	19.0	0.7243	254.1	279.1	5.2		25
2	14.25	0.6269	220.6	245.6	14.3	13.4	400
3	17.75	0.5100	207.2	232.2	4.8	4.0	25
4	15.50	0.4333	142.6	167.6	43.2	40.2	480
5	21.75	0.3453	136.6	161.6	4.3	4.2	25
5	22.00	0.3447	226.2	251.2	(1)		
6	19.25	0.2939	208.0	233.0	15.1	14.0	284
7	16.25	0.2511	195.3	220.3	13.2	12.3	375
7	16.5	0.2506	286.0	311.0	(1)		
8	16.5	0.2093	119.0	144.0	188.0	175.0	525

(1) More reaction gas added.

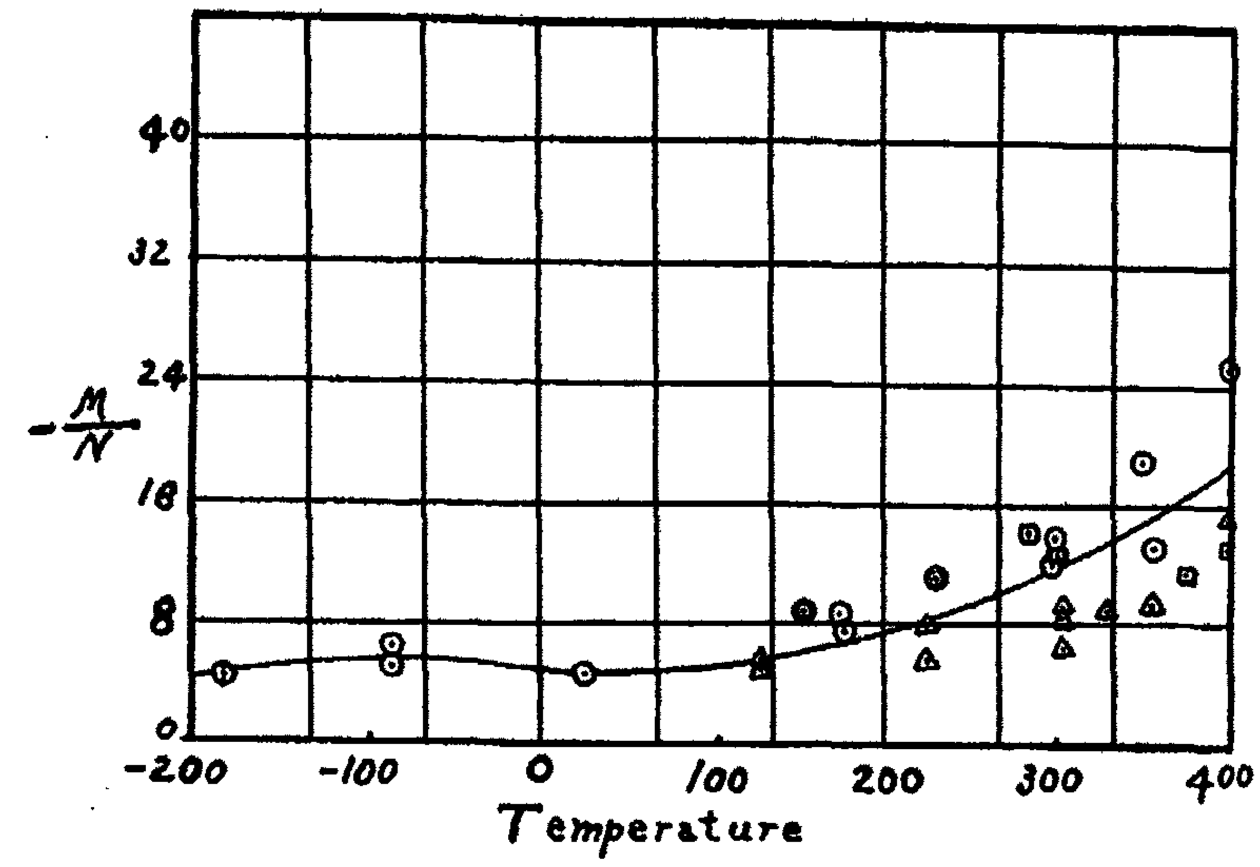

FIG. 4

ray bulb and reaction sphere are calibrated for ionization by means of reaction rate of electrolytic mixture at 25°C. The detailed results of two of these experiments at various temperatures are given in tables 4 and 5.

One experiment was carried out in a closed static system consisting of a sphere and short connecting tube all enclosed at the reaction temperature 300°C. so as to test the complete correction for a known amount of water vapor. Assuming 100 per cent efficiency of the ions of water vapor gave the value $M/N = 14$, in good agreement with those of the circulating method, thus proving the rôle of water vapor ions and their 100 per cent efficiency in promoting synthesis.

In figure 4 are plotted the results of a number of experiments at temperatures ranging from −183°C. to 400°C. From this curve are calculated the temperature coefficients which are shown in table 6 along with photochemical results for purposes of comparison.

TABLE 6

Comparison of radiochemical and photochemical temperature coefficients

TEMPERATURE INTERVAL	TEMPERATURE COEFFICIENTS				
	Radiochemical	Photochemical			
		Direct	Mercury sensitized		
			$P_{mm.\ Hg}$ 0.0004	$P_{mm.\ Hg}$ 0.0035	$P_{mm.\ Hg}$ 0.020
degrees C.					
183 to 25	1.00	—	—	—	—
100 to 200	1.039	1.045	—	—	—
200 to 300	1.043	1.07	—	—	—
300 to 400	1.047	1.07	1.12	1.09	1.05
400 to 500	1.047	—	—	—	—
400 to 490	—	1.13	1.08	1.07	1.05

DISCUSSION

The most outstanding feature of the temperature coefficient of this reaction is the complete absence of any influence of temperature from −185°C. to 25°C., a range of more than 200°C. On account of the lack of influence of temperature on the primary step, ionization, it might be supposed that any reaction resulting immediately and quantitatively from ionization should show no temperature coefficient. The fact that it does not in the lower temperature range furnishes evidence of two types of reaction, the stably quantized type, and at higher temperature, a chain mechanism of some kind.

For convenience one may assume for the low temperature range the ion "cluster" type such as has already been proposed for this and other reactions. At higher temperatures one would hardly expect the clusters to increase in size or efficiency of reaction, and it seems more probable to assume a breaking down of the cluster and a transition to some type of chain mechanism which ultimately leads to explosion. It is not improbable that the cluster mechanism persists and overlaps the chain mechanism, which gradually becomes predominant toward higher temperatures.

The complete efficiency of ions of water vapor in promoting the reaction is interesting, especially in view of the low efficiency (14 per cent) found by Rosenblum (9) of carbon dioxide ions in promoting the oxidation of carbon monoxide. In other cases however, there was ample analogy to support 100 per cent efficiency of foreign gas ions, also in this reaction (loc. cit.).

SUMMARY

The combination of hydrogen and oxygen under alpha radiation was studied at temperatures varying from −185°C. to +500°C., with radon mixed with the reacting gases and with radon in an alpha-ray bulb, with and without circulation of the gases.

The results obtained for the reaction at 25°C. agree with those previously obtained, viz., three molecules of water formed per ion pair (calculations being based on higher values of intensity of ionization than formerly). The reaction is found to proceed with approximately this same ion pair yield at −185°C. and at −78°C.

A positive temperature effect sets in above room temperature. The temperature coefficient is found to vary between 1.02 and 1.05. These values are compared with those found for the photochemical reaction.

The method of applying the correction for reaction due to ionic catalyst (water vapor) present in the system is considered. It is found that the ions of water vapor possess the same efficiency in producing reaction as the ions of the reacting gases themselves.

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THE THERMODYNAMICS OF THE ELECTROCAPILLARY CURVE. II

THE VARIATION OF THE ELECTROCAPILLARY CURVE WITH COMPOSITION

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I. INTRODUCTION

In the preceding paper on this subject,[1] the following general equation was deduced for the electrocapillary curve (I, p. 126):

$$d\sigma = -s^{\omega}dT - \sum_{i=1}^{p^{\alpha}} \Gamma_i^{\alpha} d\mu_i^{\alpha} - \sum_{i=1}^{p^{\beta}} \Gamma_i^{\beta} d\mu_i^{\beta} - \sum_{k=1}^{r} \Gamma_k d\mu_k - \epsilon^{\alpha} d[(\varphi^{\alpha} - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^{\beta}) - \mathfrak{T}] \qquad (40)$$

It is the purpose of the present paper to deduce from this equation the special equations describing the variation of the electrocapillary curve with composition. The results are of value because they show how electrocapillary measurements are to be interpreted thermodynamically so as to yield the maximum amount of information about the composition of the electric double layer.

The system to which equation 40 applies is made up of three parts as follows: (1) two phases α and β constituting a perfectly polarizable system (I, p. 112 ff.); (2) a piece of some metal Me and a series of contiguous phases connecting it with α (I, p. 126); (3) another piece of the same metal Me and a series of contiguous phases connecting it with β. In general the composition of each of the parts 1, 2, and 3 is to be regarded as independently variable.

As regards the two phases α and β of the perfectly polarizable system proper, it will be recalled that they may have no charged components X_i in common (I, p. 116), i.e., that

$$p = p^{\alpha} + p^{\beta} \qquad (1)$$

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[1] This Journal 38, 111 (1934); this paper will henceforth be referred to as I, the present paper as II. The equations in I and II are numbered as a single series: I contains equations 1 to 43 inclusive; II equations 44 to 168 inclusive. The reader is referred to I for the meaning of all mathematical symbols except those used for the first time in II.

Furthermore, in practice one of the two phases is always metallic, the other nonmetallic. Therefore the electrically neutral components X_k, being insoluble in metals under ordinary conditions, are in practice always confined to the nonmetallic phase, i.e., if, as is the case throughout this paper, α denote the metallic, β the nonmetallic phase, then (I, p. 117) $r^\alpha = 0$ and

$$r = r^\beta \tag{5}$$

Thus in practice the two phases never have any components, charged or neutral, in common, and therefore the composition of each phase interior may be varied independently of the other. Restricting equation 40 in accordance with equation 5 yields

$$\begin{aligned} d\sigma = -s^\omega dT - \sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha - \sum_{i=1}^{p^\beta} \Gamma_i^\beta d\mu_i^\beta - \sum_{k=1}^{r^\beta} \Gamma_k^\beta d\mu_k^\beta \\ - \epsilon^\alpha d[(\varphi^\alpha - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^\beta) - \mathfrak{E}] \end{aligned} \tag{40.1}$$

This paper will be confined to the consequences of equation 40.1.

Throughout this paper it is assumed that the metallic phase α and the arbitrary metal Me are in *direct* contact without intervening phases. Besides the variation of α and β it is therefore necessary to consider only the variation in the above-mentioned part of the system. This part of the system shall henceforth be designated as the reference electrode (cf. I, p. 111). For example, if the system under consideration is

I α β II
Me | Hg | 1 N KNO_3 solution | 1 N HCl solution | AgCl | Ag | Me

then the reference electrode is

Me | Ag | AgCl | 1 N HCl solution

The problem is thus reduced to that of the independent variations of α, of β, and of the reference electrode. The effects of these three kinds of variation on the behavior of the system are accordingly considered separately below.

It is to be noted in advance that the equations derived below are perfectly exact only for the case in which the pressures P^α and P^β of α and β, respectively, are each constant, and that in order to apply these equations to the electrocapillary curves determined in the Lippmann electrometer, in which P^α varies slightly, it is necessary to assume that the quantities μ_i^α (equation 40.1) are independent of P^α within the limits defined by the inequality 42 (I, p. 127). The fact that equation 43 (I, p. 127), which rests upon this assumption, is experimentally verified, may be regarded as direct proof that there is no appreciable error connected with the assumption.

II. VARIATION OF THE ELECTROCAPILLARY CURVE WITH THE COMPOSITION OF THE REFERENCE ELECTRODE

Let the surface tension σ, the temperature T, the pressures P^α, P^β, and the composition of the phases α and β be kept constant, and let the reference electrode be varied as regards both the number and the composition of all its phases. Then equation 40.1 reduces to

$$d[(\varphi^\alpha - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^\beta) - \mathfrak{E}] = 0 \tag{44}$$

whence

$$(\varphi^\alpha - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^\beta) - \mathfrak{E} = \text{constant}^{[2]} \tag{45}$$

$$\mathfrak{E} = -\text{constant} + (\varphi^\alpha - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^\beta) \tag{46}$$

Now consider two different reference electrodes which may be represented by

$$\mathrm{Me}_1 \underset{1}{|||} \quad \text{and} \quad \mathrm{Me}_2 \underset{2}{|||}$$

where the three vertical lines with the subscripts 1 and 2 indicate the presence of an arbitrary number of different phases in each case. For these two reference electrodes equation 46 may be written as

$$\mathfrak{E}_1 = -\text{constant} + (\varphi^\alpha - \varphi^{\mathrm{I}})_1 + (\varphi^{\mathrm{II}} - \varphi^\beta)_1 \tag{47.1}$$

$$\mathfrak{E}_2 = -\text{constant} + (\varphi^\alpha - \varphi^{\mathrm{I}})_2 + (\varphi^{\mathrm{II}} - \varphi^\beta)_2 \tag{47.2}$$

Subtraction of equation 47.2 from equation 47.1 gives

$$\mathfrak{E}_1 - \mathfrak{E}_2 = (\varphi^{\mathrm{I}} - \varphi^\alpha)_2 + (\varphi^\alpha - \varphi^{\mathrm{I}})_1 + (\varphi^{\mathrm{II}} - \varphi^\beta)_1 + (\varphi^\beta - \varphi^{\mathrm{II}})_2 \tag{48}$$

The quantity on the right side of equation 48 is evidently the E.M.F. of the combination

$$\mathrm{Me}_2 \,|\, \alpha \,|\, \mathrm{Me}_1 \underset{1}{|||}\, \beta \,\underset{2}{|||}\, \mathrm{Me}_2$$

which, since α is metallic, has the same E.M.F. as the cell formed out of the two reference electrodes by joining them through β. Changing from one reference electrode to another therefore displaces the electrocapillary curve of a given perfectly polarizable system horizontally by an amount equal to the E.M.F. of the cell formed by joining the two reference electrodes through β.

III. VARIATION OF THE ELECTROCAPILLARY CURVE WITH THE COMPOSITION OF THE METALLIC PHASE

Let the temperature T, the pressures P^α, P^β, the composition of the nonmetallic phase β and the composition of the reference electrode be

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[2] Comparison of equation 45 with equation 39 (I, p. 126) shows that constant = $(\varphi^\alpha - \varphi^\beta)$.

regarded as constant, and only the composition of the metallic phase α and the applied potential $\mathfrak{E}$ be varied. Under these conditions the terms in T, μ_i^β, μ_k^β and $(\varphi^{\mathrm{II}} - \varphi^\beta)$ vanish from equation 40.1 leaving

$$d\sigma = -\sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha - \epsilon^\alpha d\,(\varphi^\alpha - \varphi^{\mathrm{I}}) + \epsilon^\alpha d\mathfrak{E} \tag{49}$$

A. The case $p^\alpha = 2$

This case, the simplest possible, is trivial for the purpose in hand, because the interior of α can consist only of a single metal and is therefore incapable of variations of composition. The terms in μ_i^α and $(\varphi^\alpha - \varphi^{\mathrm{I}})$ accordingly drop out of equation 49, leaving the Lippmann-Helmholtz equation 41.

B. The general case of any number of charged components p^α

In this case the interior of α consists of a solution of a number q^α of metals such that (I, p. 116)

$$q^\alpha = p^\alpha - 1 \tag{2.1}$$

For this general case equation 49 is reducible to a simple form, first, because α being metallic all its charged components are of the same sign (positive) except one, namely the electron, and second, because α and Me being in *direct* contact, it is always the electron with respect to which α and Me are in electrochemical equilibrium.

Let μ_{j+}^α and $\mu_\ominus^\alpha$ be the chemical potentials (per equivalent) of the cations of the j^{th} metal and of the electrons, respectively, in the interior of α and let Γ_{j+}^α, $\Gamma_\ominus^\alpha$ be the corresponding surface densities (in equivalents per unit area). The sum in equation 49 may then be written as

$$\sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha = \sum_{j=1}^{q^\alpha} \Gamma_{j+}^\alpha d\mu_{j+}^\alpha + \Gamma_\ominus^\alpha d\mu_\ominus^\alpha \tag{50}$$

The introduction of the necessary relation

$$\mu_{j+}^\alpha = \mu_j^\alpha - \mu_\ominus^\alpha \tag{51}$$

where μ_j^α is the chemical potential per equivalent of the j^{th} metal, into equation 50 gives

$$\sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha = \sum_{j=1}^{q^\alpha} \Gamma_{j+}^\alpha d\mu_j^\alpha - \left(\sum_{j=1}^{q^\alpha} \Gamma_{j+}^\alpha - \Gamma_\ominus^\alpha\right) d\mu_\ominus^\alpha \tag{52}$$

From equation 33.1 it is evident that

$$\sum_{j=1}^{q^\alpha} \Gamma_{j+}^\alpha - \Gamma_\ominus^\alpha = \frac{\epsilon^\alpha}{F} \tag{53}$$

The substitution of equation 53 into equation 52 and of the result into equation 49 gives

$$\mathrm{d}\sigma = -\sum_{j=1}^{q^\alpha} \Gamma^\alpha_{j+}\mathrm{d}\mu^\alpha_j + \epsilon^\alpha \mathrm{d}\,\frac{\mu^\alpha_\ominus}{F} - \epsilon^\alpha \mathrm{d}\,(\varphi^\alpha - \varphi^\mathrm{I}) + \epsilon^\alpha \mathrm{d}\mathfrak{E} \tag{54}$$

Now since α and Me are in electrochemical equilibrium as regards the electron,

$$\varphi^\alpha - \varphi^\mathrm{I} = \frac{\mu^\alpha_\ominus - \mu^\mathrm{I}_\ominus}{F} \tag{55}$$

where $\mu^\mathrm{I}_\ominus$ is the chemical potential of the electron in Me. But since the composition of the reference electrode and therefore that of Me is constant, $\mu^\mathrm{I}_\ominus$ is constant and hence

$$\mathrm{d}\,(\varphi^\alpha - \varphi^\mathrm{I}) = \mathrm{d}\,\frac{\mu^\alpha_\ominus}{F} \tag{56}$$

so that equation 54 becomes

$$\mathrm{d}\sigma = -\sum_{j=1}^{q^\alpha} \Gamma^\alpha_{j+}\mathrm{d}\mu^\alpha_j + \epsilon^\alpha \mathrm{d}\mathfrak{E} \tag{57}$$

The μ^α_j in this equation are of course subject to the Gibbs-Duhem relation at constant T and P^α, which may be written as

$$\sum_{j=1}^{q^\alpha} N^\alpha_j \mathrm{d}\mu^\alpha_j = 0 \tag{58}$$

where N^α_j is the equivalent fraction of the j^{th} metal, defined in analogy to the mole fraction by

$$N^\alpha_j = \frac{n^\alpha_j}{\sum\limits_{j'=1}^{q^\alpha} n^\alpha_{j'}} \tag{59}$$

n^α_j and $n^\alpha_{j'}$ being the number of *equivalents* of the j^{th} and the j'^{th} metal in a given mass of the interior of the phase α. The simultaneous equations 57 and 58 give a complete thermodynamic account of the case of any number of metals at constant temperature and pressure.

C. The case $p^\alpha = 3$

In this case the interior of α consists of a solution of two metals. Let the subscript 1 refer to the solvent metal; subscript 2 to the solute metal. Then equations 57 and 58 become, respectively,

$$d\sigma = -\Gamma^{\alpha}_{1+}d\mu^{\alpha}_{1+} - \Gamma^{\alpha}_{2+}d\mu^{\alpha}_{2+} + \epsilon^{\alpha}d\mathfrak{E} \tag{60}$$

$$N^{\alpha}_{1}d\mu^{\alpha}_{1} + N^{\alpha}_{2}d\mu^{\alpha}_{2} = 0 \tag{61}$$

The elimination of the chemical potential of the solvent metal, μ^{α}_{1}, from equations 60 and 61 gives

$$d\sigma = \left(\frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha}_{1+} - \Gamma^{\alpha}_{2+}\right)d\mu^{\alpha}_{2} + \epsilon^{\alpha}d\mathfrak{E} \tag{62}$$

This equation yields for the vertical shift of the electrocapillary maximum with μ^{α}_{2} (by setting $\epsilon^{\alpha} = 0$ according to equation 41)

$$\frac{\partial\sigma^{\max}}{\partial\mu^{\alpha}_{2}} = \frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha\,\max}_{1+} - \Gamma^{\alpha\,\max}_{2+} \tag{63}$$

for the vertical shift of the electrocapillary curve

$$\left(\frac{\partial\sigma}{\partial\mu^{\alpha}_{2}}\right)_{\mathfrak{E}} = \frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha}_{1+} - \Gamma^{\alpha}_{2+} \tag{64}$$

for the horizontal shift of the electrocapillary curve

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\alpha}_{2}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left(\frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha}_{1+} - \Gamma^{\alpha}_{2+}\right) \tag{65}$$

For sufficiently small values of N^{α}_{2} the terms in $\frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha}_{1+}$ in equations 63, 64, and 65 may be neglected; this yields the approximate relations

$$\frac{\partial\sigma^{\max}}{\partial\mu^{\alpha}_{2}} = -\Gamma^{\alpha\,\max}_{2+} \tag{66}$$

$$\left(\frac{\partial\sigma}{\partial\mu^{\alpha}_{2}}\right)_{\mathfrak{E}} = -\Gamma^{\alpha}_{2+} \tag{67}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\alpha}_{2}}\right)_{\sigma} = \frac{\Gamma^{\alpha}_{2+}}{\epsilon^{\alpha}} \tag{68}$$

so that from the shift of the curve with composition, the adsorption of the solute metal ions in a sufficiently dilute metallic solution may be calculated if the thermodynamic properties of the solution are known. It is to be noted that the equations lead to no relation giving Γ^{α}_{1+} or Γ^{α}_{e} in terms of experimentally observable quantities, so that the knowledge of the composition of the metallic side of the double layer obtainable from thermodynamics alone, while valuable, is incomplete. Equation 67 is essentially identical with an equation given by Frumkin (2).

IV. VARIATION OF THE ELECTROCAPILLARY CURVE WITH THE COMPOSITION OF THE NONMETALLIC PHASE

Let the temperature T, the pressures P^α, P^β the composition of the metallic phase α, and the composition of the reference electrode be kept constant, and only the composition of the nonmetallic phase β and the applied potential $\mathfrak{E}$ be varied. Under these conditions the terms in T, μ_i^α, and $(\varphi^\alpha - \varphi^\mathrm{I})$ vanish from equation 40.1, leaving

$$d\sigma = -\sum_{i=1}^{p^\beta} \Gamma_i^\beta d\mu_i^\beta - \sum_{k=1}^{r^\beta} \Gamma_k^\beta d\mu_k^\beta - \epsilon^a d(\varphi^{\mathrm{II}} - \varphi^\beta) + \epsilon^a d\mathfrak{E} \qquad (69)$$

Owing to the possibility of more than one kind of charged component of each sign in β as well as of neutral components, and furthermore of various types of electrochemical behavior at the junction between β and the reference electrode, this case is more complicated than that of the metallic phase α. As a result equation 69, in contrast to equation 49, is not reducible to a simpler form without added restrictions. The discussion is therefore profitably limited to a number of special cases of physical interest.

A. The case $p^\beta = 2$

This case, the simplest possible, is trivial because the interior of β can consist only of a single electrolyte[3] dissociating into two kinds of ions (e.g., a molten salt), so that variations of composition are impossible. Equation 69 reduces to the Lippmann-Helmholtz equation (41).

B. The case $p^\beta = 2$, $r^\beta = 1$

In this case the interior of β contains one electrolyte dissociating into two kinds of ions and one nonelectrolyte. The best examples are electrolyte solutions in certain organic solvents, e.g., lithium chloride in acetone. Aqueous electrolyte solutions come under this case only in so far as the dissociation of the water may be neglected; as shown later (II, p. 361) this is possible without serious error in certain special cases. In the following treatment the nonelectrolyte is regarded as the solvent in the interior of β, the electrolyte as the solute, because this is the situation met with in practice.

Let μ_+^β and μ_-^β be the chemical potentials (per equivalent) of the cation and anion of the electrolyte, and μ_0^β the chemical potential (per mole) of

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[3] In the present discussion of the nonmetallic phase, the term "electrolyte" will be used in its special, and usual, sense, and not in the general sense of "electrolyte component," as defined in I, p. 115.

the nonelectrolyte. Let Γ^β_+, Γ^β_-, and Γ^β_0 be the corresponding surface densities. Equation 69 then becomes

$$d\sigma = -\Gamma^\beta_+ d\mu^\beta_+ - \Gamma^\beta_- d\mu^\beta_- - \Gamma^\beta_0 d\mu^\beta_0 - \epsilon^\alpha d(\varphi^{\mathrm{II}} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{70}$$

The substitution of

$$\mu^\beta_+ = \mu^\beta - \mu^\beta_- \tag{71.1}$$

or alternatively of

$$\mu^\beta_- = \mu^\beta - \mu^\beta_+ \tag{71.2}$$

where μ^β is the chemical potential per equivalent of electrolyte, yields

$$d\sigma = -\Gamma^\beta_0 d\mu^\beta_0 - \Gamma^\beta_\pm d\mu^\beta \pm (\Gamma^\beta_+ - \Gamma^\beta_-)\, d\mu^\beta_\mp - \epsilon^\alpha d(\varphi^{\mathrm{II}} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{72}$$

where the two alternative equations are written as a single equation with double signs. Since by equations 33.2 and 10.2

$$\Gamma^\beta_+ - \Gamma^\beta_- = \frac{\epsilon^\beta}{F} \tag{73.1}$$

$$= -\frac{\epsilon^\alpha}{F} \tag{73.2}$$

equation 72 becomes

$$d\sigma = -\Gamma^\beta_0 d\mu^\beta_0 - \Gamma^\beta_\pm d\mu^\beta \mp \epsilon^\alpha d\frac{\mu^\beta_\mp}{F} - \epsilon^\alpha d(\varphi^{\mathrm{II}} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{74}$$

The chemical potentials μ^β_0 and μ^β are subject to the Gibbs-Duhem relation

$$N^\beta_0 d\mu^\beta_0 + N^\beta d\mu^\beta = 0 \tag{75}$$

in which N^β_0, N^β are defined similarly to mole fractions by

$$N^\beta_0 = \frac{n^\beta_0}{n^\beta_0 + n^\beta} \qquad N^\beta = \frac{n^\beta}{n^\beta_0 + n^\beta} \qquad (76.1)\ (76.2)$$

where n^β_0 and n^β are the number of moles of nonelectrolyte and equivalents of electrolyte, respectively, in a given mass of the interior of β. Since the nonelectrolyte is regarded as the solvent, it is expedient to eliminate μ^β_0 from equations 74 and 75; this gives

$$d\sigma = \left(\frac{N^\beta}{N^\beta_0}\Gamma^\beta_0 - \Gamma^\beta_\pm\right) d\mu^\beta \mp \epsilon^\alpha d\frac{\mu^\beta_\mp}{F} - \epsilon^\alpha d(\varphi^{\mathrm{II}} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{77}$$

For the vertical shift of the electrocapillary maximum ($\epsilon^\alpha = 0$) with μ^β, equation 77 yields

$$\frac{\partial\sigma^{\max}}{\partial\mu^\beta} = \frac{N^\beta}{N^\beta_0}\Gamma^{\beta\max}_0 - \Gamma^{\beta\max}_\pm \tag{78}$$

The double sign remaining in this equation can be eliminated, because on setting $\epsilon^\alpha = 0$ in equation 73.2 it appears that

$$\Gamma_{+}^{\beta\max} = \Gamma_{-}^{\beta\max} \tag{79}$$

so that it is permissible to set

$$\Gamma_{\pm}^{\beta\max} = \Gamma_{\text{electrolyte}}^{\beta\max} \tag{80}$$

and equation 78 becomes

$$\frac{\partial\sigma^{\max}}{\partial\mu^\beta} = \frac{N^\beta}{N_0^\beta}\,\Gamma_0^{\beta\max} - \Gamma_{\text{electrolyte}}^{\beta\max} \tag{81}$$

In sufficiently dilute solutions of the electrolyte the term $\frac{N^\beta}{N_0^\beta}\,\Gamma_0^{\beta\max}$ is negligible and equation 81 becomes

$$\frac{\partial\sigma^{\max}}{\partial\mu^\beta} = -\,\Gamma_{\text{electrolyte}}^{\beta\max} \tag{82}$$

This equation may be taken as the basis for the distinction between capillary-inactive $\left(\frac{\partial\sigma^{\max}}{\partial\mu^\beta} \sim 0\right)$ and capillary-active $\left(\frac{\partial\sigma^{\max}}{\partial\mu^\beta} < 0\right)$ electrolytes in a given nonelectrolyte solvent.

The further consequences of the alternative equations 77 depend upon the electrochemical behavior of the junction between the phase β (of variable composition) and the reference electrode (of constant composition). The following two cases are of physical interest:

Special case 1. The potential difference $(\varphi^{\text{II}} - \varphi^\beta)$ is given either by the equation

$$\varphi^{\text{II}} - \varphi^\beta = \text{constant} + \frac{\mu_+^\beta}{F} \tag{83.1}$$

or by the equation

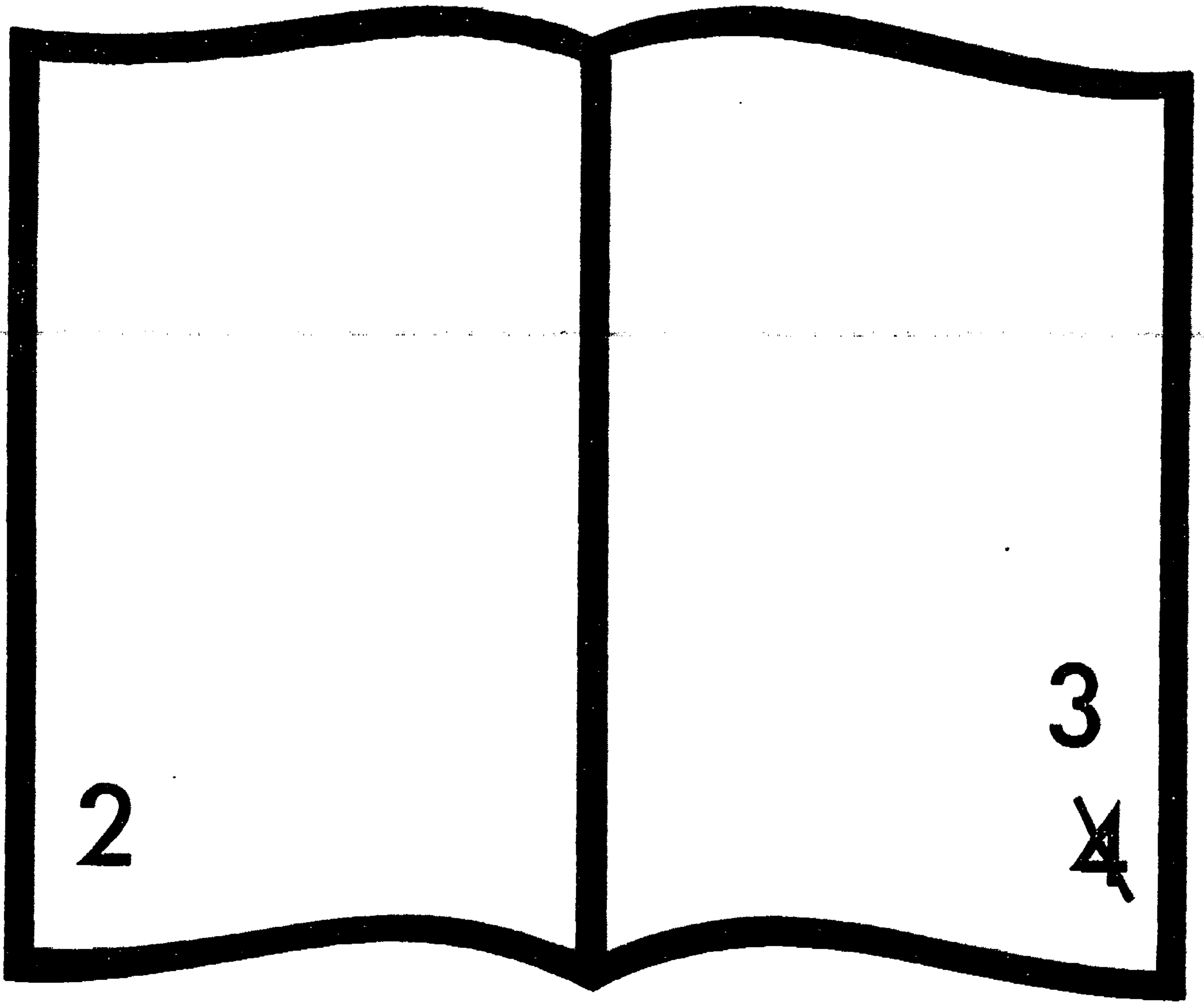
$$\varphi^{\text{II}} - \varphi^\beta = \text{constant} - \frac{\mu_-^\beta}{F} \tag{83.2}$$

If $(\varphi^{\text{II}} - \varphi^\beta)$ is given by equation 83.1, then the reference electrode will be said to *respond simply to the cation* of β. Example:

$$\overset{\text{I}}{\text{Me}} \mid \overset{\alpha}{\text{Hg}} \mid \text{KNO}_3 \text{ solution of } \overset{\beta}{\text{variable}} \text{ concentration} \mid \text{K amalgam of constant}$$
$$\text{concentration} \mid \overset{\text{II}}{\text{Me}}$$

And if $(\varphi^{\text{II}} - \varphi^\beta)$ is given by equation 83.2, the reference electrode will be said to *respond simply to the anion* of β. Example:

$$\overset{\text{I}}{\text{Me}} \mid \overset{\alpha}{\text{Hg}} \mid \text{KCl solution of } \overset{\beta}{\text{variable}} \text{ concentration} \mid \text{HgCl} \mid \text{Hg} \mid \overset{\text{II}}{\text{Me}}$$


2
3
~~4~~

Special case 2. The junction between β and the reference electrode is a "liquid-liquid junction." Example:

$$\overset{\mathrm{I}}{\mathrm{Me}}\mid\overset{\alpha}{\mathrm{Hg}}\mid\overset{\beta}{\mathrm{KNO_3\ solution\ of\ variable\ concentration}}\mid\overset{\gamma}{1N\ \mathrm{H_2SO_4}}\mid\mathrm{Hg_2SO_4}\mid\mathrm{Hg}\mid\overset{\mathrm{II}}{\mathrm{Me}}$$

in which the solvent[4] in the phases β and γ is the same.

Of these two special cases, the first is the simpler theoretically, but special case 2 is the only one which has hitherto been investigated experimentally.

Special case 1. The reference electrode responds simply either to the cation or the anion of β. If it responds simply to the cation it follows from equation 83.1 that

$$\mathrm{d}\,(\varphi^{\mathrm{II}} - \varphi^{\beta}) = \mathrm{d}\,\frac{\mu_{+}^{\beta}}{F} \tag{84.1}$$

and hence from equation 77 with the lower sign that

$$\mathrm{d}\sigma = \left(\frac{N^{\beta}}{N_0^{\beta}}\,\Gamma_0^{\beta} - \Gamma_{-}^{\beta}\right)\mathrm{d}\mu^{\beta} + \epsilon^{\alpha}\mathrm{d}\mathfrak{E} \tag{85.1}$$

If, on the other hand, the reference electrode responds simply to the anion of β, it follows from equation 83.2 that

$$\mathrm{d}\,(\varphi^{\mathrm{II}} - \varphi^{\beta}) = -\,\mathrm{d}\,\frac{\mu_{-}^{\beta}}{F} \tag{84.2}$$

and hence from equation 77 with the upper sign that

$$\mathrm{d}\sigma = \left(\frac{N^{\beta}}{N_0^{\beta}}\,\Gamma_0^{\beta} - \Gamma_{+}^{\beta}\right)\mathrm{d}\mu^{\beta} + \epsilon^{\alpha}\mathrm{d}\mathfrak{E} \tag{85.2}$$

Equations 85.1 and 85.2 yield the following relations for the shift of the electrocapillary curve with μ^{β}: if the reference electrode responds simply to the

cation of β	*anion of β*	
$\left(\frac{\partial\sigma}{\partial\mu^{\beta}}\right)_{\mathfrak{E}} = \frac{N^{\beta}}{N_0^{\beta}}\Gamma_0^{\beta} - \Gamma_{-}^{\beta}$	$\left(\frac{\partial\sigma}{\partial\mu^{\beta}}\right)_{\mathfrak{E}} = \frac{N^{\beta}}{N_0^{\beta}}\Gamma_0^{\beta} - \Gamma_{+}^{\beta}$	(86.1) (86.2)
$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\beta}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left(\frac{N^{\beta}}{N_0^{\beta}}\Gamma_0^{\beta} - \Gamma_{-}^{\beta}\right)$	$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\beta}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left(\frac{N^{\beta}}{N_0^{\beta}}\Gamma_0^{\beta} - \Gamma_{+}^{\beta}\right)$	(87.1) (87.2)

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[4] In so far as the solutions used in the examples for the above cases 1 and 2 are considered to be aqueous, the electrolytc dissociation of the water is neglected here. As shown in II, p. 361, this assumption leads to no serious error in a number of cases.

For sufficiently small values of N^β equations 86.1 to 87.2 lead to the approximate relations

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{E}} = -\Gamma_-^\beta \qquad \left(\frac{\partial\sigma}{\partial\nu^\beta}\right)_{\mathfrak{E}} = -\Gamma_+^\beta \qquad (88.1)\ (88.2)$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = \frac{\Gamma_-^\beta}{\epsilon^\alpha} \qquad \left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = \frac{\Gamma_+^\beta}{\epsilon^\alpha} \qquad (89.1)\ (89.2)$$

so that from the shift of the curve with composition, the adsorption of the solute cation or anion in a sufficiently dilute solution may be calculated, if the thermodynamic properties of the solution are known. Any one of the equations 88.1 to 89.2 together with equations 73.1 and 73.2 and the Lippmann-Helmholtz equation (41) evidently leads to a complete knowledge of the ionic content of the nonmetallic side of the double layer in this case.

Special case 2. The junction between β and the reference electrode is a liquid-liquid junction. This case may be represented schematically as follows:

$$\overset{\text{I}}{\text{Me}} \,|\, \alpha \,|\, \beta \,|\, \gamma \,|||\, \overset{\text{II}}{\text{Me}}$$

in which Me ||| γ is the reference electrode, and the liquid-liquid junction β | γ is made up in some definite and reproducible manner. The system thus represented will be referred to as system S. In order to apply equation 77 it is expedient to consider besides system S also the following cell, henceforth designated as system S′:

$$\overset{\text{III}}{\text{Me}} \,\underset{1}{|||}\, \beta \,|\, \gamma \,|||\, \overset{\text{IV}}{\text{Me}}$$

In this cell the electrode Me ||| γ and the liquid-liquid junction β | γ are supposed to be identical with the reference electrode and the junction β | γ, respectively, in system S. The electrode Me $\underset{1}{|||}$ of system S′ is supposed to be any electrode whatever which responds simply to either the cation or the anion of β as defined under special case 1 (II, p. 347), and will henceforth be referred to as electrode 1. The Roman numerals I, II, III, IV serve merely to label, for the purposes of discussion, the four separate pieces of the *same* metal Me which form the terminals of S and S′.

The quantity $(\varphi^{\text{II}} - \varphi^\beta)$ occurring in equation 77 may now be transformed as follows:

$$\varphi^{\text{II}} - \varphi^\beta = (\varphi^{\text{II}} - \varphi^\beta)_S = (\varphi^{\text{IV}} - \varphi^\beta)_{S'} \qquad (90)$$

$$= (\varphi^{\text{III}} - \varphi^\beta)_{S'} + (\varphi^{\text{IV}} - \varphi^{\text{III}})_{S'} \qquad (91)$$

$$= (\varphi^{\text{III}} - \varphi^\beta)_{S'} + \mathfrak{E}' \qquad (92)$$

where the subscripts S and S′ indicate the systems to which the corresponding quantities in parenthesis refer, and $\mathfrak{E}'$ is the E.M.F. of the cell, system S′, defined by

$$\mathfrak{E}' = (\varphi^{\mathrm{IV}} - \varphi^{\mathrm{III}})_{S'} \tag{93}$$

The introduction of equation 92 into equation 77 gives

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_\pm^\beta\right)d\mu^\beta \mp \epsilon^a d\frac{\mu_\mp^\beta}{F} - \epsilon^a d(\varphi^{\mathrm{III}} - \varphi^\beta)_{S'} - \epsilon^a d\mathfrak{E}' + \epsilon^a d\mathfrak{E} \tag{94}$$

If now electrode 1 responds simply to the cation of β it follows in analogy to equation 84.1 that

$$d(\varphi^{\mathrm{III}} - \varphi^\beta)_{S'} = d\frac{\mu_+^\beta}{F} \tag{95.1}$$

and hence from equation 94 with the lower sign that

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta\right)d\mu^\beta - \epsilon^a d\mathfrak{E}' + \epsilon^a d\mathfrak{E} \tag{96.1}$$

Similarly if electrode 1 responds simply to the anion of β it follows in analogy to equation 84.2 that

$$d(\varphi^{\mathrm{III}} - \varphi^\beta)_{S'} = -d\frac{\mu_-^\beta}{F} \tag{95.2}$$

and hence from equation 94 with the upper sign that

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta\right)d\mu^\beta - \epsilon^a d\mathfrak{E}' + \epsilon^a d\mathfrak{E} \tag{96.2}$$

Equations 96.1 and 96.2 yield the following relations for the shift of the electrocapillary curve with μ^β : if electrode 1 responds simply to the

cation of β

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{E}} = \frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta - \epsilon^a\frac{\partial\mathfrak{E}'}{\partial\mu^\beta} \tag{97.1}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = -\frac{1}{\epsilon^a}\left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta\right) + \frac{\partial\mathfrak{E}'}{\partial\mu^\beta} \tag{98.1}$$

anion of β

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{E}} = \frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta - \epsilon^a\frac{\partial\mathfrak{E}'}{\partial\mu^\beta} \tag{97.2}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = -\frac{1}{\epsilon^a}\left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta\right) + \frac{\partial\mathfrak{E}'}{\partial\mu^\beta} \tag{98.2}$$

In sufficiently dilute solutions the terms in $\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta$ may be neglected as in special case 1.

The comparison of equations 97.1 to 98.2 with equations 86.1 to 87.2 shows that special case 2 leads to exactly the same information regarding the double layer as special case 1, provided $\frac{\partial \mathfrak{E}'}{\partial \mu^\beta}$ is known. In general, the only way of obtaining accurate values of $\frac{\partial \mathfrak{E}'}{\partial \mu^\beta}$ is by experiment, because the cell S′ contains a liquid–liquid junction (variable with β) and the exact thermodynamic equations for the E.M.F. of such cells contain so many unknown factors as to be useless practically. The situation may be illustrated by considering a particular system, for instance, the system given as an example of special case 2 in II, p. 348. A possible choice for the corresponding system S′ is the following:

III β
Me | K amalgam of constant concentration | KNO$_3$ solution of variable concentration—
γ IV
1 N H$_2$SO$_4$ | Hg$_2$SO$_4$ | Hg | Me

The exact equations for the E. M. F. $\mathfrak{E}'$ of this cell are:[5]

$$\mathfrak{E}' = \mathfrak{E}_{\mathrm{El}} + \mathfrak{E}_{\mathrm{D}} + \mathfrak{E}_{\mathrm{S}} \tag{99}$$

where

$$\mathfrak{E}_{\mathrm{El}} = \mathfrak{E}_0 - \frac{RT}{F}\ln c^\beta_{\mathrm{K}^+} - \frac{RT}{2F}\ln c^\gamma_{\mathrm{SO}_4^=} \tag{100}$$

$$\begin{aligned}\mathfrak{E}_{\mathrm{D}} = \frac{RT}{F}\Bigg\{\int_\gamma^\beta t_{\mathrm{K}^+}\mathrm{d}\ln c_{\mathrm{K}^+} + \int_\gamma^\beta t_{\mathrm{H}^+}\mathrm{d}\ln c_{\mathrm{H}^+} - \int_\gamma^\beta t_{\mathrm{NO}_3^-}\mathrm{d}\ln c_{\mathrm{NO}_3^-} \\ - \tfrac{1}{2}\int^\beta t_{\mathrm{SO}_4^=}\mathrm{d}\ln c_{\mathrm{SO}_4^=}\Bigg\}\end{aligned} \tag{101}$$

$$\begin{aligned}\mathfrak{E}_{\mathrm{S}} = \frac{3RT}{2F}\Bigg\{\int_\gamma^\beta t_{\mathrm{K}^+}\mathrm{d}\ln f_{\mathrm{K}^+,\,\mathrm{SO}_4^=} + \int^\beta t_{\mathrm{H}^+}\mathrm{d}\ln f_{\mathrm{H}^+,\,\mathrm{SO}_4^=} \\ + \int_\gamma^\beta t_{\mathrm{NO}_3^-}\mathrm{d}\ln\left[(f_{\mathrm{K}^+,\,\mathrm{NO}_3^-})^{-\frac{4}{3}}\cdot f_{\mathrm{K}^+,\,\mathrm{SO}_4^=}\right] - \ln f^\beta_{\mathrm{K}^+,\,\mathrm{SO}_4^=}\Bigg\}\end{aligned} \tag{102}$$

$\mathfrak{E}_{\mathrm{El}}$ is the ideal value of that part of the total E.M.F. which is due to the two electrode potentials of the cell S′, $\mathfrak{E}_{\mathrm{D}}$ is the ideal value of the diffusion

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[5] The exact thermodynamic treatment of cells with liquid–liquid junctions is due to P. B. Taylor (5) and E. A. Guggenheim (3). Equations 99 to 102 were derived by the methods of these authors, so that the inclusion of the derivation here is unnecessary.

potential at the liquid-liquid junction between β and γ, and $\mathfrak{E}_S$ takes account of the deviations of the two electrode potentials and of the diffusion potential from their ideal values; c and t denote the concentration in equivalents per liter of solution and the transference number in equivalents per faraday, respectively, of the ion indicated in the subscript; f denotes the mean activity coefficient of the salt corresponding to the ions indicated in the subscript; $\mathfrak{E}^0$ is a constant. The evaluation of the integrals in equations 101 and 102 necessitates a knowledge of the values of c, t, and f both in the interiors of β and γ and at every point of the intermediate diffusion layer, and is therefore at present impossible. It follows that the calculation of accurate values of $\frac{\partial \mathfrak{E}'}{\partial \mu^\beta}$ from such equations as 99 to 102 is also impossible at the present state of knowledge. As a rule, therefore, the complete thermodynamic interpretation of the electrocapillary data in special case 2 necessitates supplementary measurements of the E. M. F. of cells of the type S′.

In at least one case of physical interest, however, the theoretical expression for $\frac{\partial \mathfrak{E}'}{\partial \mu^\beta}$ is simple enough to be of practical value. This case is defined by the following two conditions: (1) The phase γ of the reference electrode contains only one electrolyte which is the same as that in β. (2) The reference electrode responds simply to either the cation or the anion of γ, i.e., if the concentration of the electrolyte in γ were varied, then

$$(\varphi^{II} - \varphi^{\gamma})_s = (\varphi^{IV} - \varphi^{\gamma})_{s'} = \begin{cases} \text{either: constant} + \frac{\mu^\gamma_+}{F} & (103.1) \\ \text{or: constant} - \frac{\mu^\gamma_-}{F} & (103.2) \end{cases}$$

The simplicity of this case arises from the circumstance that electrode 1 of system S′ may always be chosen so that the ion of β to which it responds simply is the same as the ion of γ to which the reference electrode responds simply; for such cells S′ it is readily shown[6] that

$$d\mathfrak{E}' = -\frac{t^\beta_-}{F}\, d\mu^\beta \text{ if the two electrodes respond simply to the cation} \qquad (104.1)$$

$$d\mathfrak{E}' = \frac{t^\beta_+}{F}\, d\mu^\beta \text{ if the two electrodes respond simply to the anion} \qquad (104.2)$$

An example of a system S fulfilling the above conditions is

$$\begin{array}{cccccccc} \text{I} & \alpha & & \beta & & \gamma & & \text{II} \\ \text{Me} \mid & \text{Hg} \mid & \text{KCl solution of variable concentration} & \mid & 1\,N\ \text{KCl} & \mid \text{HgCl} \mid & \text{Hg} \mid & \text{Me} \end{array}$$

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[6] By the methods used in deriving equations 99 to 102. See II, footnote 5; also reference 4.

The corresponding system S′ is

III β γ IV
Me | Hg | HgCl | KCl solution of variable concentration | 1 *N* KCl | HgCl | Hg | Me

which obeys equation 104.2. The introduction of equations 104.1 and 104.2 respectively into equations 96.1 and 96.2 yields the equations

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta + \frac{\epsilon^\alpha t_-^\beta}{F}\right)d\mu^\beta + \epsilon^\alpha d\mathfrak{E} \qquad (105.1)$$

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta - \frac{\epsilon^\alpha t_+^\beta}{F}\right)d\mu^\beta + \epsilon^\alpha d\mathfrak{E} \qquad (105.2)$$

which give for the shift of the electrocapillary curve, if the reference electrode responds simply to the

cation of γ

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{E}} = \frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta + \frac{\epsilon^\alpha t_-^\beta}{F} \qquad (106.1)$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = -\frac{1}{\epsilon^\alpha}\left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta\right) - \frac{t_-^\beta}{F} \qquad (107.1)$$

anion of γ

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{E}} = \frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta - \frac{\epsilon^\alpha t_+^\beta}{F} \qquad (106.2)$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = -\frac{1}{\epsilon^\alpha}\left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta\right) + \frac{t_+^\beta}{F} \qquad (107.2)$$

In sufficiently dilute solutions the terms in $\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta$ may be neglected as before.

Finally a semiquantitative general result useful in dilute solutions is obtainable by the following approximations: (1) The deviation of the solution in β from ideality is neglected. (2) The liquid–liquid junction between β and γ is neglected. (3) The term $\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta$ is neglected. From approximation 1 it follows that

$$d\mu_+^\beta = \frac{RT}{z_+^\beta}\,d\ln c^\beta \qquad (108.1)$$

$$d\mu_-^\beta = -\frac{RT}{z_-^\beta}\,d\ln c^\beta \qquad (108.2)$$

$$d\mu^\beta = \frac{z_-^\beta - z_+^\beta}{z_+^\beta z_-^\beta}\,RT\,d\ln c^\beta \qquad (109)$$

where z_{+}^{β}, z_{-}^{β} are the valences (with sign included) of the cation and anion in β and c^{β} is the equivalent concentration of the electrolyte. Furthermore from equation 93 it follows that

$$\mathrm{d}\mathfrak{E}' = \mathrm{d}(\varphi^{\mathrm{IV}} - \varphi^{\mathrm{III}})_{s'} \tag{110}$$

$$= -\,\mathrm{d}(\varphi^{\mathrm{III}} - \varphi^{\beta})_{s'} + \mathrm{d}(\varphi^{\mathrm{IV}} - \varphi^{\beta})_{s'} \tag{111}$$

which on introduction of equation 95.1 or 95.2 becomes

$$\mathrm{d}\mathfrak{E}' = -\,\mathrm{d}\,\frac{\mu_{+}^{\beta}}{F} + \mathrm{d}(\varphi^{\mathrm{IV}} - \varphi^{\beta})_{s'} \text{ if electrode 1 responds simply to the cation of } \beta \tag{112.1}$$

$$\mathrm{d}\mathfrak{E}' = \mathrm{d}\,\frac{\mu_{-}^{\beta}}{F} + \mathrm{d}(\varphi^{\mathrm{IV}} - \varphi^{\beta})_{s'} \text{ if electrode 1 responds simply to the anion of } \beta \tag{112.2}$$

By approximation 2 the term $\mathrm{d}(\varphi^{\mathrm{IV}} - \varphi^{\beta})_{s'}$ drops out; the substitution of equations 108.1 and 108.2 respectively into equations 112.1 and 112.2 then gives

$$\mathrm{d}\mathfrak{E}' = -\frac{RT}{z_{+}^{\beta}F}\,\mathrm{d}\ln c^{\beta} \tag{113.1}$$

$$\mathrm{d}\mathfrak{E}' = -\frac{RT}{z_{-}^{\beta}F}\,\mathrm{d}\ln c^{\beta} \tag{113.2}$$

Introducing equation 113.1 into equation 96.1, equation 113.2 into equation 96.2, and furthermore equation 109 and approximation 3 into both equation 96.1 and 96.2 yields the *alternative* equations

$$\mathrm{d}\sigma = RT\left[\frac{z_{+}^{\beta} - z_{-}^{\beta}}{z_{+}^{\beta}z_{-}^{\beta}}\,\Gamma_{\pm}^{\beta} + \frac{\epsilon^{\alpha}}{z_{\mp}^{\beta}F}\right]\mathrm{d}\ln c^{\beta} + \epsilon^{\alpha}\mathrm{d}\mathfrak{E} \tag{114}$$

That these equations (114) are alternative is proved by the fact that one of them is obtainable from the other by the substitution of

$$\Gamma_{\pm}^{\beta} = \Gamma_{\mp}^{\beta} \mp \frac{\epsilon^{\alpha}}{F} \tag{115}$$

obtained from equation 73.2.

Equation 114 gives for the shift of the electrocapillary curve with concentration

$$\frac{\partial\sigma^{\max}}{\partial\ln c^{\beta}} = RT\,\frac{z_{+}^{\beta} - z_{-}^{\beta}}{z_{+}^{\beta}z_{-}^{\beta}}\,\Gamma_{\text{electrolyte}}^{\beta_{\max}} \tag{116}$$

$$\left(\frac{\partial\sigma}{\partial\ln c^{\beta}}\right)_{\mathfrak{E}} = RT\left[\frac{z_{+}^{\beta} - z_{-}^{\beta}}{z_{+}^{\beta}z_{-}^{\beta}}\,\Gamma_{\pm}^{\beta} + \frac{\epsilon^{\alpha}}{z_{\mp}^{\beta}F}\right] \tag{117}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\ln c^{\beta}}\right)_{\sigma} = RT\left[\frac{z_{-}^{\beta} - z_{+}^{\beta}}{z_{+}^{\beta}z_{-}^{\beta}}\cdot\frac{\Gamma_{\pm}^{\beta}}{\epsilon^{\alpha}} - \frac{1}{z_{\mp}^{\beta}F}\right] \tag{118}$$

For the special case of a capillary-inactive electrolyte at points along the electrocapillary curve sufficiently far removed from the maximum equation 118 may be integrated with the aid of a further approximation. In such an electrolyte the adsorption Γ_+^β, Γ_-^β of the two ions is due wholly to the electrostatic attraction of the charged metal surface, specific chemical forces being absent. Along the ascending branch $\epsilon^\alpha > 0$, so that the metal surface attracts anions and repels cations, whence $\Gamma_-^\beta > 0$, $\Gamma_+^\beta < 0$. At points far removed from the maximum, where ϵ^α is relatively large, Γ_+^β, because it is negative and the solution is dilute, is still relatively small numerically, so that for the lower part of the ascending branch the ratio $\frac{\Gamma_+^\beta}{\epsilon^\alpha}$ becomes negligible in equation 118. Setting $\frac{\Gamma_+^\beta}{\epsilon^\alpha} = 0$ in equation 118 (upper sign) gives

$$\left(\frac{\partial \mathfrak{E}}{\partial \ln c^\beta}\right)_\sigma = -\frac{RT}{z_-^\beta F} \tag{119.1}$$

which may be integrated at constant σ, giving for the horizontal displacement of the ascending branch with concentration,

$$\mathfrak{E}_2 - \mathfrak{E}_1 = -\frac{RT}{z_-^\beta F} \ln \frac{c_2^\beta}{c_1^\beta} \tag{120.1}$$

Similarly for the lower part of the descending branch $\frac{\Gamma_-^\beta}{\epsilon^\alpha}$ may be neglected and equation 118 (lower sign) gives

$$\left(\frac{\partial \mathfrak{E}}{\partial \ln c^\beta}\right)_\sigma = -\frac{RT}{z_+^\beta F} \tag{119.2}$$

$$\mathfrak{E}_2 - \mathfrak{E}_1 = -\frac{RT}{z^\beta F} \ln \frac{c_2^\beta}{c_1^\beta} \tag{120.2}$$

Equations 120.1 and 120.2 have already been given by Frumkin (1, 2).

C. The case $p^\alpha = 3$

In this case the interior of β consists of two electrolytes of two ions each, one of these ions being common to both electrolytes. The common ion may be either a cation or an anion. The best examples are aqueous solutions of acids (cation H^+ in common) and of metallic hydroxides (anion OH^- in common).

Special case 1. The common ion is a cation. In this case equation 69 becomes

$$d\sigma = -\Gamma_+^\beta d\mu_+^\beta - \Gamma_{1-}^\beta d\mu_{1-}^\beta - \Gamma_{2-}^\beta d\mu_{2-}^\beta - \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{121}$$

in which the subscript + refers to the cation, and the subscripts 1 − and 2 − to the anions of the solvent and the solute respectively. The substitution into equation 121 of the two relations

$$\mu_{1-}^{\beta} = \mu_1^{\beta} - \mu_+^{\beta} \tag{122.1}$$

$$\mu_{2-}^{\beta} = \mu_2^{\beta} - \mu_+^{\beta} \tag{122.2}$$

where μ_1 and μ_2 are the chemical potentials per equivalent of solvent and solute respectively, yields

$$d\sigma = -\Gamma_{1-}^{\beta} d\mu_1^{\beta} - \Gamma_{2-}^{\beta} d\mu_2^{\beta} - (\Gamma_+^{\beta} - \Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta})\, d\mu_+^{\beta} - \epsilon^{a} d(\varphi^{\mathrm{II}} - \varphi^{\beta}) + \epsilon^{a} d\mathfrak{E} \tag{123}$$

From equations 33.2 and 10.2 it follows that

$$\Gamma_+^{\beta} - \Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta} = \frac{\epsilon^{\beta}}{F} \tag{124.1}$$

$$= -\frac{\epsilon^{a}}{F} \tag{124.2}$$

and hence from equation 123 that

$$d\sigma = -\Gamma_{1}^{\beta}\text{-}d\mu_1^{\beta} - \Gamma_2^{\beta} - d\mu_{2-}^{\beta} + \epsilon^{a} d\frac{\mu_+^{\beta}}{F} - \epsilon^{a} d(\varphi^{\mathrm{II}} - \varphi^{\beta}) + \epsilon^{a} d\mathfrak{E} \tag{125}$$

which, on elimination of μ_1^{β} by means of the Gibbs-Duhem relation:

$$N_1^{\beta} d\mu_2^{\beta} + N_2^{\beta} d\mu_2^{\beta} = 0 \tag{126}$$

gives

$$d\sigma = \left(\frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta}\right) d\mu_2^{\beta} + \epsilon^{a} d\frac{\mu_+^{\beta}}{F} - \epsilon^{a} d(\varphi^{\mathrm{II}} - \varphi^{\beta}) + \epsilon^{a} d\mathfrak{E} \tag{127}$$

where N_1^{β} and N_2^{β} are the equivalent fractions (cf. equation 59) of solvent and solute respectively.

For the shift of $\sigma^{\max}$ with μ_2^{β} equation 127 yields

$$\frac{\partial\sigma^{\max}}{\partial\mu_2^{\beta}} = \frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta\max} - \Gamma_{2-}^{\beta\max} \tag{128}$$

in which the term $\frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta\max}$ is negligible in sufficiently dilute solutions, giving the approximate relation

$$\frac{\partial\sigma^{\max}}{\partial\mu_2^{\beta}} = -\Gamma_{2-}^{\beta\max} \tag{129}$$

The further consequences of equation 127 depend upon the nature of the junction between β and the reference electrode. The following four special cases 1α, 1β, 1γ, 1δ are of physical interest.

Special case 1α. The reference electrode responds simply to the cation of β, i.e.,

$$d(\varphi^{\mathrm{II}} - \varphi^{\beta}) = d\,\frac{\mu_{+}^{\beta}}{F} \tag{130}$$

The introduction of equation 130 into equation 127 gives

$$d\sigma = \left(\frac{N_2^{\beta}}{N_1^{\beta}}\,\Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta}\right) d\mu_2^{\beta} + \epsilon^{\alpha} d\mathfrak{E} \tag{131}$$

This equation yields for the shift of the electrocapillary curve with μ_2^{β}

$$\left(\frac{\partial\sigma}{\partial\mu_2^{\beta}}\right)_{\mathfrak{E}} = \frac{N_2^{\beta}}{N_1^{\beta}}\,\Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta} \tag{132}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu_2^{\beta}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left(\frac{N_2^{\beta}}{N_1^{\beta}}\,\Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta}\right) \tag{133}$$

in which the term $\frac{N_2^{\beta}}{N_1^{\beta}}\,\Gamma_{1-}^{\beta}$ may be neglected in sufficiently dilute solutions giving the approximate relations

$$\left(\frac{\partial\sigma}{\partial\mu_2^{\beta}}\right)_{\mathfrak{E}} = -\Gamma_{2-}^{\beta} \tag{134}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu_2^{\beta}}\right)_{\sigma} = \frac{\Gamma_{2-}^{\beta}}{\epsilon^{\alpha}} \tag{135}$$

Special case 1β. The reference electrode responds simply to the anion of the solvent in β, i.e.,

$$d(\varphi^{\mathrm{II}} - \varphi^{\beta}) = -d\,\frac{\mu_{1-}^{\beta}}{F} \tag{136}$$

The substitution of the relation

$$\mu_{+}^{\beta} = \mu_{1}^{\beta} - \mu_{1-}^{\beta} \tag{137}$$

into equation 127, and of equations 136 and 126 into the result yields

$$d\sigma = \left[\frac{N_2^{\beta}}{N_1^{\beta}}\left(\Gamma_{1-}^{\beta} - \frac{\epsilon^{\alpha}}{F}\right) - \Gamma_{2-}^{\beta}\right] d\mu_2^{\beta} + \epsilon^{\alpha} d\mathfrak{E} \tag{138}$$

This equation gives for the shift of the electrocapillary curve with μ_2^{β}

$$\left(\frac{\partial\sigma}{\partial\mu_2^{\beta}}\right)_{\mathfrak{E}} = \frac{N_2^{\beta}}{N_1^{\beta}}\left(\Gamma_{1-}^{\beta} - \frac{\epsilon^{\alpha}}{F}\right) - \Gamma_{2-}^{\beta} \tag{139}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu_2^{\beta}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left[\frac{N_2^{\beta}}{N_1^{\beta}}\left(\Gamma_{1-}^{\beta} - \frac{\epsilon^{\alpha}}{F}\right) - \Gamma_{2-}^{\beta}\right] \tag{140}$$

in which the term $\frac{N_2^{\beta}}{N_1^{\beta}}\left(\Gamma_{1-}^{\beta} - \frac{\epsilon^{\alpha}}{F}\right)$ may be neglected in sufficiently dilute solution giving again equations 134 and 135.

Special case 1γ. The reference electrode responds simply to the anion of the solute, i.e.,

$$d(\varphi^{II} - \varphi^{\beta}) = -d\,\frac{\mu^{\beta}_{2-}}{F} \tag{141}$$

The substitution of the relation

$$\mu^{\beta}_{+} = \mu^{\beta}_{2} - \mu^{\beta}_{2-} \tag{142}$$

into equation 127, and of equation 141 into the result yields

$$d\sigma = \left(\frac{N^{\beta}_{2}}{N^{\beta}_{1}}\Gamma^{\beta}_{1-} - \Gamma^{\beta}_{2-} + \frac{\epsilon^{\alpha}}{F}\right)d\mu^{\beta}_{2} + \epsilon^{\alpha}d\mathfrak{E} \tag{143}$$

This equation gives for the shift of the electrocapillary curve with μ^{β}_{2}

$$\left(\frac{\partial\sigma}{\partial\mu^{\beta}_{2}}\right)_{\mathfrak{E}} = \frac{N^{\beta}_{2}}{N^{\beta}_{1}}\Gamma^{\beta}_{1-} - \Gamma^{\beta}_{2-} + \frac{\epsilon^{\alpha}}{F} \tag{144}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\beta}_{2}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left(\frac{N^{\beta}_{2}}{N^{\beta}_{1}}\Gamma^{\beta}_{1-} - \Gamma^{\beta}_{2-}\right) - \frac{1}{F} \tag{145}$$

in which the term $\frac{N^{\beta}_{2}}{N^{\beta}_{1}}\Gamma^{\beta}_{1-}$ may be neglected in sufficiently dilute solutions giving the approximate relations

$$\left(\frac{\partial\sigma}{\partial\mu^{\beta}_{2}}\right)_{\mathfrak{E}} = -\Gamma^{\beta}_{2-} + \frac{\epsilon^{\alpha}}{F} \tag{146}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\beta}_{2}}\right)_{\sigma} = \frac{\Gamma^{\beta}_{2-}}{\epsilon^{\alpha}} - \frac{1}{F} \tag{147}$$

From equations 129, 134, 146, and 41, it is evident that from the shift of the electrocapillary curve with composition, the adsorption of the solute anion in a sufficiently dilute solution may be calculated in the cases considered, if the thermodynamic properties of the solution are known. It is to be noted that the equations lead to no relation giving Γ^{β}_{+} or Γ^{β}_{1-} in terms of experimentally observable quantities, so that the information obtainable, while valuable is incomplete. The situation regarding the nonmetallic side of the double layer for $p^{\beta} = 3$ is therefore similar to that regarding the metallic side in the case $p^{\alpha} = 3$ (II, p. 344; cf. particularly equations 128, 129, 131, 132, 133, 134 and 135 with equations 63, 66, 62, 64, 65, 67, 68).

Special case 1δ. The junction between β and the reference electrode is a liquid-liquid junction. By means of supplementary E.M.F. measurements of suitable cells this special case can always be reduced to one of the foregoing special cases 1α, 1β, 1γ, in exactly the same way as for $p^\beta = 2$, $r^\beta = 1$, special case 2 is reducible to special case 1 by means of the cells S′ (**II**, pp. 349–355).

Special case 2 (of the case $p^\beta = 3$). The common ion is an anion. The results for this special case are immediately obtainable from those for special case 1 by replacing the word "cation" in the discussion of special case 1 by "anion" and vice versa, and, in equations 121, 128, 129, 131 to 135, 138 to 140, 143 to 147, replacing the + in the subscripts by − and vice versa.

D. The case $p^\beta = 4$

This case is so complicated that a general treatment is inexpedient. There is only one special case simple enough to be worth considering here.

Special case 1. This case is defined by two conditions: (1) The interior of β consists of two electrolytes of two ions each, there being no common ion. (2) The ions of the solvent electrolyte are not specifically adsorbed. This special case is of importance because it includes the aqueous solutions of certain neutral salts.

Under condition 1 equation 69 becomes

$$\mathrm{d}\sigma = -\Gamma_{1+}^{\beta}\mathrm{d}\mu_{1+}^{\beta} - \Gamma_{-1}^{\beta}\mathrm{d}\mu_{2-}^{\beta} - \Gamma_{2+}^{\beta}\mathrm{d}\mu_{2+}^{\beta} - \Gamma_{2-}^{\beta}\mathrm{d}\mu_{2-}^{\beta} - \epsilon^{a}\mathrm{d}(\varphi^{\mathrm{II}} - \varphi^{\beta}) + \epsilon^{a}\mathrm{d}\mathfrak{E} \tag{148}$$

where the subscripts 1+, 1− refer to cation and anion of the solvent electrolyte, 2+, 2− to cation and anion of the solute electrolyte. Condition 2 means that

$$\Gamma_{1+}^{\beta} = \Gamma_{1-}^{\beta} \tag{149}$$

so that it is permissible to set

$$\Gamma_{1\pm}^{\beta} = \Gamma_{1}^{\beta} \tag{150}$$

where Γ_1^β is the surface density of the solvent molecules (in equivalents per unit area). The substitution of equation 150 and of the relation

$$\mu_{1+}^{\beta} + \mu_{1-}^{\beta} = \mu_{1}^{\beta} \tag{151}$$

into equation 148 gives

$$\mathrm{d}\sigma = -\Gamma_{1}^{\beta}\mathrm{d}\mu_{1}^{\beta} - \Gamma_{2+}^{\beta}\mathrm{d}\mu_{2+}^{\beta} - \Gamma_{2-}^{\beta}\mathrm{d}\mu_{2-}^{\beta} - \epsilon^{a}\mathrm{d}\,(\varphi^{\mathrm{II}} - \varphi^{\beta}) + \epsilon^{a}\mathrm{d}\mathfrak{E} \tag{152}$$

If the subscripts 1, 2+, 2− are replaced by 0, +, −, respectively, equation 152 becomes identical with equation 70 for the case $p^\beta = 2$, $r^\beta = 1$ (**II**, pp. 345–355). Moreover, under condition 1 above the interior of β contains only two independently variable components, so that the Gibbs-Duhem equation for the case in hand is similar to equation 75 for the case $p^\beta = 2$, $r^\beta = 1$ in that it contains only two terms, namely

$$N_{1}^{\beta}\mathrm{d}\mu_{1}^{\beta} + N_{2}^{\beta}\mathrm{d}\mu_{2}^{\beta} = 0 \tag{153}$$

where μ_1^β is given by equation 151 and μ_2 by

$$\mu_{2+}^\beta + \mu_{2-}^\beta = \mu_2^\beta \tag{154}$$

and N_1^β, N_2^β are the equivalent fractions of solvent and solute. It follows that all the consequences of equations 152 and 153 are identical in form with those of equations 70 and 75, i.e., under the above conditions 1 and 2 the effect of the dissociation of the solvent electrolyte disappears and the case $p^\beta = 4$ reduces to the case $p^\beta = 2$, $r^\beta = 1$.

Frumkin (2) has shown how it is always possible to ascertain experimentally whether the above condition 2 is approximately fulfilled by an aqueous solution of a neutral salt. The method consists in investigating the shift in the electrocapillary curve of the salt solution produced by adding to the solution a small quantity of either that acid or that metallic hydroxide of which the salt in question is the product of neutralization. The junction between the salt solution (β) and the reference electrode must be a liquid–liquid junction. If no appreciable shift is found, equation 149 applies; if there is a shift, equation 149 does not apply. The theory of the method is best explained by means of a special case, say sodium sulfate solution. For this case equation 148 becomes

$$\begin{aligned} \mathrm{d}\sigma = &- \Gamma_{\mathrm{H}^+}^\beta \mathrm{d}\mu_{\mathrm{H}^+}^\beta - \Gamma_{\mathrm{OH}^-}^\beta \mathrm{d}\mu_{\mathrm{OH}^-}^\beta - \Gamma_{\mathrm{Na}^+}^\beta \mathrm{d}\mu_{\mathrm{Na}^+}^\beta - \Gamma_{\mathrm{SO}_4^=}^\beta \mathrm{d}\mu_{\mathrm{SO}_4^=}^\beta \\ &- \epsilon^\alpha \mathrm{d}(\varphi^{\mathrm{II}} - \varphi^\beta) + \epsilon^\alpha \mathrm{d}\mathfrak{E} \end{aligned} \tag{155}$$

The substitution of.

$$\mu_{\mathrm{H}^+}^\beta = \mu_{\mathrm{H_2O}}^\beta - \mu_{\mathrm{OH}^-}^\beta \tag{156}$$

gives

$$\begin{aligned} \mathrm{d}\sigma = &(\Gamma_{\mathrm{H}^+}^\beta - \Gamma_{\mathrm{OH}^-}^\beta)\, \mathrm{d}\mu_{\mathrm{OH}^-}^\beta - \Gamma_{\mathrm{H}^+}^\beta \mathrm{d}\mu_{\mathrm{H_2O}}^\beta - \Gamma_{\mathrm{Na}^+}^\beta \mathrm{d}\mu_{\mathrm{Na}^+}^\beta - \Gamma_{\mathrm{SO}_4^=}^\beta \mathrm{d}\mu_{\mathrm{SO}_4^=}^\beta \\ &- \epsilon^\alpha \mathrm{d}(\varphi^{\mathrm{II}} - \varphi^\beta) + \epsilon^\alpha \mathrm{d}\mathfrak{E} \end{aligned} \tag{157}$$

Consider the change in σ at constant $\mathfrak{E}$ produced by adding to a sodium sulfate solution of constant concentration, say 1 N, an amount of sodium hydroxide, say 0.01 equivalent per liter, so small that the values of $\mu_{\mathrm{H_2O}}^\beta$, $\mu_{\mathrm{Na}^+}^\beta$, $\mu_{\mathrm{SO}_4^=}^\beta$, $(\varphi^{\mathrm{II}} - \varphi^\beta)$ are not appreciably affected, but yet large enough to change $\mu_{\mathrm{H}^+}^\beta$ and $\mu_{\mathrm{OH}^-}^\beta$ appreciably. For such a change equation 157 gives

$$\frac{\partial\sigma}{\partial\mu_{\mathrm{OH}^-}^\beta} \sim \Gamma_{\mathrm{H}^+}^\beta - \Gamma_{\mathrm{OH}^-}^\beta \tag{158}$$

If no shift of the curve is observed, $\dfrac{\partial\sigma}{\partial\mu_{\mathrm{OH}^-}^\beta} = 0$ and it follows that

$$\Gamma_{\mathrm{H}^+}^\beta \sim \Gamma_{\mathrm{OH}^-}^\beta \tag{159}$$

i.e., condition 2 is at least approximately fulfilled. But if an appreciable shift is observed then $\frac{\partial\sigma}{\partial\mu^{\beta}_{\mathrm{OH^-}}} \neq 0$ and

$$\Gamma^{\beta}_{\mathrm{H^+}} \neq \Gamma^{\beta}_{\mathrm{OH^-}} \tag{160}$$

Similarly it can be shown that the absence of a shift on adding a small amount of sulfuric acid to the sodium sulfate solution is also a criterion for the approximate fulfillment of condition 2. Frumkin has found that 1 *N* sodium sulfate + 0.01 *N* sulfuric acid and 1 *N* sodium sulfate + 0.01 *N* sodium hydroxide both have electrocapillary curves practically identical with that of 1 *N* sodium sulfate, and that 1 *N* potassium thiocyanate + 0.01 *N* thiocyanic acid and 1 *N* potassium thiocyanate + 0.01 *N* potassium hydroxide both have electrocapillary curves practically identical with that of 1 *N* potassium thiocyanate (2). It follows that the equations for the case $p^{\beta} = 2$, $r^{\beta} = 1$ apply to these solutions.

Case E. The concentrations in the phase β are constant save for that of a dilute, powerfully adsorbed nonelectrolyte

A typical example of this case is the system

$$\overset{\alpha}{\mathrm{Hg}}\,|\,1\,N\,\mathrm{Na_2SO_4} + 0.02N\,\mathrm{H_2SO_4} + \overset{\beta}{\text{tert.}}\,\mathrm{C_5H_{11}OH}\text{ in the concentration }c'^{\beta}$$

where $0 \leq c'^{\beta} \leq$ about 0.05 molal. The variation of c'^{β} throughout this relatively small range causes a relatively enormous variation of σ. Almost any organic nonelectrolyte in aqueous solution behaves similarly to the tertiary amyl alcohol. The equations of physical interest yielded by this case are all only approximate, but they have the advantage of applying no matter what the composition of β is. The approximation consists in neglecting the effect of variations in the concentration, c'^{β}, of the substance in question upon the chemical potentials μ^{β}_{i}, μ^{β}_{k} of the other components of β and upon the quantity $(\varphi^{\mathrm{II}} - \varphi^{\beta})$. Equation 69 shows this approximation to be the better, the smaller the concentration and the greater the absorbability of the substance is. Introducing this approximation into equation 69 gives

$$d\sigma = -\Gamma'^{\beta}d\mu'^{\beta} + \epsilon^{\alpha}d\mathfrak{E} \tag{161}$$

where Γ'^{β} and μ'^{β} are respectively the surface density in moles per unit area and the chemical potential per mole of the component of variable concentration. This equation yields for the shift of the electrocapillary curve with μ'^{β} the approximate relations

$$\frac{\partial\sigma^{\max}}{\partial\mu'^{\beta}} = -\Gamma'^{\beta}{}_{\max} \tag{162}$$

$$\left(\frac{\partial \sigma}{\partial \mu'^{\beta}}\right)_{\mathfrak{E}} = -\Gamma'^{\beta} \tag{163}$$

$$\left(\frac{\partial \mathfrak{E}}{\partial \mu'^{\beta}}\right)_{\sigma} = \frac{\Gamma'^{\beta}}{\epsilon^{\alpha}} \tag{164}$$

The equations 162, 163, 164 yield immediately useful results on setting

$$d\mu'^{\beta} = RT \, d \ln c'^{\beta} \tag{165}$$

a good approximation for most nonelectrolytes in the concentration range in which equations 161 to 164 are reasonably accurate.

V. REMARK ON THE RELATION BETWEEN THE VERTICAL AND THE HORIZONTAL SHIFT OF THE ELECTROCAPILLARY CURVE WITH COMPOSITION

In five of the cases discussed above, namely III C ($p^{\alpha} = 3$), IV B ($p^{\beta} = 2$, $r^{\beta} = 1$), IV C ($p^{\beta} = 3$), IV D, special case 1 ($p^{\beta} = 4$, special case 1), IV E (concentrations in β constant save for that of dilute, powerfully adsorbable nonelectrolyte), the state of that phase whose composition is varied is a function of but a single variable, which may be designated by λ and taken to mean the chemical potential of one of the components of the phase in question, or its mole fraction, or its equivalent concentration, or any other variable of composition. Hence in the five cases mentioned the surface tension σ is a function of only two variables, which may be taken as the arbitrary variable of composition λ and the applied potential $\mathfrak{E}$. It follows from the rules of partial differentiation that

$$\left(\frac{\partial \sigma}{\partial \lambda}\right)_{\mathfrak{E}} = -\left(\frac{\partial \sigma}{\partial \mathfrak{E}}\right)_{\lambda} \cdot \left(\frac{\partial \mathfrak{E}}{\partial \lambda}\right)_{\sigma} \tag{166}$$

But since T, P^{α}, P^{β} are constant, equation 41 gives

$$\left(\frac{\partial \sigma}{\partial \mathfrak{E}}\right)_{\lambda} = \epsilon^{\alpha} \tag{167}$$

whence

$$\left(\frac{\partial \sigma}{\partial \lambda}\right)_{\mathfrak{E}} = -\epsilon^{\alpha} \cdot \left(\frac{\partial \mathfrak{E}}{\partial \lambda}\right)_{\sigma} \tag{168}$$

Equation 168 is the general and exact relation between the vertical and horizontal shift of the electrocapillary curve with composition in the five cases enumerated above. It is seen to be fulfilled by all the above pairs of equations, either exact or approximate, in which the vertical and horizontal shifts of the curve with some variable of composition are given separately, e.g. by the pairs 64 and 65, 67 and 68, 86 and 87, 97 and 98, 117 and 118, etc.

VI. SUMMARY

In the systems giving rise to electrocapillary curves the reference electrode, the metallic phase α and the nonmetallic phase β can each be varied in composition independently. The principal equations describing the effect of each of these three kinds of variation on the electrocapillary curve are deduced for the first time, starting from a general equation derived in a previous paper. As regards variations of the reference electrode and of the metallic phase α, the general equations describing their effect upon the electrocapillary curve (equations 48 and 57, 58, respectively) are relatively simple. But for variations of the nonmetallic phase β the possibilities are so diverse that no simple general expression can be obtained, and it is therefore necessary to consider the chief special cases separately. In many of the cases considered the surfaced ensities Γ_i, Γ_k of certain components of the electric double layer can be approximately calculated from the shift of the electrocapillary curve caused by varying the composition of α or of β.

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THE THERMAL DECOMPOSITION OF GASEOUS ETHYLENE IODIDE

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Ethylene iodide decomposes readily, even at moderate temperatures and in the absence of oxygen, into ethylene and iodine. This thermal decomposition has been studied recently by several investigators. Pollissar (5) used carbon tetrachloride as a solvent and found that iodine was a catalyst for the reaction, the rate being proportional to the product of the ethylene iodide concentration and the square root of the iodine concentration. He concluded that iodine atoms were the real catalytic agents, and he devised some equations to satisfy the kinetics of the reaction. Schumacher and Wiig (6) made a photochemical study of the influence of iodine atoms on the decomposition. In 1928 Mooney and Ludlam (4) published a paper dealing with the dissociation pressure of ethylene iodide, the gaseous equilibria of the gases ethylene iodide, iodine, and ethylene at different temperatures in the presence of solid ethylene iodide and iodine, and a few experiments on the velocity of decomposition of gaseous ethylene iodide, and of the substance dissolved in carbon tetrachloride, in which they concluded that iodine played the part of a catalyst. Mooney (4) recently carried out some experiments on the synthesis of ethylene iodide from ethylene and iodine, and found that the reaction took place on the surface of the solid iodine, and that the glass surface of the reaction vessel was not, in itself, catalytic unless covered with a layer of alcohol. A satisfactory investigation of the rate of decomposition of the purely gaseous substance does not seem to have been undertaken. This paper is a record of some experiments we have carried out under these conditions, and of our own conclusions, which differ in some respects from those of previous workers.

We found, at the outset, that ethylene iodide which was in the slightest degree impure was quite useless for quantitative work. We prepared the pure substance by passing ethylene into an alcoholic solution of iodine containing powdered glass, which was a very efficient catalyst, though not all varieties of glass were found suitable for this purpose. The substance was recrystallized several times from alcohol, was of a pure white appearance, and melted sharply at 82°C.

The reaction was carried out in a glass vessel (figure 1) and the change in pressure recorded on a simple glass manometer. It will be seen from the figure that one side of this could be opened continuously to the vacuum system if necessary. The manometric liquid was a very concentrated solution (at 65°C.) of orthophosphoric acid, obtained by partially dehydrating the ordinary commercial phosphoric acid. It was heated under the vacuum until dissolved gases were removed. After opening T_1 (figure 1) to the vacuum system, and closing T_2 for a time, no perceptible pressure difference was detected.

We carried out some preliminary tests and found that neither iodine vapor nor ethylene were appreciably soluble in this liquid. It was the only one of a number we experimented with which satisfactorily fulfilled these conditions. The manometer was read from outside the thermostat, in which both it and the reaction vessel were immersed, by means of a cathetometer.

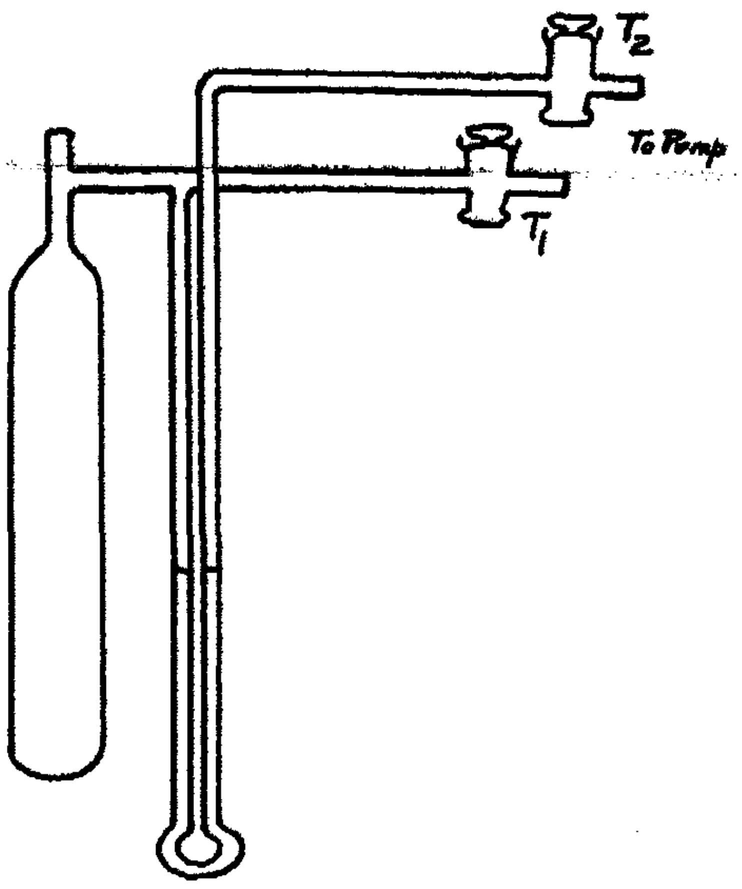

FIG. 1. GLASS REACTION VESSEL

The reaction vessel was cleaned in the usual way with chromic acid, etc., but in some cases we used hydrofluoric acid. These modes of treating the glass surface have a marked influence on the reaction rate. No attempt was made to bake out the vessel at a temperature much higher than that of the reaction itself.

The taps T_1 and T_2 were lubricated with graphite and metaphosphoric acid, and in some experiments we discarded T_1 and sealed off directly.

The decomposition was studied at 65°C. and 75°C. The procedure was this: A small quantity of ethylene iodide was introduced through the top of the reaction vessel, which was then sealed up and evacuated with a Hyvac pump. The solid ethylene iodide remained at the bottom of the vessel and was prevented from vaporizing completely by cooling with a freezing mixture of ice and salt. The final pressure under these conditions was not much more than the limit obtained by the pump, namely, 0.001 mm. of mercury. We tried solid carbon dioxide as a cooling agent, but found that ethylene iodide was too unstable at this low temperature; some decomposition took place as was apparent from the brown color developed by the ethylene iodide on the side adjacent to the cold glass

TABLE 1

The decomposition of ethylene iodide at 65°C.

Experiment no. 9. Induction period pronounced

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2 \times 10^4$	$k_1(\sqrt{I_2}) \times 10^5$	$k_1(I_2) \times 10^6$
minutes	*mm.* H_3PO_4					
10	19.6					
15	19.9					
25	20.4					
30	20.7					
40	20.7					
50	20.7					
60	22.4	170	372			
70	23.2	125	280		33	90
80	24.0	110	252		30	79
90	24.5	95			27	64
100	25.6	98	255		30	65
110	26.5	97	238		31	61
120	27.8	101	261		36	61
130	28.6	99	261		37	51
140	29.6	101	271		40	56
150	30.8	102	291		46	55
160	31.9	101	307		51	54
170	32.8	100	318		56	52
180	33.7	99	330		62	51
190	34.5	97	341		69	50
200	35.3	94	354		77	49
210	35.7	92	350	869	80	46
220	36.3	89	358	914		46
230	36.7	85	358	919		44
240	36.9	80	349	1007		43
250	37.4	78	357	1023		42
260	37.6		351	1009		41
270	37.7		339	998		39
280	37.8		330	945		37
310	38.0					
320	38.0					

surface. It may be that the excessive refrigeration condenses some very volatile substance which acts as a catalyst for the decomposition, or there is another crystalline form of ethylene iodide which is unstable. Unless the ethylene iodide used is very pure, the reaction will not exhibit the special features now to be described.

The reaction vessel was plunged into the thermostat at 65°C. and immediate readings of the manometer taken. As the ethylene iodide vaporized and acquired the temperature of the thermostat, the pressure rose and remained steady for a while. No trace of iodine vapor could be detected in the vessel. The pressure began to increase again, and plotting the pressure against the time, we obtained the type of curve shown in figure 2 (curve A). Towards the end of the reaction a definite violet vapor filled the reaction vessel. If the ethylene iodide used was partially decomposed or if a small crystal of iodine was introduced into the reaction vessel before sealing up, the form of the curve was different (figure 2,

TABLE 2

The decomposition of ethylene iodide at 65°C.

Experiment no. 13. Induction period pronounced

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2(I_2) \times 10^5$	$k_2 \times 10^6$
minutes	*mm.* H_3PO_4				
10	(9.3)				
15	9.1				
20	9.2				
25	9.2				
30	9.2				
35	9.2				
45	9.8	(60)			
60	10.1	36		174	
75	10.8	40	208	145	
90	11.2	36	194	130	
105	11.8	36	198	122	
120	12.2	35	202	109	
135	12.5	33	193	96	
165	13.3	32	197	92	
180	13.7	31	201	88	
195	14.1	31	206	84	
210	14.4	30	207	79	808
225	14.6	28	202	65	813
285	15.2	24	194	56	797
330	15.4	21	165	53	762
360	15.7	20		45	805
390	15.9	19			820
405	15.9				
420	15.9				

curve B). The pressure never remained steady at any time. Undoubtedly the portion ab of the curve A indicates an induction period, and it seemed reasonable, at first, to attribute this to the lack of the necessary catalytic agent, presumably iodine, which, however, soon begins to accumulate in the system, with consequent increase in the speed of decomposition. We would expect the reaction to be bimolecular and to follow an equation of the second order, involving either the iodine concentration or its square root. But this does not seem to be the case. The results of a number of our experiments have been tabulated. We calculated the velocity constants k_0, k_1, k_2 (I_2), k_2 ($\sqrt{I_2}$) and k_2, for the zero order, monomolecular, bimolecular (catalyzed), and bimolecular (uncatalyzed), respectively.

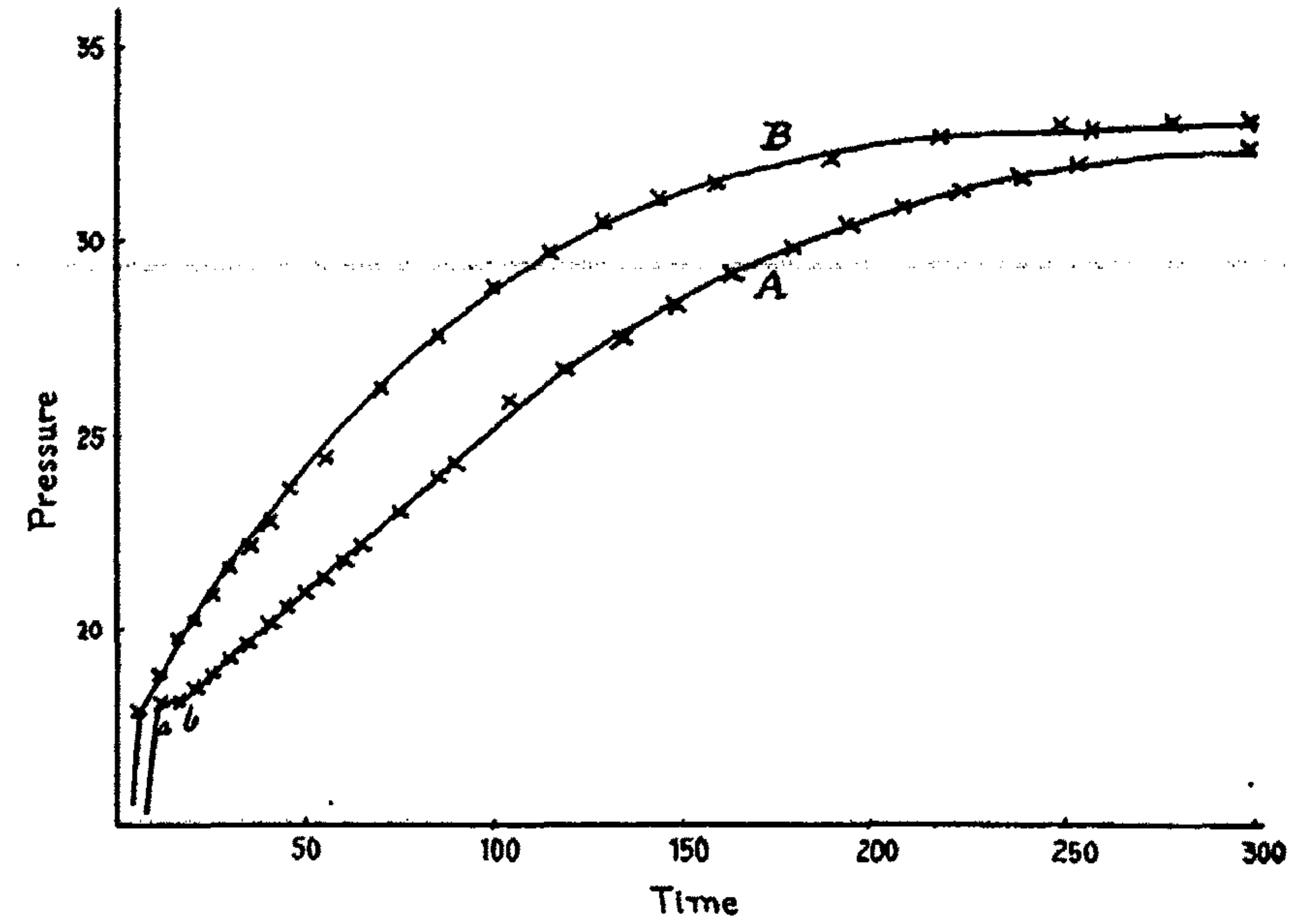

FIG. 2. DECOMPOSITION OF ETHYLENE IODIDE AT 65°C.

Curve A, experiment no. 14; curve B, experiment no. 15

If a = initial concentration of ethylene iodide (in millimeters of phosphoric acid), x = concentration of iodine formed, and t = time in minutes, then

$$\frac{dx}{dt} = -\frac{d(a-x)}{dt} = K \qquad (K = K_0, \text{ zero order}) \qquad (1)$$

$$\frac{dx}{dt} = K(a-x),\ K = \frac{1}{t}\ln\frac{a}{a-x} \qquad (K = K_1, \text{ monomolecular}) \qquad (2)$$

$$\frac{dx}{dt} = K(a - x)x,\ K(t_2 - t_1) = \frac{1}{a}\left(\ln \frac{x_2\,(a - x_1)}{x_1\,(a - x_2)}\right)$$

$$(K = K_3\ (\mathrm{I_2})\ \text{bimolecular catalyzed}) \qquad (3)$$

$$\frac{dx}{dt} = K(a - x)\sqrt{x},\ K(t_2 - t_1) = \frac{1}{\sqrt{a}}\left(\ln \frac{(\sqrt{a} + \sqrt{x_2})\,(\sqrt{a} - \sqrt{x_1})}{(\sqrt{a} - \sqrt{x_2})\,(\sqrt{a} + \sqrt{x_1})}\right)$$

$$(K = K_3\ (\sqrt{\mathrm{I_2}})\ \text{bimolecular catalyzed}) \qquad (4)$$

$$\frac{dx}{dt} = K(a - x)^2,\ K = \frac{1}{t}\,\frac{x}{a(a - x)} \qquad (K = K_2,\ \text{bimolecular uncatalyzed}) \qquad (5)$$

The initial pressure was taken to be the pressure recorded during the induction period.

The rate of decomposition is best represented by the zero order equation in the first stage, and after the pressure has fallen, by the monomolecular equation, and finally by the bimolecular equation (uncatalyzed). This is characteristic of a heterogeneous reaction, where strong adsorption takes place on the walls of the vessel.

We verified the heterogeneous nature of the reaction by introducing a number of thin glass tubes into the reaction vessel. There is an increase in the velocity of decomposition, and the reaction follows the same course as before. A similar increase in the velocity is obtained by cleaning the reaction vessel with a dilute solution of hydrofluoric acid. There must be an increase in the number of active centers of adsorption as the result of this procedure, but this does not explain the induction period.

We could assume that iodine is a catalyst for the decomposition. If the reaction were mainly homogeneous it would be of the second order, as Pollissar found in carbon tetrachloride. There is undoubtedly a slow homogeneous reaction at 65°C., but the heterogeneous reaction is the more rapid, and we can only conclude that there is some reaction between the ethylene iodide and the iodine on the glass walls of the reaction vessel.

Iodine is not so strongly adsorbed on glass as on calcium fluoride, according to de Boer (1). But these effects are relative, and iodine is found to be adsorbed more readily on freshly blown glass surfaces, or on glass that has been treated with hydrofluoric acid. We find that in the vacuum system from which mercury vapor has not been removed by liquid air, and into which iodine vapor is admitted, deposits of mercuric iodide are found mostly on the internal surfaces of the glass joints that have been heated by the hand blowpipe. This is a suggestive but by no means conclusive demonstration of the selective nature of iodine adsorption on glass.

In all the experiments we observed that the reaction did not appear to go to completion; there seemed to be some undecomposed ethylene iodide remaining, as the pressure was not sufficiently great for complete decomposition. Mooney and Ludlam (4) found an equilibrium constant at 65°C. which indicated almost complete decomposition, and for this reason we felt justified in using the simple kinetic equations. We also came to the same conclusion in some preliminary experiments at 65°C., in which ethylene and iodine vapor were mixed; there was no perceptible pressure change over a considerable period. We prefer, therefore, to ascribe the anomaly to the loss of iodine in the gas phase due to adsorption, iodine being more strongly adsorbed than ethylene iodide.[1] This also accounts

TABLE 3

The decomposition of ethylene iodide at 75°C.

Experiment no. 14. Short induction period

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2 \times 10^5$	$k_1(\sqrt{I_2}) \times 10^5$	$k_1(I_2) \times 10^5$
minutes	*mm.* H_3PO_4					
10	18.1					
15	18.1					
20	18.5	80	194		171	344
25	18.9	80	197		209	252
30	19.2	73	182		215	222
35	19.6	75	188		210	211
40	20.2	84	214		197	177
45	20.6	83	215		187	171
50	21.0	83	217		175	154
55	21.3	80	211		169	144
60	21.7	80	214		167	137
65	22.2	82	223		159	122
75	23.0	82	229		157	113
85	24.0	84	245		151	108
90	24.3	83	243		153	99
105	25.9	87	272		151	89
120	26.9	82	267		135	81
135	27.5	78	265		131	75
150	28.4	74	271		128	70
165	29.2	74	275		125	66
180	29.9	72	278		121	63
195	30.5	69	279	68	116	59
210	30.9	66	274	70	112	56
225	31.3	63	270	72	106	53
240	31.6	60	264	76	106	51
255	32.0	58	264	72	93	44
300	32.4	51	238	67	82	38
345	32.6					
360	32.6					
375	32.6					

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[1] There is also the possibility of ethylene adsorption on glass. Investigators differ in the estimation of the magnitude of this effect.

in part for the prolongation of the induction period, which has the appearance of a steady state, rather than of a slow chemical reaction. The iodine adsorption evidently reaches saturation at low pressures. The rate of reaction is therefore independent of the iodine pressure, and does not appear to be of the second order. But we would expect the apparent incompleteness of the reaction to be more pronounced the greater the activity of the surface, and this is not the case.

TABLE 4

The decomposition of ethylene iodide at 75°C.

Experiment no. 15. No induction period

TIME	PRESSURE	$k_0 \times 10^2$	$k_1 \times 10^5$	$k_2 \times 10^3$	$k_2(\sqrt{I_2}) \times 10^5$	$k_2(I_2) \times 10^6$
minutes	*mm.* H_3PO_4					
5	17.9					
10	18.9	125	298		429	595
15	19.7	144	353		↓	↓
20	20.2	129	319		↓	↓
25	20.9	132	332		↓	↓
30	21.6	133	346		↓	↓
35	22.2	130	346		↓	↓
40	22.8	129	349		↓	↓
45	23.6	133	370		↓	↓
55	24.4	122	350		↓	↓
70	26.2	122	374		↓	↓
85	27.5	115	375		↓	↓
100	28.8	110	385		↓	↓
115	29.7	104	379		↓	↓
130	30.5		376	84	↓	↓
145	31.1		366	87	↓	↓
160	31.5		348	87	↓	↓
195	32.1		322	86	↓	↓
220	32.7		305	88	106	48
250	33.0			86		
310	33.0					
355	33.0					
385	33.0					

We cannot be certain, therefore, if the glass surface itself without iodine is also catalytic to some extent. The introduction of freshly made glass tubing increases the velocity so much that no observation of an induction period is possible. There is not sufficient time for thermal equilibrium to be established and readings on the manometer are unsatisfactory.

There remains the question as to whether the anomalous final pressure is due to some polymerization process. We do not believe this to be the case because of certain independent experiments we carried out. Ethylene iodide was sealed up in a glass vessel and the equilibrium pressure at 35°C.

found to be 22 mm. of mercury. The vessel was then cooled to 16°C. (pressure 5 mm.) and afterwards heated to a much higher temperature, 65°C. It was then allowed to drop to room temperature again, and after some time heated to 35°C. (final pressure 22 mm.). If any irreversible polymerization had taken place during the decomposition at the higher temperature, the initial and final pressures at 35°C. would not have been the same.

The addition of ethylene seems to have a slight accelerating effect on the reaction. It is not easy to explain this, but as a chain mechanism is not altogether improbable for this reaction the ethylene could have some influence in delaying the breaking of the chains at the walls.

TABLE 5

The decomposition of ethylene iodide at 65°C.

Experiment no. 19. Ethylene (29.2 mm.) added at beginning of reaction. Short induction period

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2 \times 10^5$	$k_2(\sqrt{I_2}) \times 10^5$	$k_3(I_2) \times 10^5$
minutes	*mm.* H_3PO_4					
5	26.5					
10	27.2					
15	27.2					
20	28.1	(180)	292			
25	28.6	140	230		236	434
30	29.9	(180)	302			
35	30.6	(170)	290			
51	31.0	106	187			
65	33.7	130	237			
80	35.4	126	239			
95	36.9	121	239			
125	40.0	116	251			
140	41.5	114	259			
155	42.4	109	253			
170	43.6	106	258	36		
185	44.0		246	35		
230	45.8		232	37	↓	↓
245	46.2		226	37	69	27
275	46.8			36		
305	47.0			34		
335	47.0					

For such a chain mechanism we could write:

$$I\ (\text{glass}) + C_2H_4I_2 = I{-}I\ (\text{glass}) + C_2H_4I \qquad (1)$$
$$C_2H_4I + C_2H_4I_2 = C_2H_4 + I_2 + C_2H_4I \qquad (2)$$
$$C_2H_4I = C_2H_4 + I \qquad (3)$$
$$C_2H_4I_2 + I = C_2H_4I + I_2 \qquad (4)$$
$$C_2H_4 + I = C_2H_4I \qquad (5)$$
$$I\ (\text{glass}) + C_2H_4I = C_2H_4 + I{-}I\ (\text{glass}) \qquad (6)$$
$$I\ (\text{glass}) + I = I{-}I\ (\text{glass}) \qquad (7)$$
$$I + I_2 = I_3 \qquad (8)$$

It seems doubtful if reaction 1 is exothermic, and reactions 2, 4, and 5 are certainly endothermic, and require more energy of activation. Reactions 6, 7, and 8 are the chain-breaking reactions. But the energy of the C—I bond is not known with any certainty, and it would be unwise to generalize about any such chain mechanisms.

The great increase in reaction velocity brought about by the introduction of a larger glass surface is only consistent with the idea that the chains begin at the walls to a greater extent than they end there.

TABLE 6

The decomposition of ethylene iodide at 65°C.

Experiment 21. Enhanced activity of surface. Ethylene 17 mm. No induction period

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_1 \times 10^5$
minutes	*mm.* H_3PO_4			
5	14.2			
10	23.2	330	685	
13	24.1			
15	24.7			
17	25.5			
20	26.3			
23	27.1			
25	27.9			
30	29.3			
35	30.6		↓	
40	32.1	↓	718	
45	33.3	292		110
50	34.1			112
55	34.8			114
60	35.6			119
75	37.2			125
108	38.5			110
120	38.9			107
165	38.9			

From experiments at 65°C. and 75°C. it should be possible to calculate the energy of activation. But we have never found a satisfactory reproducibility for any one set of values of the velocity constant at either temperature. The catalytic surface does not necessarily remain constant from one experiment to another, and only gross comparisons can be made. But we estimate that the activation energy, calculated[2] from the zero-

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[2] This calculation is only possible if the density of the manometric liquid does not vary appreciably, which, in this case, is only approximately correct. We can also calculate the energy of activation from the monomolecular constants. In any case, it is not of a high order.

TABLE 7

The decomposition of ethylene iodide at 65°C.

Experiment no. 22. No ethylene

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$
minutes	*mm.* H_3PO_4		
3	13.4		
7	18.1		
12	18.9	133	333
17	19.5	150	312
23	20.3	138	358
27	20.8	144	363
35	21.6	135	363
37	22.3	139	
57	25.0	140	
72	26.9	138	
87	29.0	136	
102	30.5	136	
117	31.5	130	
132	32.0		
177	33.2		

TABLE 8

The decomposition of ethylene iodide at 65°C.

Experiment no. 25. Glass capillary tubing in reaction vessel

TIME	PRESSURE
minutes	*mm.* H_3PO_4
5	8.5
7	13.9
10	21.1
12	24.8
17	31.5
22	34.8
27	38.3
32	41.9
37	44.9
42	47.4
48	48.2
59	48.5

Velocity constants indeterminate.

TABLE 9

The decomposition of ethylene iodide at 65°C.

Experiment no. 17. Free iodine at the beginning of reaction

TIME	PRESSURE
minutes	*mm.* H_3PO_4
2	11.8
7	39.2
12	42.2
17	46.2
22	49.9
27	52.8
32	55.7
37	58.3
42	60.0
47	60.8
62	64.2
77	63.8
82	63.8

Velocity constants indeterminate

order constants, is not greater than 12,000 calories. The heat of the endothermic reaction

$$C_2H_4I_2 = C_2H_4 + I_2$$

is 20,000 calories, calculated from the thermal data, assuming the heat of sublimation of ethylene iodide to be 15,000 calories (4), and the heat of combustion of ethylene, 344,000 calories (2).

We hope to explore more deeply the main features of this reaction, particularly as it is affected by the shape of the reaction vessel and the material of the catalytic surface.

We do not wish to express any definite opinion as to the mechanism of the reaction, as it is obvious that there are a number of factors involved.

SUMMARY

The decomposition of gaseous ethylene iodide at 65°C. and 75°C. in a glass vessel seems to be heterogeneous and to a great extent autocatalytic; iodine adsorbed on the glass is a probable catalyst.

There is a short induction period which disappears when traces of iodine are present at the beginning of the reaction, and when the catalytic surface is greatly increased.

The reaction is of zero order after the induction period, and follows higher orders as the pressure diminishes.

A chain mechanism is suggested for the reaction, but this has not yet been completely verified.

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FORMATION OF BENZENE BY THE PHOTOCHEMICAL POLYMERIZATION OF ACETYLENE AT HIGH TEMPERATURES

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The formation of benzene by the photochemical polymerization of acetylene has been reported by Sechi Kato (5), who demonstrated the presence of benzene by means of its distinctive absorption spectrum. Kato claims that the formation of benzene, relative to that of cuprene, is favored by temperatures above 270°C. or by the absorption of light of short wave length. Since these results were in apparent contradiction to the results of a number of other observers (1, 2, 6, 8) who obtained cuprene as the only product of the photochemical reaction, it seemed worth while to repeat Kato's experiments under slightly different conditions. The results of the present work confirm her claim that benzene is formed when acetylene at temperatures above 270°C. is irradiated with ultra-violet light.

APPARATUS AND PROCEDURE

The source and purification of the acetylene were similar to those described by Lind and Livingston (6). The reaction system is represented in figure 1. The reaction vessel was a quartz tube 24.5 cm. long and 2.2 cm. in diameter; it was sealed at the lower end and connected to the line by a graded seal at the upper end. The upper half of this tube was wrapped with a nichrome wire coil, spaced at about half-centimeter intervals. The back and side of the coil were covered by a loosely fitting heavy-walled asbestos shield. The light source, a vertical quartz-mercury arc, was placed opposite the shield at a distance of about 3 cm., and was run "hot" to minimize the probability of a mercury sensitized reaction. The lower part of the reaction vessel was immersed in a mixture of solid carbon dioxide and acetone. The approximate temperature of the acetylene was determined indirectly by measuring the current flowing through the heating coil. These temperature determinations were based upon a series of calibrations, in which a tube with dimensions identical with the reaction vessel was inserted in the heating coil. The upper end of this tube was not constricted but was closed by an asbestos plug through which a thermometer was inserted. The Dewar tube containing the carbon dioxide–

acetone mixture, the asbestos shield, and the mercury arc were arranged as during reaction periods. The temperatures corresponding to current readings were measured from 250°C. to 400°C. The temperature of the irradiated gas was not uniform, but varied from the center to the ends of the heating coil by as much as 50°C. The recorded temperatures all correspond to maximum values, and were measured after steady-state conditions had been attained.

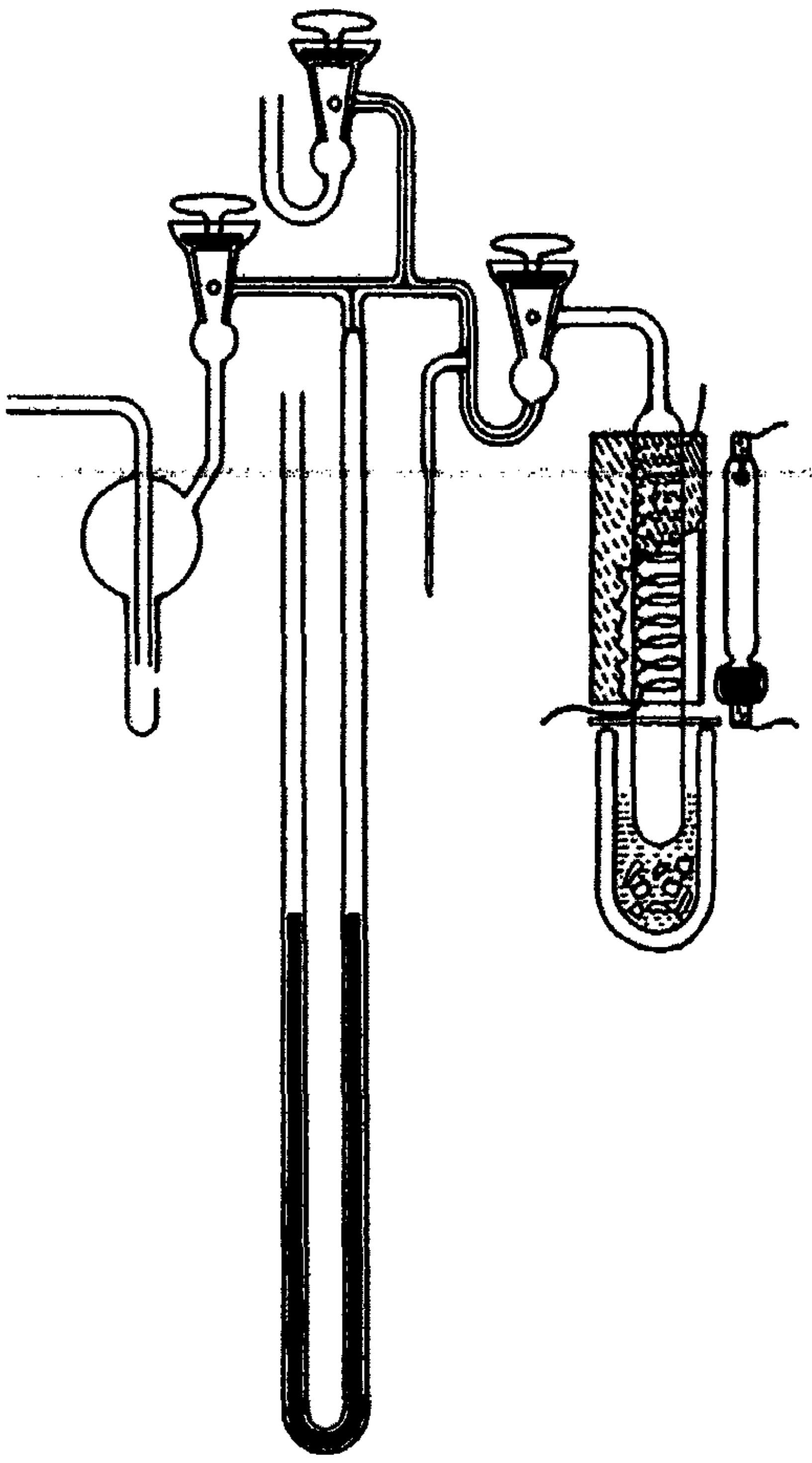

FIG. 1. THE REACTION SYSTEM

Before each experiment air was admitted to the reaction cell, which was then heated to burn out any non-volatile substance. After the system had been evacuated (pressure less than 10^{-4} mm.), sufficient acetylene was admitted to make the pressure approximately 1 atmosphere at the temperature of the experiment. The pressure was then determined with the whole system at room temperature. The cooling bath was put in place and the heating current started. After sufficient time (about an hour) had elapsed for temperature equilibrium to be attained, the arc was started and was run from three to four and one-half hours. In some experiments an attempt was made to follow the change of pressure during the experiment; in others the manometer was closed off as soon as temperature equilibrium was reached. After each exposure the whole system was allowed to return to room temperature and the pressure was determined and corrected for any change in room temperature.

RESULTS

In all of the photochemical experiments a decrease in pressure was observed and a variety of products was formed. Two of the products were non-volatile solids; one of these resembled cuprene, and the other was a hard dark yellow film, like a film of dried varnish. The cuprene seemed to be evenly distributed and was particularly evident in the irradiated and heated part of the tube. It was insoluble in ether and burned very readily in air. The dark yellow film occurred in the cooler part of the tube, both above the heated zone and in the bottom of the tube. When heated in vacuum it charred, but did not sublime. It was partly soluble in ether, coloring the ether dark yellow; it formed a dense and adherent coating which burned in air only with difficulty. A small quantity of a volatile liquid was always found frozen in the bottom of the tube. This liquid was yellow and viscous. When the bottom of the tube was immersed in liquid air there was no detectable residual pressure, which indicates the absence of hydrogen and methane. No other attempt was made to isolate gaseous products.

While the experimental method did not allow exact measurement of the rate of change, it was demonstrated that the rate was initially at a maximum and became negligible after three or four hours. This was probably due to the absorption of the incident light by the cuprene which accumulated on the walls of the tube. The decrease in pressure varied from 3.5 per cent for a 3-hour exposure at 270°C. to 9.3 per cent for a 4.5-hour exposure at 375°C. These changes are apparently much greater than those which would have been obtained at room temperature under otherwise similar conditions. No measurements were made at temperatures below 270°C. or above 376°C.

That the reaction was truly photochemical and not thermal was demonstrated by two independent blank experiments. In one the quartz reaction vessel was replaced by a Pyrex tube of similar dimensions. All other conditions were identical with those used in the photochemical experiments; at the end of two and one-half hours there was no measurable change of pressure nor visible accumulation of products. In another experiment the quartz tube was used but the arc was not started. The temperature was maintained at 350°C. for 4 hours, at the end of which time there was no evidence of any reaction having occurred.

The following experiments were performed in an attempt to determine the nature of the volatile liquid products. The liquids were frozen with carbon dioxide-acetone mixture and the gas was pumped off. A capillary side tube was then immersed in liquid air and the more volatile liquids were allowed to distil over. The distillate always consisted of a few cubic millimeters of a non-viscous liquid, which was clear or faintly yellow (depending on the time allowed for distillation). After one of the experiments, which was performed at 345°C., the capillary side tube and manometer were sealed off from the reaction vessel, and the side tube was immersed in an acetone bath which was cooled with solid carbon dioxide. The vapor pressure measurements given in table 1 were made. While the vapor pressure values given are not in sufficiently close agreement with the published values for benzene to make it possible to identify the distillate as benzene, it does seem probable that the distillate is a mixture consisting chiefly of benzene. Under the conditions of the experiment the distillate appeared to melt over the range −9°C. to −15°C. At temperature above −5°C. the volume of the liquid was very small and it had a distinct yellowish color.

TABLE 1

Vapor pressure of the distillate

TEMPERATURE OF THE BATH	VAPOR PRESSURE OF DISTILLATE	VAPOR PRESSURE OF BENZENE (4)
degrees C.	*mm.*	*mm.*
−24 to −25	4.3	3.6
−19 to −20	6.6	5.5
−14 to −15	10.1	8.2
−9 to −10	14.2	12.1
−5.5 to −6	18.6	16.1

To obtain definite evidence of the presence (or absence) of benzene, the distillate was transferred in vacuum to a quartz absorption cell, which was 5 cm. long and was equipped with a side tube. The absorption spectrum was photographed with a Steinheil spectrograph, using a hydrogen arc as a light source (7). When the cell was at room temperature a continuous absorption set in at about 2225 A.U., with a region of partial transmission between 2140 and 2270 A.U. In the region between 2225 A.U. and 2650 A.U. (the long wave length limit of the spectrograph), several bands were noticeable which coincided with the benzene bands recorded by

Henri (3). When the side tube of the cell was maintained at −37°C. the continuous absorption vanished; a regular series of bands was noticeable between 2275 and 2603 A.U. Fourteen of these bands were identified as benzene bands. We may conclude from these results that the distillate consisted of benzene and some less volatile substance which exhibited a continuous absorption in the ultra-violet.

CONCLUSIONS

It is noteworthy that the products of the photochemical polymerization of acetylene at high temperatures resemble those of the thermal polymerization (9) much more nearly than they do those of the low temperature photochemical reaction. At the present time any attempt to give a detailed analysis of the reaction mechanism would be premature. It seems probable that not all of the detailed analysis of Kato (5) will prove to be correct. Her assumption that the apparent continuum on the long wave length side of the banded absorption corresponds to a region of predissociation seems unlikely. It is quite possible that the continuous absorption was due to some impurity present in the acetylene. It is very probable that the solid condensate which is formed in the photochemical reaction is a true polymer rather than the dehydrogenated product $(C_7H_6)_n$, assumed by Kato. In the absence of any information on the intensity of the light absorbed at the different frequencies used in Kato's experiments, it is difficult to decide whether her conclusion that light of short wave length favors benzene formation is justifiable.

SUMMARY

The photochemical polymerization of acetylene at temperatures above 270°C. has been studied qualitatively. In confirmation of the results of Kato (5), benzene has been identified as one of the reaction products.

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THE ADSORPTION OF THE VAPORS OF CERTAIN DICHLORO HYDROCARBONS BY ACTIVATED CHARCOAL. IV

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In the previous papers reports have been made of studies of the adsorption of the vapors of methane and its chlorine derivatives (6), and of ethyl, propyl, isopropyl, *n*-butyl, and *tertiary*-butyl chlorides (7). Since all of these adsorptions have been made on samples from the same stock of acid-washed, ash-free, steam-activated charcoal, the results should be comparable and significant.

The extremely uneven nature of the charcoal surface gives rise to a great variation in the nature of the adsorption forces emanating from the surface atoms. The surface is composed chiefly of capillary pores, cracks, and fissures; the surface atoms may be those of unbroken benzene rings, exposed carbon chains, and projecting peaks of single carbon atoms. Obviously, the degree of unsaturation of the surface forces, and hence the intensity of the adsorption forces, will be greatest for the projecting atoms. The influence of the fine capillary structure upon adsorption is shown by the calculations of Magnus (3). Assuming that the attractive force exerted upon a molecule decreases with the sixth power of the distance from the surface element, he finds that a molecule situated in a hemispherical concavity of about equal size is attracted about three times more strongly than by a plane surface.

The forces operative in the adsorption of vapors and gases at charcoal surfaces may be those of simple adsorption due chiefly to van der Waals forces, or they may be more of an electrical nature. The latter follows from the fact that the electrical field at a distance of 1 A.U. from a surface atom is of the order of 1×10^9 volts per centimeter. This field is capable of orienting and attracting vapor molecules possessing permanent dipole moments; it is capable not only of increasing dipole moments already present, but also of inducing dipoles in neutral molecules and quadripoles. The induced dipole will be greater, the greater the ease of deformation of the electronic orbits of the constituent atoms. In this way many nonpolar molecules may become as highly adsorbed as those of a highly polar nature.

In the interpretation of the previous results we have assumed that the attraction between the surface of the adsorbent and the vapor molecules is largely influenced by an attraction for some particular atom or group of atoms within the molecule adsorbed. It has been assumed that the chlorine atom plays the dominant rôle in the adsorption of the alkyl chloride vapors. If our assumption is correct, we should expect that for any alkyl chloride series the number and position of the chlorine atoms in the molecule, as well as the shape and volume of the molecule, should be important factors in the intensity of the adsorption and in the relative amounts of the different vapors adsorbed under corresponding conditions. With the normal compounds, the chlorine atom should be attracted toward the surface of the adsorbent, with the hydrocarbon chain extending outward into space. The surface cover-power of all normal alkyl chloride molecules should be the same.

On the basis of the assumption that adsorption takes place through the ~~chlorine atom, the intensity of the adsorption should increase with the~~ number of chlorine atoms in the molecule. If two chlorine atoms are present, the intensity and magnitude of the adsorption will depend upon their position. If the two are joined to the same carbon atom, the molecule will probably be adsorbed on a single point or elementary space, unless the points are sufficiently close together to attract the chlorine atoms separately. On the other hand, if the two chlorine atoms are attached to two different carbon atoms, the molecule should lie flat upon the surface. The surface covering power of these molecules will be greater than for those with the chlorine atoms attached to the same carbon atom.

The present paper gives a brief statement of the results obtained in a study of the adsorption of the vapors of ethylene, ethylidene, propylene, and trimethylene chloride vapors.

The dichloro compounds used were Eastman's products of highest purity. They were further purified by means of a special fractional distillation apparatus (2, 8). The liquids finally used were fractions of 75 to 100 cc. collected over a range of 0.01° to 0.10°C. and having the correct boiling points.

The apparatus and the technique employed were the same as that described in the previous papers (6, 7). It should be stated that before use each sample of charcoal was first outgassed at 525°C., then flushed one or more times with the vapor to be adsorbed, and finally outgassed at 525°C.

DISCUSSION

The results obtained are collected in tables 1 to 4. In these x/m is the number of cubic centimeters of vapor (N.T.P.) adsorbed by one gram of charcoal under the equilibrium pressures p (in millimeters). The 0°C. and 40°C. isotherms were carried up to the saturation pressures of the pure liquids at these temperatures. The equilibrium pressures at the higher temperatures were limited to the saturation pressures at 50°C.,—the temperature of the air bath. Each pressure recorded is the mean of three or four readings taken at 30-minute intervals during which the increase in pressure did not exceed the limits of accuracy of the large precision cathetometer. Duplicate series on entirely different samples of charcoal showed that pressure equilibria are easily reproducible at all temperatures and pressures. As with the monochloro vapors, the dichloro vapors decompose with measurable speed at about 180°C.

TABLE 1

The adsorption of ethylene chloride vapor by charcoal at various temperatures

At 0°C.													
p	0.15	0.25	0.35	2.03	5.78	11.45	17.70	20.61	20.76				
x/m	30.05	57.42	72.79	97.51	103.72	109.60	114.25	117.71	124.68				
At 40.00°C.													
p	0.15	0.25	0.30	0.45	0.75	2.13	6.75	16.88	40.80	73.21			
x/m	8.95	17.78	26.51	43.49	64.37	79.12	88.06	93.10	97.89	102.14			
p	105.38	138.98	146.18	149.25	152.58	152.88	153.07						
x/m	106.52	110.13	110.82	110.99	112.14	112.72	113.83						
At 63.96°C.													
p	0.15	0.50	0.80	1.34	2.38	4.42	10.82	26.06	53.61	99.37	135.16	139.88	142.06
x/m	11.86	26.06	38.31	49.61	61.05	69.13	78.10	84.20	88.05	91.36	93.17	93.69	95.16
At 79.50°C.													
p	0.50	1.00	1.73	3.12	5.60	11.05	26.61	67.34	103.61	142.06	179.32	193.24	196.32
x/m	16.68	29.20	41.36	52.37	61.51	70.92	79.92	86.22	88.83	90.61	91.01	92.43	92.73
At 99.48°C.													
p	1.24	2.68	5.80	9.27	18.43	39.00	72.79	122.93	165.30	186.80	220.30	222.33	
x/m	19.18	33.47	45.13	53.22	64.18	73.26	79.15	83.11	84.93	85.62	87.21	89.62	
At 136.20°C.													
p	3.47	10.26	18.73	32.84	62.43	115.30	141.28	190.37	195.47				
x/m	16.45	32.15	41.87	52.03	61.71	70.15	72.27	75.31	76.20				

In his development of a quantitative theory of adsorption, Langmuir (1) has deduced six relations, each applicable to definite limiting conditions. These relations satisfy the different possible configurations of the surface atoms and the number of molecules which each elementary space may adsorb. The simplest of these involves the simple adsorption of vapor molecules on a plane surface possessing only one kind of elementary space, and each space capable of holding only one adsorbed molecule. For this condition the amount of gas adsorbed by one gram of charcoal is given by the relation,

$$\frac{x}{m} = \frac{abp}{1 + ap}, \quad \text{or} \quad \frac{p}{x/m} = \frac{1}{ab} + \frac{p}{b} \tag{1}$$

TABLE 2

The adsorption of ethylidene chloride vapor by charcoal at various temperatures

At 0°C.											
p........	0.25	0.50	1.50	4.86	10.90	22.55	38.25	49.50	57.92	66.00	70.66
x/m......	28.89	57.48	85.50	95.12	98.87	103.05	107.82	110.48	113.66	116.48	120.53
At 40.00°C.											
p........	0.25	0.70	1.70	4.67	11.66	24.77	52.12	125.43	179.18	248.18	319.21
x/m......	24.38	43.24	59.43	70.99	78.48	83.14	87.08	91.48	93.77	96.85	100.11
At 64.00°C.											
p........	0.60	2.08	5.00	10.60	22.89	47.37	102.57	107.59	255.33	398.98	479.74
x/m......	24.20	42.53	56.62	66.23	73.88	79.30	84.06	86.98	89.01	91.60	93.05
At 79.50°C.											
p........	0.95	3.37	8.47	21.60	50.24	89.44	164.56	263.46	407.30	497.80	505.51
x/m......	17.01	35.68	51.39	64.99	74.02	78.87	83.54	85.48	87.87	89.27	91.71
At 99.50°C.											
p........	2.08	6.64	17.19	36.32	68.78	111.20	169.96	237.94	367.22	493.86	504.57
x/m......	20.01	36.41	50.35	61.04	68.14	72.77	76.11	78.52	80.54	82.41	85.20
At 136.65°C.											
p........	3.86	13.87	28.00	53.51	90.78	141.17	274.41	356.96	478.16	565.12	
x/m......	15.47	27.87	36.14	43.98	50.55	55.68	65.50	64.68	66.89	68.52	

Here, $1/b$ is the slope of the straight line plot and $1/ab$ is the intercept on the ordinate at zero pressure.

Charcoal, however, is a highly porous solid with a variety of projecting points, crags, crevices, capillaries, and minute elementary surface spaces, all of which may be unlike. The relation which Langmuir has derived for amorphous adsorbents represents a complicated function whose exact form can not be determined with our present knowledge of the nature of charcoal surfaces.

Since the plots of the log x/m against the log p show that the Freundlich equation does not hold for any of these vapors, we have chosen the only alternative possible and have plotted our isotherms in accordance with equation 1. These isotherms for the four dichloro compounds are shown in figures 1 and 2. Within the pressure range indicated by the experimental points the adsorption relations for these vapors are satisfactorily expressed by the Langmuir equation. At lower pressures than those indicated the values of $p(x/m)$ appear to diminish rapidly with diminishing pressure and the simple adsorption equation 1 no longer applies.

TABLE 3

The adsorption of propylene chloride vapors by charcoal at various temperatures

At 0°C.											
p........	0.10	0.20	0.30	0.40	2.03	5.75	8.23	12.20	12.88		
x/m......	36.14	53.98	67.61	76.94	84.17	90.63	93.49	96.49	100.15		
At 40.00°C.											
p........	0.25	0.40	1.59	6.06	12.61	24.27	42.98	56.58	65.12	79.02	84.53
x/m......	36.82	57.50	72.10	78.61	80.67	83.51	86.83	89.08	90.65	92.99	95.40
At 63.88°C.											
p........	0.35	1.30	7.58	26.70	60.95	91.32	124.37	134.48			
x/m......	32.58	57.61	69.18	74.36	77.53	79.64	81.68	84.20			
At 79.20°C.											
p........	0.30	1.00	3.45	8.00	21.90	29.15	45.00	105.70	138.30		
x/m......	22.97	44.03	56.45	62.09	66.99	68.18	69.76	73.14	75.72		
At 99.22°C.											
p........	0.55	2.58	6.89	15.26	40.68	85.28	125.56	136.80			
x/m......	25.78	44.07	54.80	61.33	66.92	70.35	72.04	74.96			
At 136.20°C.											
p........	2.03	7.33	16.65	35.23	67.60	105.65	136.60	138.15			
x/m......	21.74	34.46	42.81	49.62	54.09	56.91	58.62	60.35			

McBain and Britton (4) have studied the adsorption of nitrous oxide, ethylene, and nitrogen by charcoal at different temperatures and under pressures up to 40 and 60 atmospheres. They find that equation 1 adequately expresses the adsorption relations throughout the whole pressure range. McBain, Lucas, and Chapman (5) find that a plot of $(p/p_0)/(x/m)$ against the relative humidity, p/p_0, gives a straight line throughout the pressure range studied for toluene, hexane, octane, decane, acetone, and acetic acid vapors. It appears to fail, however, for methyl alcohol vapor at low pressures, and the authors attribute the deviations to the presence of residual impurities.

The study of the adsorption of vapors of the kind here used and the possibility of drawing definite conclusions as to the influence of the structure and complexity of the vapor molecules upon adsorption is hampered by the fact that the study is limited to temperatures at which liquefaction is possible. This is particularly true at the lower temperatures employed at which the forces operative in condensation may coëxist along with those of adsorption. The orientation and adsorption of the vapor molecules is opposed by thermal agitation. Since the amount of vapor adsorbed diminishes as the temperature is raised, there should be for each vapor a critical temperature above which adsorption is impossible. A satisfactory comparison of adsorption magnitudes on a given surface can only be made when the thermal energies of the vapor molecules are equal.

TABLE 4

The adsorption of trimethylene chloride vapor by charcoal at various temperatures

At 0°C.										
p	0.05	0.10	0.15	0.30	1.50	3.12	3.72	3.77	3.82	
x/m	23.82	50.45	66.42	81.35	89.67	94.15	98.73	109.11	119.83	
At 40.00°C.										
p	0.10	0.15	0.35	3.62	8.30	15.75	23.80	26.75	31.02	33.00
x/m	21.39	42.90	63.18	78.71	81.77	85.08	88.23	89.24	90.51	92.00
At 63.85°C.										
p	0.15	0.25	0.50	3.32	12.34	19.32	36.96	45.24	50.05	
x/m	27.64	44.57	57.72	72.77	77.91	79.82	82.96	84.23	85.98	
At 79.10°C.										
p	0.15	0.35	0.90	2.23	7.18	15.41	36.07	47.57	50.15	
x/m	25.90	42.93	54.35	63.93	69.99	73.32	76.74	77.94	79.15	
At 99.50°C.										
p	0.30	0.75	2.38	6.65	19.32	40.73	50.44			
x/m	24.07	41.38	55.71	65.27	72.03	75.52	77.35			
At 136.20°C.										
p	0.80	3.27	8.67	18.33	35.58	49.95				
x/m	20.36	36.42	48.38	56.43	61.95	64.56				

Although the critical adsorption temperatures may not be identical with their critical temperatures, we have assumed nevertheless that the boiling points of the liquids are corresponding adsorption temperatures. We have assumed also that the variation of the adsorption with the temperature is linear through the narrow interval between the experimental isotherms just above and below the boiling points. In this way we have calculated the isotherm data of table 5 for the vapors of all of the chlorine substituted compounds studied thus far. The natural boiling point isotherms plotted from these data are shown in figure 3. The relative amounts of the different vapors adsorbed at their boiling points should be significant.

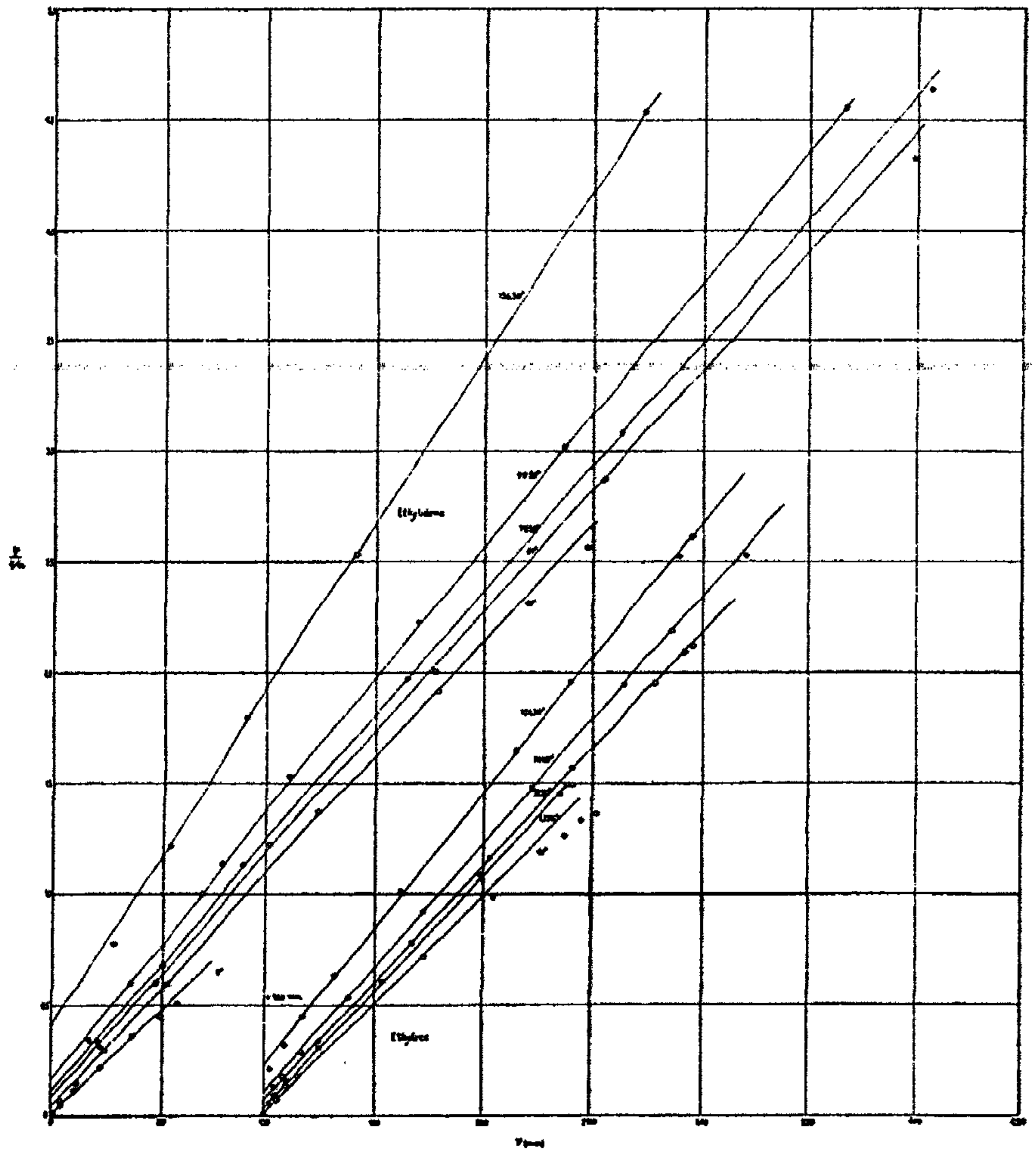

FIG. 1. THE LANGMUIR ADSORPTION ISOTHERMS FOR ETHYLENE AND ETHYLIDENE CHLORIDE VAPORS AT VARIOUS TEMPERATURES

A study of figure 3 shows certain definite regularities. Under an equilibrium pressure of 1 mm. ethyl chloride is more highly adsorbed than is methyl chloride, and both are more highly adsorbed than n-propyl and n-butyl chloride. Of the latter two the propyl chloride is the more highly adsorbed. At still lower pressures the order of increasing adsorption is methyl, ethyl, n-propyl, n-butyl. This is exactly the order of their respective molecular weights, boiling points, and dipole moments. At higher pressures the order of adsorption is exactly reversed; methyl chloride is the most highly adsorbed and butyl chloride the least.

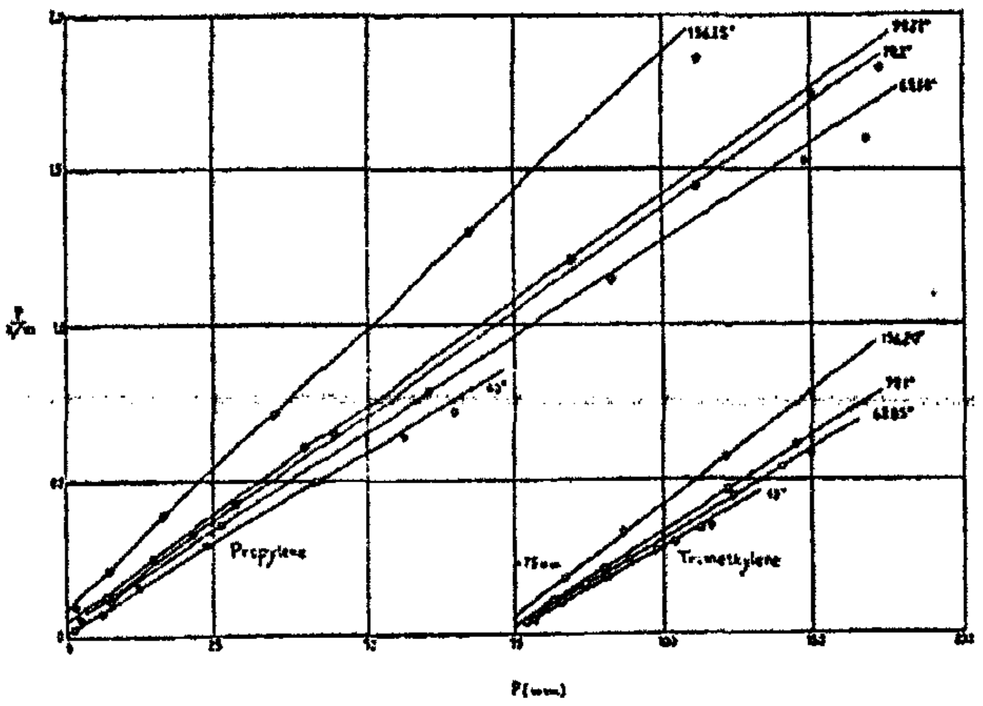

FIG. 2. THE LANGMUIR ADSORPTION ISOTHERMS FOR PROPYLENE AND TRIMETHYLENE CHLORIDE VAPORS AT VARIOUS TEMPERATURES

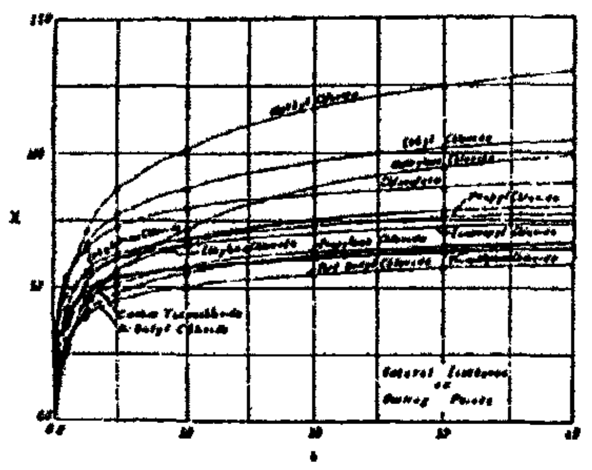

FIG. 3. THE NATURAL ISOTHERMS OF VARIOUS CHLORINE DERIVATIVES OF THE ALIPHATIC HYDROCARBONS AT THEIR BOILING POINTS

The isopropyl and *tertiary*-butyl chloride vapors, as we might expect, from their greater surface covering power, are less adsorbed at all pressures than the corresponding normal vapors.

Chloroform is more highly adsorbed than methyl chloride below 1.3 mm.

and more highly adsorbed than methylene chloride below 17 mm. From the trend of the isotherms we may infer that carbon tetrachloride is more highly adsorbed than chloroform at very low pressures. At higher pressures, however, the order of increasing adsorption is that of decreasing molecular volume, namely, $CCl_4 < CHCl_3 < CH_2Cl_2 < CH_3Cl$.

Ethylidene chloride is more highly adsorbed than ethylene chloride up to 19 mm. Above this pressure they are adsorbed to practically the same extent at all pressures. The greater adsorption of the lower boiling ethylene chloride at the lower pressures is interpreted as being due to the fact that the two chlorine atoms are attached to the same carbon atom. Thus, the attraction for the vapor molecule is increased, and since the radical extends outward, more molecules may be adsorbed.

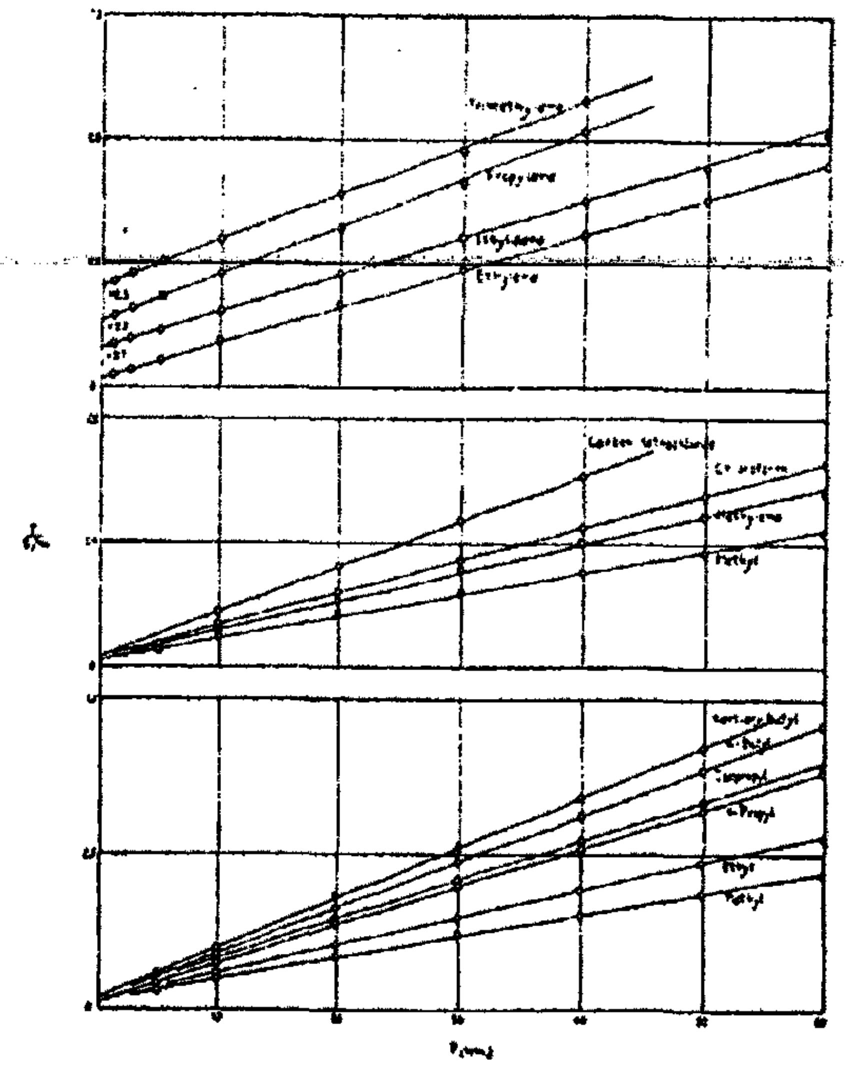

FIG. 4. THE LANGMUIR ADSORPTION ISOTHERMS OF VARIOUS CHLORINE DERIVATIVES OF THE ALIPHATIC HYDROCARBONS AT THEIR BOILING POINTS

Ethylene chloride is less adsorbed than propylene chloride at pressures below 2.5 mm.; it is less adsorbed than trimethylene chloride below 1.7 mm. The latter, in turn, is less adsorbed than propylene chloride below 2.5 mm. Above the pressures indicated the order of adsorption is: ethylene > propylene > trimethylene. This is exactly the order to be predicted from the respective surface covering powers of the three vapors on the assumption that the adsorption is due to the attraction of the surface forces for the chlorine atoms.

While we have discussed the adsorption with respect to four series of chlorine substituted vapors, the relative adsorbability of the vapors of the different series may be easily noted from figure 3. In general, it may be stated that for any one of the series of vapors, the higher boiling, heavier molecules are most highly adsorbed at low pressures. The adsorption of these quickly approaches a maximum and then increases but slightly with further increase in pressure. At relatively high pressures the more simple the molecule is, the greater is the tendency of the adsorbent to adsorb additional vapor as the pressure is increased.

We have plotted the boiling point isotherms corresponding to the simple adsorption equation of Langmuir. These are shown in figure 4. Because of the approximate equality of the adsorption magnitudes of the ethylene and ethylidene chloride vapors, and of those of propylene and trimethylene chloride, it was necessary to displace the plots upward by definite space intervals.

Within the limits indicated by the experimental points, the Langmuir equation for simple adsorption on a plane surface adequately expresses the adsorption for the chlorine compounds studied. At lower pressures the values of $p/(x/m)$ fall rapidly below the straight line plot. This is not surprising since the Langmuir equation (1) applies only to adsorption on a plane surface. Charcoal surfaces are exceedingly irregular; they are made up of points, edges, and capillaries, and the atoms of each possess adsorption forces of widely varying intensity. Upon exposing the gas-free charcoal surface to a vapor it is the more intense forces emanating from the surface atoms that are first saturated. Only when these points have become covered with vapor molecules will the adsorption approximate in nature that on a plane surface. Then and only then should the simple adsorption equation apply to the adsorption of vapors on charcoal surfaces.

The heats of adsorption of the four dichloro vapors studied in this research were calculated from the slopes of the isosteres. The heats of adsorption obtained are: ethylene chloride, 11,500 calories; ethylidene chloride, 10,965 calories; propylene chloride, 13,160 calories; trimethylene chloride, 13,700 calories. Since the heats of adsorption of these vapors have not been determined experimentally, we can only state that the above values are probably of the right order of magnitude. In general, however, it has been found that heats of adsorption calculated from the isosteres are usually lower than those experimentally obtained.

SUMMARY

The adsorption of the vapors of ethylene chloride, ethylidene chloride, propylene chloride, and trimethylene chloride on charcoal has been studied

at several temperatures between 0°C. and 136°C. Within the pressure range employed, the adsorption magnitudes are satisfactorily expressed by the simple Langmuir equation for adsorption on plane surfaces.

Both the natural and the Langmuir isotherms have been plotted for these vapors and for the chlorine derivatives previously studied at temperatures corresponding to the boiling points of the pure liquids. The Langmuir equation applies for the pressure range studied. The Freundlich equation does not hold for any of the vapors.

For any one series the amount of vapor adsorbed at very low pressures is always greatest for that vapor having the greatest molecular weight, the largest molecular volume, and the highest boiling point; it is least for the simpler, lower boiling liquids. Similar relations obtain with increase in the number of chlorine atoms within the molecule. At higher pressures the order of the adsorption magnitudes is exactly reversed.

The influence of the number and position of the chlorine atoms has been determined.

The heats of adsorption of the vapors have been calculated from the slope of the isosteres.

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THE EFFECT OF TEMPERATURE ON THE VISCOSITY OF BINARY MIXTURES WITH ABNORMAL VISCOSITIES

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The effect of temperature on the abnormal viscosities of certain binary mixtures has received both experimental and theoretical consideration. In a general way, experimental evidence indicates that at higher temperatures the abnormality diminishes and the viscosity of the mixture tends to follow the law of mixtures. Further, the constancy or variation in the composition at which the abnormality occurs, when the temperature is changed, has been used to determine the cause of this abnormal behavior. Most cases can be explained on the assumption of (1) compound formation, (2) complex formation, (3) association, and (4) dissociation.

Drucker and Kassel (3) in their investigation of systems with maximum viscosities, find in all cases investigated that an increase in temperature decreases the sharpness of the maximum point. Kurnakov and Krotkov (6) in an investigation of some twenty mixtures, find that not only is the sharpness of the maximum point decreased with increasing temperature, but also there is a shift in the composition of the maximum viscosity mixture in the direction of higher concentration of the more viscous component. De Carli (2) and Errera (5) report similar behavior in systems they have investigated.

Dunstan and Thole (4) have investigated the effect of temperature on the viscosity maximum shown by the system water–acetic acid, up to temperatures of 30°C. Taakalatos (7) has investigated the system pyridine–acetic acid over about the same temperature range. J. Wagner (8) has studied the system nitrobenzene–*n*-butyl alcohol. The first two systems mentioned show a maximum viscosity point, the last a minimum. In the data reported on these systems there appears to be little if any shift in the composition of the mixture having the maximum viscosity at higher temperatures.

This paper deals largely with an extension of the existing data on these three systems to higher temperatures.

APPARATUS

Drucker type viscosimeters were used. Pressure–time products were checked for each viscosimeter.

The vapor thermostat, suggested by Daniels, Mathews, and Williams (1) was used to secure the various constant temperatures. Carbon disulfide (b.p. 46.2°C.), acetone (b.p. 56.5°C.), methyl alcohol (b.p. 66°C.) and benzene, (b.p. 80.38°C.) were used in the vapor thermostat.

Vacuum jacketed 10-cc. pycnometers, calibrated with distilled water, were used for density measurements.

All thermometers used were carefully checked against thermometers calibrated by the U. S. Bureau of Standards.

MATERIALS

Freshly boiled, twice distilled water was used in preparing the acetic acid-water mixtures and for standardizing the pycnometers and viscosimeters.

A standard C.P. brand of glacial acetic acid was purified by repeated fractional crystallization.

Commercial grades of pyridine, nitrobenzene, and *n*-butyl alcohol were purified by repeated fractional distillation.

METHOD

Mixtures of the two components, with composition expressed in mole per cent, were made up covering the entire range of composition. Densities of the various mixtures were determined from room temperature to about 80°C., using the vapor thermostat. The time of flow for an equal volume of water or mixture was measured over this temperature range. The same volume of liquid was used in the viscosimeter at all temperatures. Volumes of water or mixture were brought into the viscosimeter after having been previously brought to the desired temperature. Relative viscosities of mixtures were calculated from densities and times of flow of the mixtures and water at corresponding temperatures. Absolute viscosities were calculated from relative viscosities, using density and viscosity data for water from the International Critical Tables.

EXPERIMENTAL RESULTS

Tables 1, 2, and 3 and figures 1, 2, and 3 show the viscosities of the three systems over a temperature range from 35°C. to 75°C. in intervals of 10°C. These data, at even temperatures, were taken from large scale graphs of the experimental values for temperatures obtained with the vapor thermostat.

Reference to figure 1 shows that in the case of the acetic acid-water system, the composition of the mixture having maximum viscosity remains practically constant at 55 mole per cent acid. Figure 2 shows this also to be the case of the system pyridine-acetic acid. The viscosity isotherms

TABLE 1

The viscosity of acetic acid–water mixtures at various temperatures

ACETIC ACID	VISCOSITY × 10^3 C.G.S. UNITS					
	At 35°C.	At 45°C.	At 55°C.	At 65°C.	At 75°C.	At 80°C.
mole per cent						
100	10.12	8.53	7.46	6.60	5.82	5.40
80	15.24	12.26	10.30	8.77	7.47	6.92
60	18.10	14.33	11.63	9.74	8.20	7.52
55	18.48	14.50	11.82	9.82	8.28	7.60
50	18.47	14.49	11.80	9.80	8.27	7.59
40	17.68	14.03	11.32	9.32	7.83	7.24
20	13.03	10.95	9.00	7.60	6.48	5.95
0	7.18	5.97	5.07	4.36	3.80	3.57

TABLE 2

The viscosity of pyridine–acetic acid mixtures at various temperatures

PYRIDINE	VISCOSITY × 10^3 C.G.S. UNITS					
	At 35°C.	At 45°C.	At 55°C.	At 65°C.	At 75°C.	At 80°C.
mole per cent						
100	7.80	6.60	5.88	5.35	4.84	4.65
80	10.52	8.96	7.88	6.82	6.20	5.83
60	12.70	10.70	9.20	7.80	7.10	6.70
40	19.28	15.20	12.65	10.80	9.35	8.73
30	25.50	19.85	15.80	13.05	10.93	10.00
25	28.87	22.00	17.55	14.30	11.75	10.70
20	31.70	23.80	18.60	15.00	12.57	11.15
15	32.00	23.50	18.20			
0	10.12	8.53	7.46	6.60	5.82	5.40

TABLE 3

The viscosity of nitrobenzene–n-butyl alcohol mixtures at various temperatures

NITROBENZENE	VISCOSITY × 10^3 C.G.S. UNITS					
	At 35°C.	At 45°C.	At 55°C.	At 65°C.	At 75°C.	At 80°C.
mole per cent						
100	16.01	13.27	11.24	9.80	8.78	8.27
95	14.53	12.52	10.81	9.46	8.47	8.05
90	14.03	11.96	10.35	9.06	8.10	7.70
80	13.50	11.47	9.86	8.54	7.60	7.22
60	13.39	11.09	9.31	8.02	7.06	6.65
40	14.11	11.28	9.49	8.07	6.87	6.33
20	15.80	12.70	10.13	8.36	7.11	6.60
0	20.24	15.53	12.23	9.94	8.10	7.33

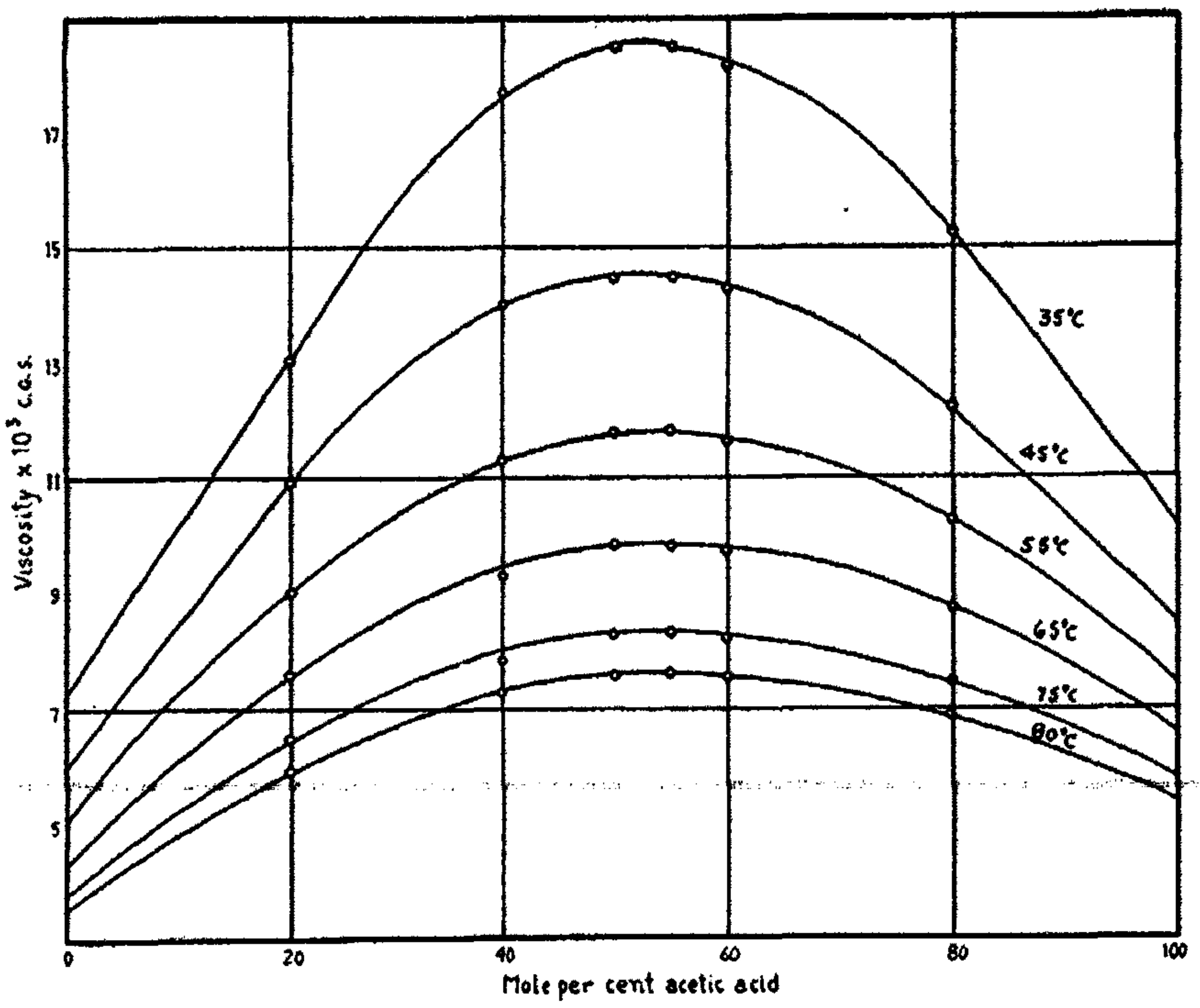

FIG. 1. VISCOSITY ISOTHERMS FOR ACETIC ACID-WATER MIXTURES

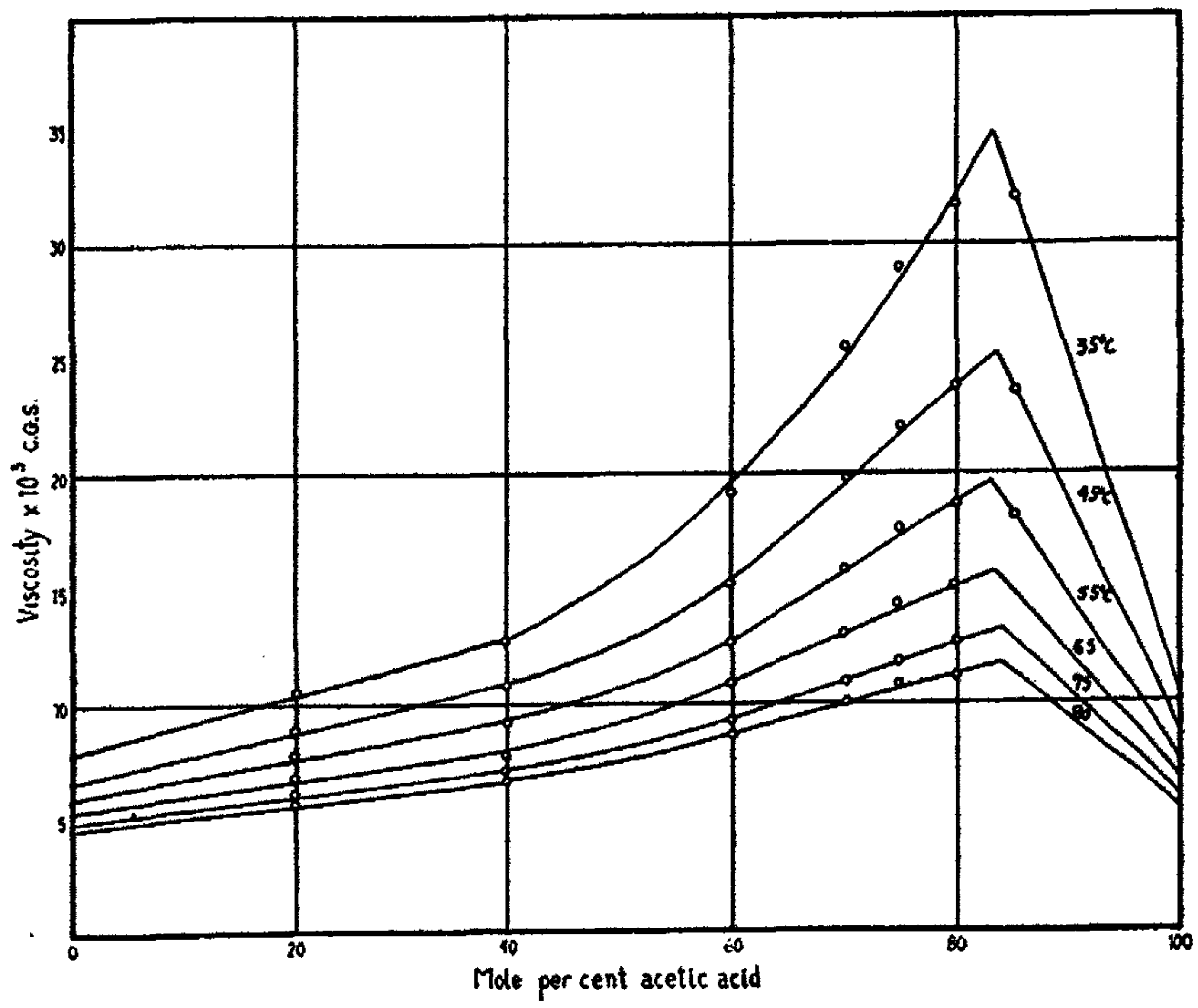

FIG. 2. VISCOSITY ISOTHERMS FOR PYRIDINE-ACETIC ACID MIXTURES

flatten considerably at the higher temperatures, but the maximum is clearly in evidence at a fixed composition in each case.

The viscosity isotherms for the system nitrobenzene–*n*-butyl alcohol show a minimum present for all temperatures investigated. In contrast with the two preceding cases, as the temperature is raised, this system shows a marked and quite regular shift in the composition of the mixture having minimum viscosity. The isotherms are quite flat at the higher temperatures.

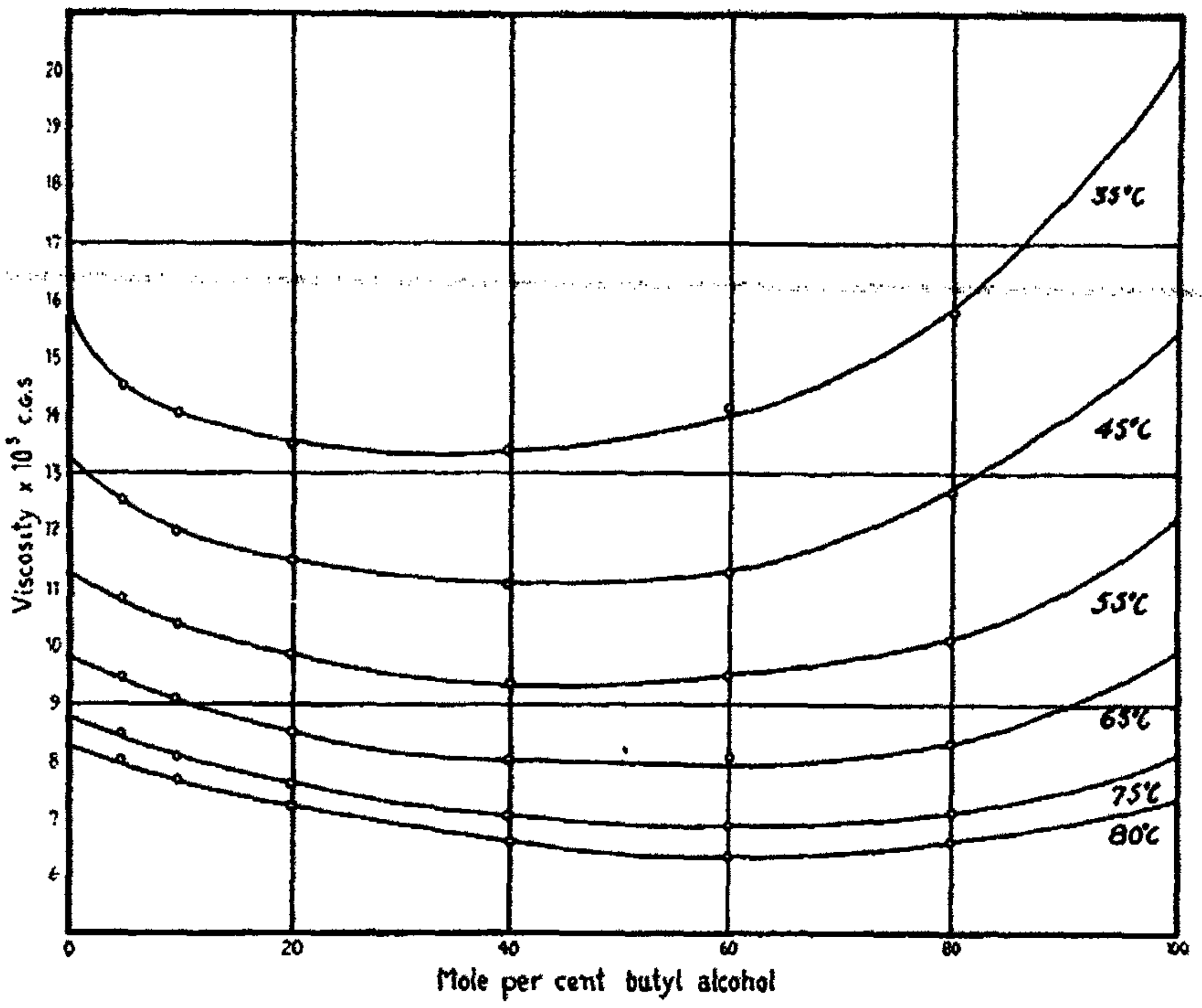

FIG. 3. VISCOSITY ISOTHERMS FOR NITROBENZENE-*n*-BUTYL ALCOHOL MIXTURES

SUMMARY

The effect of temperature on the composition of mixtures having maximum or minimum viscosity has been studied for the systems acetic acid–water, pyridine–acetic acid, and nitrobenzene–*n*-butyl alcohol.

The first two systems show the maximum to occur at fixed compositions for temperatures as high as 80°C. The third system shows a minimum point, occurring at varying compositions, depending on the temperature.

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139-26

ELECTROKINETIC POTENTIALS AND MINERAL FLOTATION[1]

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There has been much speculation as to the rôle which electrostatic charges play in ore flotation (2, 7, 9, 10, 16). The attempts to determine these charges experimentally have yielded various methods as well as various results. The majority of these measurements have dealt with the electrokinetic potential (ζ), while there is some more recent work dealing with thermodynamic potential of galena immersed in various solutions (15). In studying potentials these two must not be confused (11). Ince (14) made use of a Burton cataphoretic tube. Burtsch (5) investigated the problem by means of electroösmosis. Bull (3) utilized the Dorn effect to study the potentials on galena particles.

EXPERIMENTAL

We employed cataphoretic technique in our studies and made use of a modification (4) of a micro cell developed by Buzágh (6). It consisted simply of a groove 1 mm. deep, 1.25 cm. wide and 16.5 cm. long cut in a strip of plate glass which had two small holes ground into it on each end to act as an outlet and inlet for the suspension of ore particles. A thin cover glass was sealed over this groove with sealing wax. Cork slivers were inserted at either end of the groove to a certain distance to prevent contamination of the contents of the cell. Copper electrodes consisting of copper wire in a saturated sodium nitrate–agar agar gel were slipped in behind the cork dams and the whole sealed in place. In accord with Smoluchowski's (17) treatment the measurement of the velocity of the particles was made one-fifth the distance from the top and bottom. The distribution of velocities with the distance from the bottom was not a

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[1] This research was made possible by a grant from the Graduate School of the University of Minnesota. The experimental work was done in the Division of Agricultural Biochemistry of the University of Minnesota. Part of the discussion was furnished by Dr. N. W. Taylor, Chairman of the Department of Ceramics, Pennsylvania State College.

completely symmetrical parabola as demanded by theory, the particles one-fifth the distance from the top always traveling a little more slowly than those at the corresponding position at the bottom. The readings recorded in this paper are those obtained at one-fifth the distance from the bottom of the cell.

In making this study of the effect of electrolytes on the electrokinetic properties of galena, we tried to follow as closely as possible the condition of the flotation experiments as conducted by Taylor and Bull (18) in order to discover any simple relationship between the toxic effect of the cations and the electrokinetic potential. The $M/10$ solutions of electrolytes were prepared from pure chemicals. The hydrochloric acid and nitric acid solutions were carefully standardized. The pH values of the solutions noted on the graph were determined by means of the quinhydrone-platinum electrode.

The galena ore, a 300-g. lot as pure as could be obtained,[2] was ground in an agate mortar (diameter of particles in cell varied from 3μ to 25μ) and the whole thoroughly mixed and stored in closed bottles out of direct contact with air. The other minerals used, pyrite, quartz, anglesite, sphalerite, cerussite, and rhodochrosite were the purest naturally occurring ores obtainable.

The technique of the measurement was to add 0.574 g. of galena or 0.201 g. of quartz, as the case might be, to 500 cc. of the solution investigated. This was shaken and allowed to stand 15 minutes. In this way only smaller particles were obtained which permitted a measurement of their cataphoretic velocity to be made without the particles settling out of focus of the microscope. As mentioned before, the readings were taken one-fifth the distance from the bottom of the cell. The velocities of migration of the particles are expressed in μ per second per volt per centimeter. The readings were obtained within a temperature range of 26.5° to 28.5°C. Eucalyptus oil was not included in the general procedure as used by Taylor and Bull (18). Parallel experiments were run, however, which included the effect of eucalyptus oil in pure water and also in the presence of aluminum nitrate, silver nitrate, lead nitrate, and thorium nitrate on the cataphoretic velocity of galena and of quartz in the presence of aluminum nitrate. A series of experiments was conducted in which the oil was added to the suspension of the mineral in the electrolyte, and another series was investigated where the oil was added to a pure water suspension of the mineral and the electrolyte added afterwards. In no case was there any observable difference in the electrokinetic potential between the two series, nor was there any observable difference whether the eucalyptus oil was present or not.

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[2] Kindly contributed by Dr. Gruner of the Department of Geology of the University of Minnesota.

RESULTS

The effect of potassium ethyl xanthate on the electrokinetic potential of galena and quartz was investigated. In the concentration normally used in flotation (1/10 lb. per ton of ore), there was no observable effect. In more concentrated solutions the negative potential is increased. In concentrations about one hundred times as large as that normally employed a peculiar phenomenon takes place. There is a flocculation of small particles (2μ in diameter) into single needles of approximate dimensions of 2μ $\times$ 2μ $\times$ 10μ. These needles have a negative electrokinetic potential almost twice that of the original small particles.

The cataphoretic velocity of all the minerals suspended in pure water may be summarized as given in table 1. It is interesting that the carbonates carry a positive charge. This is probably due to a hydrolysis of the carbonate in the following manner:

TABLE 1

Cataphoretic velocity of minerals suspended in pure water

MINERAL	VELOCITY	MINERAL	VELOCITY
	μ/sec./volt/cm.		*μ/sec./volt/cm.*
Sphalerite	−2.82	Galena	−2.34
Pyrite	−1.95	Galena exposed to air for 5 days	−2.36
Anglesite	0.0		
Cerussite	+3.13	PbO_2	+1.21
Malachite	+0.63	$PbSO_4$	+1.82
Rhodochrosite	+1.91	PbO	+1.05

$$PbCO_3 + H_2O \rightarrow PbHCO_3^+ + OH^-$$

The effect of the addition of electrolytes on the electrokinetic potential of galena is shown in figure 1 and their effects on quartz and sphalerite in figure 2.

DISCUSSION

It should be emphasized that though the endeavor was made to maintain the same condition in this study as used by Taylor and Bull (18) in their flotation experiments there were some differences, and these must always be kept in mind in interpreting the cataphoretic studies in terms of flotation. In the flotation experiments a 50-g. lot of galena was present in about the same amount of suspension as 0.57 g. in these experiments. There was undoubtedly some adsorption of electrolyte which will therefore alter concentrations and also, although purest galena obtainable was used in both cases, we cannot be sure we had exactly the same degree of purity.

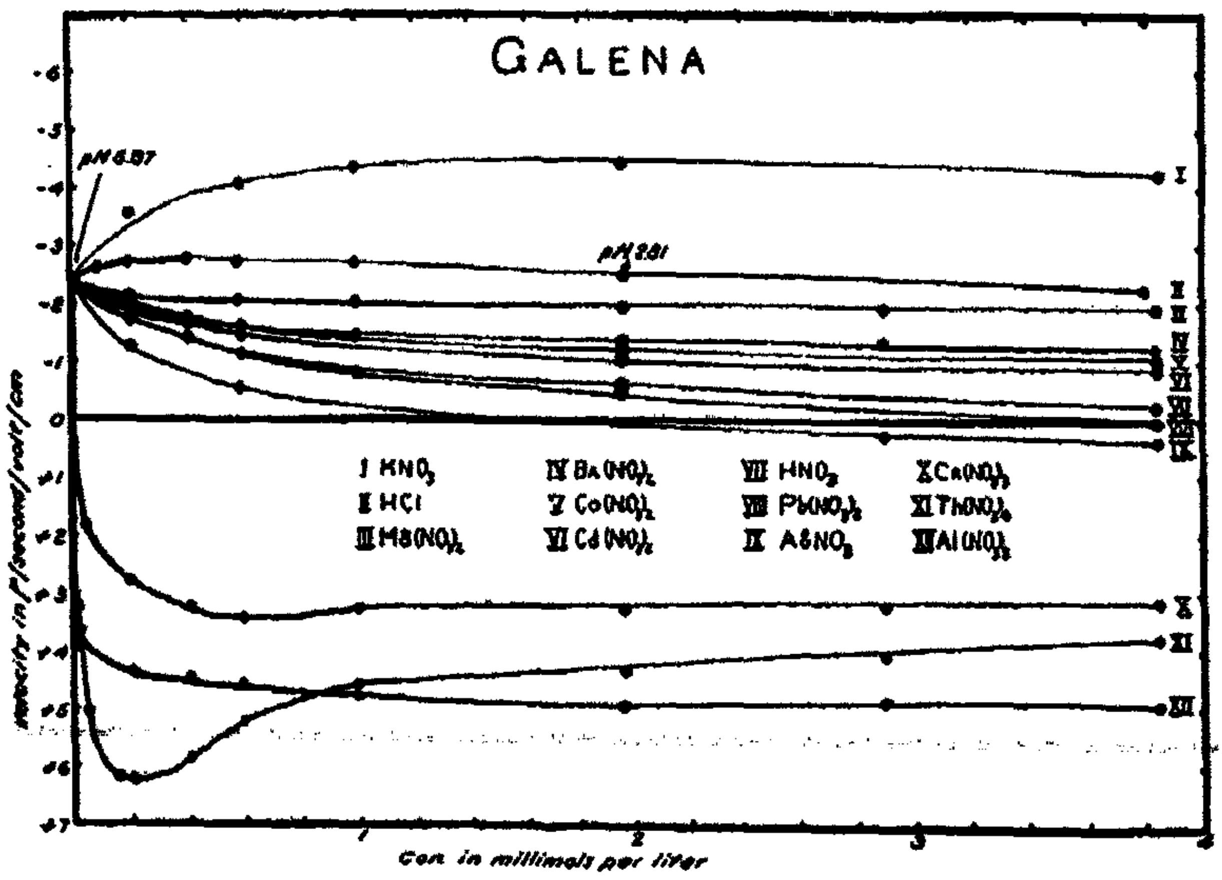

FIG. 1. SHOWING THE EFFECT OF ELECTROLYTES ON THE MOBILITY OF GALENA

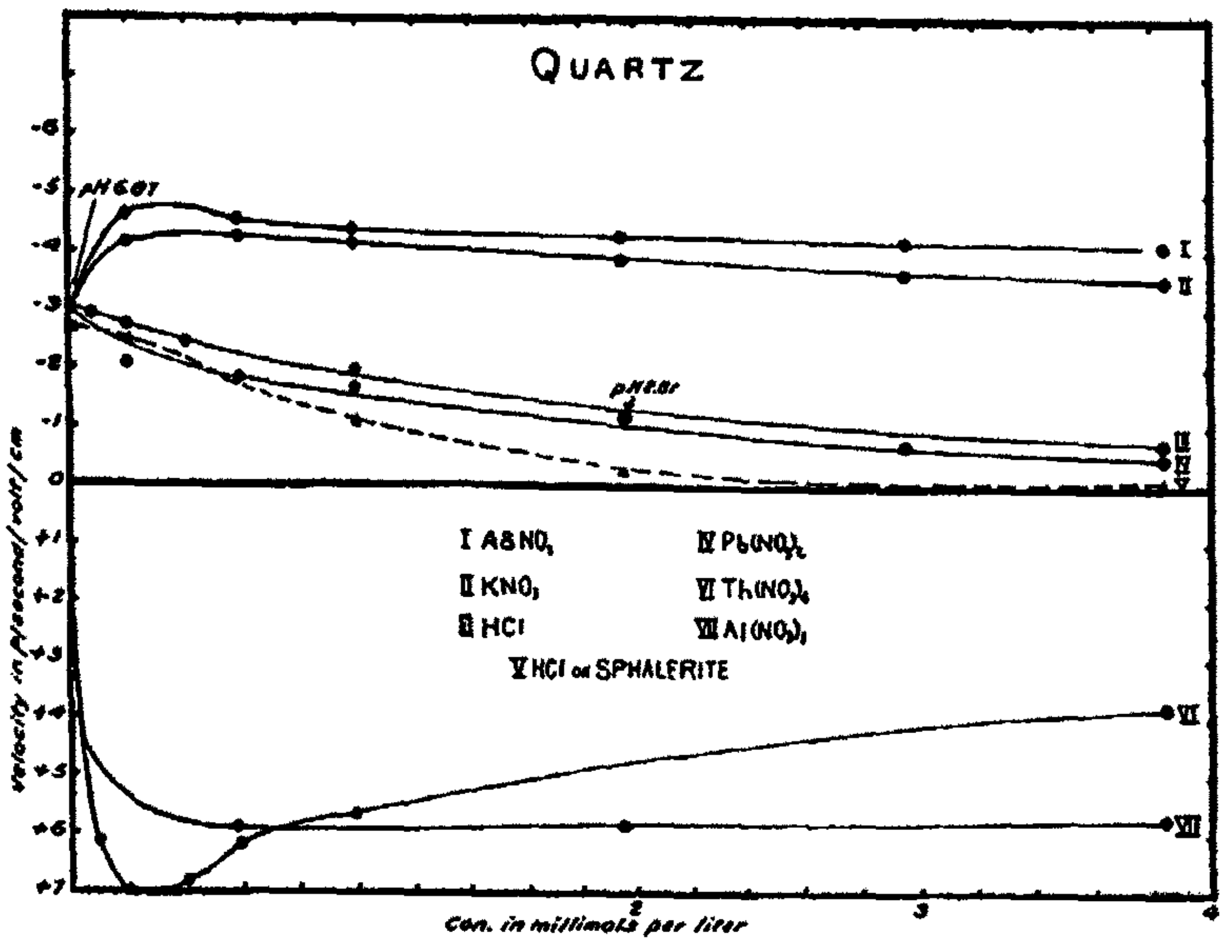

FIG. 2. SHOWING THE EFFECT OF ELECTROLYTES ON THE MOBILITY OF QUARTZ

However, in spite of these factors, the results do enable us to answer some earlier suggestions. For example, once an air bubble has become mineralized the charges of particles already attached may tend to keep other particles from attaching, owing to repulsion by like charges. If this alone were the cause of the loss of galena in flotation in the presence of certain cations then figure 1 would indicate that galena with eucalyptus oil in pure water should float less readily than when the nitrates of Mg^{++}, Ba^{++}, CO^{++}, Cd^{++}, and Pb^{++} are present. Furthermore the floatability of galena in presence of silver nitrate should pass through a maximum at a certain concentration where the charge on the particle is zero. On the other hand, these salts all reduce the floatability of galena by eucalyptus oil (18). Figure 1 would also indicate that potassium nitrate might be as toxic as thorium nitrate.

We find that floatability of galena varies directly as the potential on the particles in the case of Ag^+, Pb^{++}, Cd^{++}, Co^{++}, Ba^{++} and Mg^{++}, and further that the order of the toxicity of the nitrates $Ag > Pb > Cd > Co$ is exactly that of ability of the cations to reduce the electrokinetic potential on the galena. This would indicate that flotation is a matter of peptization rather than flocculation, and it may be interpreted that the larger surface of the peptized material offers greater opportunity for collecting agents to become adsorbed and build up a nonpolar coating. Later these coated particles are taken up by the air bubbles. This view harmonizes with certain statements in Gaudin's excellent book (12). "Far from considering general flocculation is necessary, it would seem as though reasonably good dispersion is desirable for successful flotation, because if it does not obtain, the opportunity to react with the reagents and to adhere to air bubbles is not fully presented to particles that occur within the floccules. The production of a dispersed pulp would then appear as the first requisite in a slimy pulp, and treatment with proper reagents to bring the selection of certain minerals should come next."

The inhibition of flotation by the nitrates of thorium, aluminum, and chromium may be due to formation of hydroxides which are more hydrophilic than the original sulfide.

It seems to be rather generally believed that galena surfaces oxidize to give a surface of lead sulfate (1, 8, 13). According to information supplied by Gaudin (12) this oxidation takes place rapidly. The effect of atmospheric oxidation of galena on the cataphoretic velocity was studied by determining the potential immediately on rapid grinding and then allowing the galena to remain exposed to air for five days. The loss in negative potential was not more than 5 per cent. Then the galena was heated to 300°C. in a stream of air for two hours and the negative potential had been reduced by 20 per cent. Pure anglesite ($PbSO_4$) exhibited no potential; pure cerussite ($PbCO_3$) gave a relatively large positive potential equivalent to a velocity of 3.1μ per second per volt per centimeter. Laboratory chemicals PbO, PbO_2, and $PbSO_4$, all exhibited positive potentials. Since the electrokinetic potential is a surface phenomenon, these experiments seem to indicate that the oxidation is by no means rapid.

It is interesting to note the effect of hydrochloric acid on the cataphoretic velocity of galena as contrasted with that of nitric acid. The increased potential with hydrochloric acid is possibly due to the tendency to adsorb chloride ions because lead chloride is more insoluble. It is also interesting that silver nitrate lowers the potential very much. This may be due to the large adsorption of the silver ion, since silver sulfide is very insoluble.

The previous results reported by Bull (3) on the electrostatic charge on galena using the Dorn effect have not been confirmed.

SUMMARY

1. Cataphoretic studies have been made on a number of pure minerals suspended in pure water. The study has been extended in the case of galena, quartz, and sphalerite to include several electrolytes at various concentrations.

2. Comparison of the data on surface charge of galena with our earlier work on flotation under similar conditions of added electrolytes shows that peptization rather than flocculation is a necessary requisite for good flotation, to be followed by the addition of suitable collecting agents.

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NEW BOOKS

Grenzflächen-Katalyse. By MARTIN KRÖGER. 22 × 15 cm.; viii + 387 pp. Leipzig: S. Hirzel, 1933. Price: 10.50 M.

This book consists of a series of papers dealing with measurements of various physical properties of finely divided solids in relation to catalysis and adsorption, and, as such, presents a valuable and very considerable body of experimental material due to the work of Professor Kröger and his collaborators.

The physical variants studied include changes in the electrical conductivity, in the dielectric constant, and in the magnetic properties of catalysts during reaction and adsorption. These certainly offer some indication of the condition of the catalyst during the process in question; and Professor Kröger is to be congratulated on the thoroughness with which the measurements have been carried out. At the same time, the correlation of catalyst composition with the reaction mechanism is frequently difficult. This is also true of the interpretation of the changes in the velocity and intensity of sound waves, which have been used in the investigation of the condition of gases during reactions in contact with finely divided solids.

Of special interest in connection with the energetics of catalysis is the section dealing with the limitation of the oxidative degradation of naphthalene. The function of catalysts such as vanadium pentoxide in inducing not merely a process of gross oxidation but also the effective stoppage of the oxidation at the phthalic anhydride stage is certainly of primary importance in the understanding of the general mechanism of all reactions of this type.

Probably the outstanding feature of the series of papers lies in the unusual nature of some of the methods of attack.

E. B. MAXTED.

Fundamentals of Fibre Structure. By W. T. ASTBURY. 15 × 22 cm.; ix + 187 pp. London: Oxford University Press (Humphrey Milford), 1933. Price: 8/6 net.

Mr. Astbury has here made available in book form a series of six university extension lectures which he gave to Yorkshire textile students early in 1932. The author is an acknowledged authority on the structure of fibres, particularly protein fibres of the animal body, such as hair and wool, and a wide range of readers will welcome this account. Reprinted lectures, while preserving the freshness of the spoken word, always suffer from the special nature of the audience for which they were prepared. In this case the reader may or may not welcome seventy-six pages on the nature of matter and radiation, the invisible fibres of the world of molecules, and an elementary account of how atoms make spatial patterns. The remaining three lectures deal in a vital way with the author's own researches and those of his colleagues. The general reader will feel that precision has been brought into a very difficult field of organic chemistry, and the specialist will marvel that so much precise information has been obtained from such fuzzy x-ray photographs. The crystallites of hair and wool are very minute and the remaining amorphous matter increases the difficulties of inpretation. Mr. Astbury shows how the extensibilities of hair and wool are due to the unfolding of the keratin chains and his facts are linked up in a novel way with the technical processes of the woolen industry. The book is appropriately introduced by Sir William Bragg and concludes with a useful bibliography.

J. T. RANDALL.

Pour Comprendre la Chimie Moderne. By E. Cattelain. 18 × 11 cm.; 254 pp. Paris: G. Doin & Cie., 1933. Price: 15 francs.

There are some who will condemn this book merely because the theory of atomic structure is introduced on p. 24, whereas no mention of a buret is made until p. 150. In a book of this type addressed to the layman there is, however, something to be said for using this theory as a framework into which the facts of chemistry may be fitted, in spite of the obvious risk that the stability of the whole structure may be thought to depend on this framework. Granting this, certain features of the arrangement of the subject matter may prove useful to teachers who have to "explain" modern chemistry to those who have not had an experimental initiation into the science. On the other hand, the book should not be put into the hands of the novice who might aspire to become a serious student of Chemistry. Apart from acquiring strange ideas about the scope of organic chemistry (p. 17) and regarding the structure of an "unionised molecule" of sodium chloride (p. 236), he would be completely confused in his attempt to understand the explanation of how the volumes of gases participating in a reaction are shown by the chemical equation (p. 73), since the author habitually writes the formulas of hydrogen, oxygen and nitrogen as if their molecules were monatomic.

H. J. T. Ellingham.

Theorie der Oberlächenerscheinungen. Edited by A. R. Rabinowitsch, N. A. Bach and A. G. Passynski. Charkow, Russia: Technischer Staatsverlag, 1933.

During September 20–24, 1932, a symposium on "The Properties of Surfaces" was held at Moscow, Russia, under the auspices of the "Assoziation Physikalisch-Chemischer Forschungs-Institute im Karpow-Institut für physikalische Chemie, Moskau." The papers presented at this symposium appear in Band 4, Heft 2, pp. 139–432 (1933), of the "Physikalische Zeitschrift der Sowjetunion." All papers appear in either German or English. This Symposium may be regarded as more or less analogous to the Colloid Symposiums which have been held annually for the past ten years in the United States. The following twenty-three papers, all dealing with problems of surface chemistry or surface physics, are included in the monograph:

M. Polanyi. Adsorption und Kapillarkondensation.
M. Dubinin. Kapillarkondensation von Dämpfen an porösen Sorbenten.
M. O. Charmadarjan und W. K. Markow. Einfluss der Reaktion des Mediums im Moment der Koagulation auf die Struktur des Silikagels. I.
F. P. Bowden. On the Range of Surface Forces.
R. Burstein, P. Lewin und S. Petrow. Aktivierte Adsorption von Gasen an Kohle.
P. I. Lukirsky. Über die Austrittsarbeit der Elektronen und die photoelektrischen Eigenschaften der Metalle.
A. Frumkin. Ionenadsorption an Metallen und Kohle.
E. Lange. Über die Natur der Quecksilbertropfelektrode.
B. P. Nikolski. Die Eigenschaften der Doppelschicht und die Austauschadsorption von Ionen an nichtmetallischen Oberflächen.
L. Lepin. Die Oberflächenoxyde der Kohle und die Adsorption von Elektrolyten.
H. R. Kruyt. Kapillar-elektrische Untersuchungen an Silberhalogeniden.
A. J. Rabinowitsch. Adsorption der Elektrolyte und ζ-Potential.
L. W. Janssen. Der Aufbau der elektrischen Doppelschicht.
M. O. Charmadarjan und B. I. Perwuschin. Über einige Erscheinungen bei der Bewegung einer der Elektroden im Elektrolyten und über das elektrokinetische Potential.

F. P. Bowden and A. Dummett. The Influence of the Underlying Surface on the Cataphoretic Mobility of Adsorbed Proteins.
M. Volmer. Überspannung.
R. W. Gurney. Quantum Mechanics and Overpotential.
P. A. Rehbinder und N. Kalinowskaja. Abnahme der Grenzflächenenergie und Zunahme der Dispergierbarkeit fester Körper bei Bildung einer Adsorptionsschicht.
W. P. Berdennikow. Messung der Oberflächenspannung von festen Körpern.
D. L. Talmud. Mechanische Eigenschaften der Adsorptionsschichten und Stabilität der Schäume und Emulsionen.
B. V. Deriagin. Mechanical Properties of Thin Layers of Liquids.

Space will not permit an evaluation of the individual contributions in this review. Suffice it to say that many of the papers are of the utmost importance and should be carefully read by those interested in the properties of surfaces. The volume can be secured through the American agents, G. E. Stechert and Company, 31 E. 10th St., New York City.

Ross Aiken Gortner.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 54: Wolfram. 25 × 17.5 cm.; xi + 397 pp. Berlin: Verlag Chemie, 1933. Price: 64 M. Subscription price: 56 M.

This volume includes the sources and ores of tungsten, the preparation of the metal, including technical processes and the production of wire for the lamp industry, physical properties, chemical properties, analysis, alloys, and compounds. Among the latter the salts of tungstic acid are fully dealt with, together with the question of the basicity of the tungstic acids. The complex molybdic acids, such as borotungstic, silicotungstic, and phosphotungstic acids, are included. The volume gives a modern and very complete account of the chemistry of tungsten and is of the same high standard as its predecessors. In view of the importance of tungsten in modern industry, such a monograph is very welcome.

J. R. Partington.

Recent Advances in Physical Chemistry. By Samuel Glasstone. Second edition. 14 × 21 cm.; viii + 498 pp. London: J. and A. Churchill, 1933. Price: 15 shillings.

This well-planned and well-written summary of recent advances in physical chemistry has won for itself a place in the library of most advanced students of the subject, and the appearance of a second edition will be heartily welcomed. No change has been made in the general plan of the book, except that the chapter on solubility, perhaps the least necessary or important chapter in the former edition, has been omitted; and the space which has thus been made available has been more than used up in expansions of the remaining chapters. The groundwork of the book remains largely unchanged, although here and there certain paragraphs have been rewritten or modified, and the value of the present edition as compared with its predecessor lies in the new matter which has been inserted. The new subjects discussed include: wave mechanics and its applications to problems of valency and the calculation of energy of activation; nuclear disintegration and the discovery of the neutron and the positive electron; the influence of free and restricted rotation on dipole moments; molecular beams and their uses; potential energy curves; atomic reactions; the kinetics of photochemical reactions; activated and discontinuous adsorption; surface potentials; the mobility of surface molecules. In the case of a number of these subjects many will, perhaps, feel that the treatment is rather slight and inadequate, but even if this may be so, the discussion of the various topics, all of considerable interest at the present time, will direct the attention of the serious student to the paths along which the subject is advancing and will help him to take up the fuller study of one or more of the subjects discussed. More than this can scarcely be demanded of such a book as the one under review.

A. Findlay.

Die Lösungsgleichgewichte der Systeme der Salz ozeanischer Salzablagerung. By J. D'Ans. Quarto, 254 pp.; accompanied by 31 tables of graphs and diagrams, which are bound separately. Kali-Forschungs-Anstalt, Berlin. Verlagsgesellschaft für Ackerbau, M.B.H., Berlin S.W. 11, Dessauer Strasse.

The writer of this monograph, who worked in the laboratory of van't Hoff on this subject, has here revised and recompiled all of the information relating to it now available. It forms a complete summary of the facts known regarding the equilibria which exist between water and salts yielding chloride, sulfate, sodium, potassium, magnesium, and calcium ions, in either their simplest or most complex mixtures. In part I, one finds forty-seven pages devoted to a clear and systematic discussion of solubility determinations, methods of ascertaining the composition of the solid phases left after such determinations, and methods of fixing the constants which define invariant points; also the results of the application of the phase rule to the study of such data and discussion of the graphical methods of representing such systems. There are one hundred and eighty-eight pages devoted to the discussion of the forty-six salt systems, in which all of the data relating to combinations of water and from two to all six of the ions named, have been compiled and submitted to critical analysis. One is surprised at the large amount of such data which has accumulated since the last summary by van't Hoff.

The composition of solutions has been recalculated, where necessary, and tabulated in terms of moles or double moles per 1000 moles of water, and in many cases in grams per 100 grams of water also. These data have been plotted on coördinate paper on a scale of 2.5 moles or 2.5 degrees per centimeter, the most probable course of the corresponding graphs drawn, and the whole reduced by photographic reproduction to a series of graphs and diagrams on which one centimeter represents 5 moles or 5 degrees. It is possible therefore, with the use of a lens, to read off compositions to 0.1 mole and temperatures to 0.1 degree. These graphs and diagrams make up most of the material reproduced on the thirty-one plates of part II. The volume clearly represents the results of an enormous amount of work and gives evidence of having been thoughtfully and carefully compiled and edited.

W. C. Blasdale.

STUDIES IN AUTO-OXIDATION REACTIONS. VII

THE DATIVE OR COÖRDINATION PEROXIDE THEORY OF AUTO-OXIDATION[1]

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In a recent paper published in This Journal, Stephens (38) has advanced some arguments against the dative peroxide theory of auto-oxidation (27a, 27b) and concluded somewhat dogmatically that the initial stages postulated by this theory have no justification. It is the purpose of this paper to point out that Stephens' arguments are not entirely justifiable and in several cases are somewhat inconsistent with facts, and to bring forth additional evidence in favor of the dative peroxide theory.

When this theory was first enunciated some years ago, the present author made a careful investigation of the chemical behavior of numerous substances which are capable of auto-oxidation. This study revealed the fact that all substances capable of combining with molecular oxygen are known to be unsaturated towards reagents other than molecular oxygen. The apparent exception of saturated hydrocarbons is easily accounted for by the assumption originally made by Mardles (23) and independently by the present author (reference 27b, p. 347) that combination of molecular oxygen with saturated hydrocarbons occurs either through free radicals (highly unsaturated towards other reagents) or through the exposed electrons resulting from the activation of hydrocarbon molecules prior to their decomposition. Hydrocarbons, especially of the hexaphenylethane type, are known to split very readily into free radicals which add molecular oxygen with considerable avidity.

The presence of unsaturation in auto-oxidant molecules is confined entirely to certain atomic nuclei in each molecule known to possess loosely bound molecular valence electrons which can be easily donated to other nuclei by sharing. That these electrons are loosely bound in certain nuclei of polyatomic molecules has been recently amply demonstrated by Mulliken (29). This author gives the electronic structures of NH_3 and H_2O as $1s^2\ 2s^2\ 2p\ (\pi)^4 2p(\sigma)^2$ and $1s^2\ 2s^2\ 2pa^2\ 2pb^2\ 2pc^2$, respectively, and states that "the two $2p\ (\sigma)$ electrons in NH_3 avoid the region of the H nuclei, and as a

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[1] Contribution No. 94 from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology.

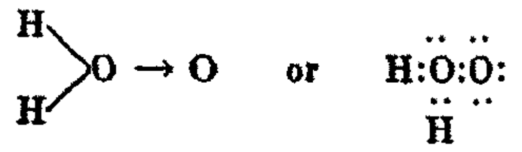
result are relatively loosely bound and reduce the energy of formation of the molecule." "Direct evidence of these electrons in NH_3 is given by the low ionization potential of this molecule, which is 11.1 volts. Many features of the chemical behavior of NH_3, e.g., the formation of NH_4^+, $H_3N \cdot BCl_3$, $Cu^{++}(NH_3)_4$, etc., are reasonably interpreted as conditioned by the stabilization of the two loosely bound $2p(\sigma)$ electrons of NH_3 under the influence of an additional nucleus." The ionization of a $2p(\pi)$ electron of NH_3 would take, according to Mulliken, 15 volts, while that of a $2s$ electron, 25 volts.

Although NH_3 reacts with oxygen only at relatively high temperatures, several of its derivatives are known to auto-oxidize quite readily. Sodamide, for example, adds molecular oxygen to form sodium amidoperoxide, $NaH_2N \cdot O_2$ (35). Several aryl amines, hydrazones, etc., can be isolated only in the form of their salts in which the $2p(\sigma)$ electrons are stabilized (reference 27a, p. 1211). Furthermore, the instability of free radicals, like the methyl radical, is, according to Mulliken (29), due to the presence in the radical of a $2p(\sigma)$ electron.

It has already been suggested elsewhere (reference 27a, p. 1211) that the tendency to auto-oxidize of the hydrides and aryl derivatives of the elements of the fifth group of the periodic table increases as the "effective nuclear charge" of the central elements increases. If the auto-oxidation of these substances proceeds through a preliminary addition of molecular oxygen to the unshared pair of electrons present in each molecule, then there ought to exist a relationship between the tendency of these substances to auto-oxidize and their ionization potentials. That such a relationship actually exists not only with the hydrides of the elements of the fifth group, but also with those of the sixth and seventh groups, has been recently pointed out by the author (28). It has been shown that as we pass down in each group from the lightest to the heaviest element, there is a regular decrease in the ionization potentials of the hydrides, which means an increase of looseness of the molecular valence electrons. With an increase of looseness of these electrons, there ought to be a corresponding increase in the tendency to auto-oxidize. This is made obvious when we compare the first ionization potentials of the alkali and alkaline earth metals with their tendency to oxidize. It has been found that with a decrease in the ionization potentials there is a corresponding increase in the tendency to auto-oxidize.

These considerations should not be confined to the inorganic substances, since the principles of oxidation and reduction apply equally well to organic substances. When molecular oxygen combines with an organic substance, the latter contributes two electrons to it, and the ease with which these electrons are contributed usually determines the reducing power or the oxidizability of the substance. Furthermore, the ease with which molecular oxygen takes up these electrons to form the peroxide group may also depend upon its electron affinity, or the energy required to remove two electrons from the peroxide ion, O_2^{--}. Unfortunately there are no data available at present which will enable us to estimate this electron affinity. Noyes and Beckman (30) have calculated the electron affinity of atomic oxygen for the first electron and found it to be 4.6 volts. Whether that of the molecular oxygen for two electrons is of the same order of magnitude is not known. As an oxygen molecule approaches an easily oxidizable substance, it is easily conceivable that it may attract electrons from the latter with a force equal to its electron affinity, or, in other words, it may reduce the ionization potential of the auto-oxidizable substance.

Some evidence in favor of the electronic structure of the reacting oxygen molecule originally proposed by the author, is to be found in the structure of hydrogen peroxide recently proposed by Maas and his students (5, 8, 21). From a study of the dielectric constant, molecular refractive power, and the parachor of hydrogen peroxide, these investigators proposed the unsymmetrical structure,



$$H_2{>}O \rightarrow O \quad \text{or} \quad \underset{\mathrm{H}}{\mathrm{H{:}\ddot{O}{:}\ddot{O}{:}}}$$

which also agrees with the ease with which hydrogen peroxide loses an oxygen atom to form water. This structure is probably in equilibrium with the symmetrical structure. Since hydrogen peroxide is known to form by the addition of hydrogen to molecular oxygen, its unsymmetrical structure provides evidence for our electronic structure of the reacting oxygen molecule. However, as has been emphasized elsewhere by the author (reference 27b, p. 300), the "odd" electronic structure proposed by Lewis should not be excluded in auto-oxidation reactions.

Although some of the molecular valence electrons, present in many of the auto-oxidant molecules, are apparently paired, it is not certain that this condition holds when these molecules are activated or excited. Moreover, several of the auto-oxidants, such as nitric oxide, the alkali metals, ferrous and chromous compounds, and free organic radicals, in general, are definitely known to possess unpaired valence electrons through which they interact with other molecules.

Auto-oxidation reactions are strongly exothermic and in numerous cases are chemiluminescent. Bäckström has clearly demonstrated that chemiluminescent reactions reveal the presence in the reaction system of molecules of exactly the same kind as are produced by the absorption of light of the same or higher frequency as the emitted light. Furthermore, the energy transferred during auto-oxidation reactions to the reactant molecules, presumably by collisions of the second kind, excites these molecules into those quantum states which are responsible for their ultra-violet spectra. That this energy is of chemical origin can be easily shown by the fact that the heat of reaction is usually greater than the energy of excitation which corresponds to the wave length of the emitted light.

In the case of benzaldehyde, for example, Bäckström has shown that the region of strong light absorption is approximately 3800 A.U., corresponding to an energy of excitation of 75 kg-cal. The heat of auto-oxidation of this substance is 140 kg-cal., which is more than sufficient to cause the excitation of benzaldehyde molecules. Another notable example is the thermal decomposition of ozone, which shows a heat of reaction of 69 kg-cal. whereas the longest wave length in its absorption spectrum corresponds to an energy of excitation of only 47 kg-cal.

If the energy of excitation in auto-oxidation reactions were entirely of vibrational origin, as Stephens seems to assert, one would expect infra-red light to have an accelerating effect in these reactions. As far as the present author is aware, there is no evidence that this is the case. On the contrary, the decomposition of hydrogen peroxide which follows a chain mechanism is totally unaffected by the absorbed infra-red light, while it is greatly accelerated by ultra-violet light (18).

Moreover, there exists a strong parallelism between the photochemical and the thermal auto-oxidations. Both have a chain mechanism; both are susceptible to the influence of negative and positive catalysts. Another parallelism closely related to this one is that between the effects of peroxides and ultra-violet light on certain chemical reactions. Both are known to accelerate auto-oxidation reactions, to induce polymerization of unsaturated substances and to affect the photographic plate. Furthermore, the recent observations of Kharasch and his students (16, 17) and of Smith (36) seem to indicate clearly that in the presence of oxygen or peroxides the olefinic bond is polarized in such a way as to influence the direction of the addition of hydrogen bromide to it. Other additional reactions to the double bond cannot be easily understood unless we assume with Lowry (22) and with Carothers (7) that the reacting molecules are polar or electrovalent, in which two of the electrons have been displaced towards one or the other carbon atom. In fact, it is because of this displacement of the electrons that we are justified in speaking of these substances as unsaturated molecules (20). The fact that the electric moment of ethylene and of other unsaturated substances is found to be zero does not disprove the assumption that the reacting unsaturated molecules are polar. This has been clearly stated recently by Smyth (37).

Finally, the foregoing considerations lead to the unescapable conclusion that the mechanism of the formation of excited molecules is the same in the dark or in photochemical auto-oxidation reactions, and that these excited molecules are produced by the simultaneous supply of vibrational and electronic energy.

AUTO-OXIDATION OF HYDROCARBONS

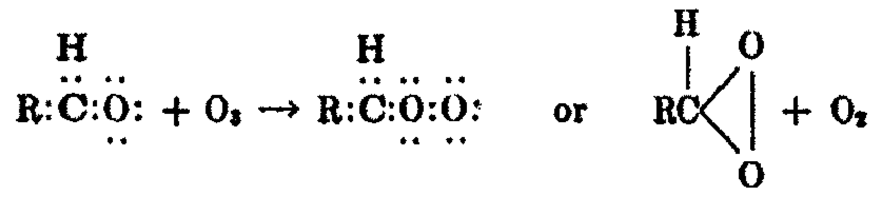
The fact that saturated hydrocarbons auto-oxidize is not at variance with the general theory proposed by the present author, as Stephens seems to insist, since the theory assumes the addition of molecular oxygen to molecular valence electrons which are exposed either as the result of excitation of the hydrocarbon molecule or of its dissociation to free radicals. Whether the final peroxide is an alkyl hydroperoxide or a dialkyl peroxide depends entirely upon the hydrocarbon in question and the relative strengths of the bonds concerned. This point has been more fully discussed by the author elsewhere.

With regard to the auto-oxidation of unsaturated hydrocarbons, there is a displacement of electrons prior to the addition of oxygen, a condition which is fulfilled only by the theory of the present author. The effective strength of the bond broken in the auto-oxidation of an ethylenic substance may be taken as the difference of the strengths of the double and the single bonds. Taking the strength of the C—C bond as 80 kg-cal. (33), and that of the C=C bond as 123 kg-cal. (39), this difference comes out as 43 kg-cal. which is not very far off from the experimentally obtained activation energy for the oxidation of ethylene, namely, 35 to 43 kg-cal. (40). This indicates that in the activated ethylene molecule the double bond is probably broken with subsequent displacement of the electrons to form the polar double bond discussed in the previous section.

AUTO-OXIDATION OF ALDEHYDES, ETC.

Pure aldehydes are not known to dehydrogenate easily, as Stephens claims; in fact, we know of no case in which aldehydes dehydrogenate easily, say, to form diketones even in the presence of dehydrogenating catalysts. Furthermore, Eyring (10) has shown recently that in the case of acetaldehyde, for example, the C—H bond is stronger than the C—C bond. Such arguments, therefore, as those proposed by Stephens are entirely irrelevant to the auto-oxidation of aldehydes in which the seat of unsaturation lies in the carbonyl group. Both Wolf (41) and Smyth (37) have concluded that the electric moment of aldehydes is inherent in the carbonyl group with the oxygen being the negative end of the dipole.

Hydrogen peroxide and ozone are stronger oxidizing agents than molecular oxygen, yet in neither case does the hydrogen of the alpha carbon atom of aldehydes oxidize easily to a hydroxyl group. In the case of hydrogen peroxide stable α-hydroxy peroxides and hydroperoxides are formed (34). Ozone, which is known to add on to unsaturated groups very much in the same manner as molecular oxygen, forms alkyledine peroxides with aldehydes (13, 12, 11). These peroxides either polymerize or, when warmed up, go over to their isomeric acids.



In the case of the auto-oxidation of aldehydes the very recent work of Bodenstein (4), of Bäckström and Beatty (2) and of Kohler and Nygaard (19) confirmed the conclusion of earlier investigators that an active moloxide is first formed which subsequently rearranges to the peracid. Bäckström and Beatty state definitely that the direct formation of a peracid or an activated form of it in one step fails to account for their experimental results; accordingly they were forced to assume the existence of an intermediate moloxide originally proposed by Bach. These and various other considerations confirm our earlier view in regard to the mechanism of the auto-oxidation of these substances.

A similar view has been adopted in the case of the addition of oxygen to the ketones and thioketones. That the double bond in thioketones and thioaldehydes is virtually broken under ordinary conditions is shown by the fact that the aliphatic thioketones and thioaldehydes are known to exist only in their dimeric or trimeric modifications (3). This conclusion is strengthened by the high electric moment recently reported for some of these substances by Hunter and Partington (14). Contrary to the assumption of Stephens, no alkyledine peroxides are known to form in the case of the auto-oxidation of thioketones.

With regard to the mechanism of the auto-oxidation of ethers, there exists ample chemical evidence on oxonium compounds (31, 32, 24) which supports the correctness of our original conclusion that an unstable oxonium or dative peroxide is initially formed.

Finally, the auto-oxidation of triethylphosphine and related substances proceeds, as has already been shown elsewhere, through the initial formation of dative or triethylphosphonium peroxide. Stephens disagreed with this view and proposed an initial peroxide in which the phosphorus atom still retains its original valence of three. This is contrary to our knowledge of the chemical behavior of this class of compounds towards oxidizing agents. The main stable product of this reaction is triethylphosphonium oxide, while secondary products formed by the interaction of this oxide with the peroxide have also been isolated (9, 15, 25). If the peroxide proposed by Stephens were the initial product, one would expect it to hydrolyze in presence of water to yield ethyl hydroperoxide. Actually, no such product is known to form. That the oxide is the main final product is clearly shown by the auto-oxidation of triethoxyphosphine, $(C_2H_5O)_3P$, to form first the peroxide and then triethoxyphosphonium oxide, $(C_2H_5O)_3PO$ (42). Another example of this type is the auto-oxidation of phosphorus trichloride, which yields phosphorus oxycloride (26).

Trimethylarsine and other alkylarsines are also auto-oxidized to yield through the intermediate peroxides alkylarsonium oxides (6).

SUMMARY

1. Additional evidence has been given in favor of the dative peroxide theory of auto-oxidation originally proposed by the author.

2. It has been shown that the recent criticism of this theory is entirely unjustifiable.

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STUDIES IN AUTO-OXIDATION. IV

THE MECHANISM OF ADDITION OF OXYGEN

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The paper immediately preceding this one (6) attempts to defend against recent criticism (14) and to substantiate further the dative peroxide theory of auto-oxidation (5). It also attempts to refute the arguments advanced by the writer (14) in favor of his own viewpoint. In view of the fact that neither the defense of the former theory nor the criticism of the latter is convincing, it becomes necessary to extend the earlier criticisms of the dative peroxide theory to include the most recent arguments of its proponent and to add to the justification of the opposing theory of the writer.

MOLECULAR VALENCE ELECTRONS

The writer has already conceded (15) that molecules such as those considered by Mulliken (9) and Birge (1) contain electrons which may be properly considered as valence electrons. It may be added that odd molecules and free radicals undoubtedly belong to this group. However, it cannot be admitted that such a capacity can be indiscriminately attributed to all unshared electrons in molecules.

In view of the fact that the foregoing article by Milas directs attention particularly to the hydrides of the elements of groups V, VI and VII in the periodic table it will be convenient to consider them here also. Taking ammonia as an example, it is assumed that its two unshared electrons are capable of functioning as valence electrons. This is true, however, only in a very restricted sense, as it is only[1] in cases involving the attachment of a proton or positive ion to the ammonia molecule, that the unshared pair of electrons in the latter plays a rôle similar to that of valence electrons. In other words, the addition reactions of ammonia are highly specific and depend upon what is called, in the absence of a more general term, the proton affinity of the molecule. In the typical case of the addition of HCl, the resultant ammonium ion acquires a positive electrovalence of one, which is merely the valence of its fourth proton,

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[1] The possibility of exceptions in the addition compounds of ammonia with the hydrides and halides of boron is, in the meantime, disregarded, owing to lack of knowledge of the structure of these erratically varied substances.

the valence of the nitrogen thus remaining unchanged. On the other hand, addition reactions of such molecules as CO, CO^+, BeF^+ etc., which admittedly contain true valence electrons, will necessarily involve valence changes. It will be obvious, then, that direct analogy between ammonia and these molecules is of extremely doubtful validity.

Following further the arguments of Milas, it is clearly implied that the formation of -onium compounds is due to "unsaturation" in the donor molecules. It has just been indicated, however, that the formation of these salts is a highly specific reaction involving the addition of a positive ion from the addendum. Typical unsaturated compounds such as ethylene and its derivatives do not show this specificity nor do their hydrohalides in any case exhibit more than a very feeble approach to the properties which we associate with salts. Consequently, the addition reactions of the ethylenes cannot be compared with those of compounds which form -onium salts. If the term "unsaturation" is used at all in the latter cases it ought to imply a special connotation. In the opinion of the writer the property in question ought to be called proton affinity and sharply distinguished from unsaturation. To illustrate the necessity for this distinction may we consider further the behavior of the group V hydrides and their derivatives.

It is common knowledge that the proton affinity of these hydrides decreases regularly with increasing atomic weight of the central element. When we reach phosphine the capacity of forming a base with water has practically disappeared and later the capacity of salt formation vanishes. A similar trend is evident in the alkyl and aryl derivatives.

Now, if we examine the tendency to auto-oxidize we find precisely the opposite trend, ammonia and the amines being the least susceptible to molecular oxygen and the activity toward oxygen increasing as we pass down the group. Trimethylstibine catches fire in air at ordinary temperature, while trimethylamine is relatively difficult to oxidize.

Furthermore, to make the argument more conclusive, the proton affinity of nitrogen increases regularly as the hydrogen atoms in ammonia are replaced successively by alkyl groups, as evidenced by the increasing strength of the corresponding bases. On the other hand, replacement by aryl groups is paralleled by a decrease in proton affinity.

Once more we find that the tendency to auto-oxidize is exactly opposite in trend, as the aryl amines are very sensitive and the alkyl amines relatively indifferent to oxygen at ordinary temperatures. The inevitable conclusion is that the auto-oxidation of the group V hydrides is not related to their proton affinity. It seems logical to conclude further that proton affinity is not related to unsaturation, because decreasing unsaturation ought to involve a decrease in the tendency to auto-oxidize. It will be evident that such arguments as those above might be extended to include other compounds which form -onium salts. These would include alcohols, ethers and aldehydes, and their sulfur analogues—in brief, the majority of the compounds used to illustrate the applicability of the dative peroxide theory.

It has just been pointed out that the tendency of the hydrides of group V to auto-oxidize is not related to proton affinity or to unsaturation. It is very obviously parallel to the thermal stability of the X—H bond and the writer feels justified in adhering to the viewpoint expressed earlier, that the point of attack in these hydrides and their organic derivatives is a vibrationally activated X—H or X—C bond. The hydrides of groups VI and VII are considered similarly, as are also those of group IV.

IONIZATION POTENTIAL AND AUTO-OXIDATION

In the preceding article by Milas it is pointed out that there exists a parallelism between the ionization potentials of the hydrides of groups V, VI, and VII and their tendency to auto-oxidize. This is compared to a similar parallelism in the alkali and alkaline earth metals.

TABLE 1

Ionization potentials

ELEMENTS	IONIZATION POTENTIAL*	HYDRIDES	IONIZATION POTENTIAL*
	volts		*volts*
Cl_2	13.2	HCl	13.8
Br_2	12.8	HBr	13.2
I_2	10.0	HI	12.8

* From Landolt-Börnstein Tabellen E. 384.

In the latter case the parallelism unquestionably involves a relationship, as the peroxides of the active metals are salts and their formation, therefore, involves an actual transfer of electrons. In the former case, however, there seems every indication that this is not so. The electron affinity is undoubtedly smaller for molecular than for atomic oxygen, which, as Milas has pointed out, has been estimated at 4.6 volts (10). Therefore if we consider, for example, the oxidation of ammonia, with an ionization potential of 11.1 volts, the activation energy necessary to accomplish the transfer of two electrons to the oxygen molecule could hardly be less than 7 volts. As this is an impossibly high value, the natural inference is that the reaction proceeds by some other mechanism, involving an activation energy more in accord with experience.

If it were justifiable to assume with Milas that auto-oxidation proceeds invariably through donation of a pair of electrons to the oxygen molecule and if, as is implied in the foregoing paper, the ease of this donation is determined by the ionization potential of the donor molecule, one would expect, for example, that the halogens in molecular form would be more readily auto-oxidized than their corresponding hydrides. The ionization potentials in question appear in table 1. It might further be expected that xenon, with an ionization potential of 11.5 volts, would be more readily auto-oxidized than any of the halogen hydrides.

POLAR STRUCTURE AND AUTO-OXIDATION

The application of the dative peroxide theory requires the assumption of polar structures for ethylene and its derivatives and for the oxygen molecule, to which the writer has objected (16). In this case it is unnecessary to argue the fundamental question of the possibility of such structures, but merely to consider the application employed by Milas. In the preceding paper it is concluded that, *in the activation of ethylene, prior to oxidation,* "the double bond is probably broken, with subsequent displacement of the electrons to form the polar double bond." May we now outline the conditions specified by the dative peroxide theory as necessary for the auto-oxidation of ethylene: (1) activation energy must be supplied; (2) the activated molecule must assume the unsymmetrical electronic structure; (3) the polar molecule will react only with a polar molecule of oxygen.

With respect to condition 2, our general knowledge of the reluctance of carbon to participate in the electrovalent type of linkage seems to preclude any possibility of a definite state with any permanence having the extreme separation of charges of the polar molecule (4). It is to be admitted, of course, that there will be a certain small probability of such an electronic configuration being found instantaneously, but there seems no possible reason for such an arrangement having any stability. Therefore, only a very small fraction of the already activated molecules of ethylene would be instantaneously in a position to react with oxygen. This fact alone ought to be sufficient to cast some doubt on the validity of condition 2, but when there is further superimposed the restriction that only the polar form of oxygen can react with the very small fraction of activated ethylene molecules which happen to be in the polar configuration, the writer feels that this interpretation reduces itself to an absurdity. The absence of electric moment in oxygen, of course, limits the maximum possible concentration of polar molecules to a very small one.

ACTIVATION IN LOW-TEMPERATURE THERMAL REACTIONS

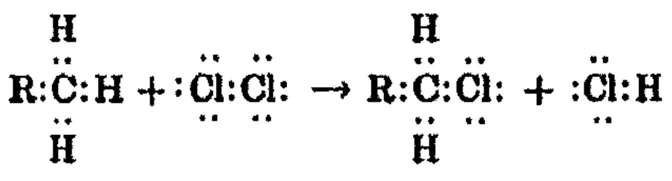
It has been pointed out by the writer (17) and elaborated upon by Milas (8) that thermal and photochemical auto-oxidations proceed through the same initial stage. It is reasonable, therefore, to assume that a similar energy of activation is required in each case. In low temperature dark reactions there is no apparent source of energy for electronic activation;

therefore the writer concluded that, as vibrational activation alone was possible in such cases, it must also account for photochemical oxidations. Milas attempts to discredit this viewpoint by pointing out the fact that the heat of oxidation, which may be transferred during the propagation of chains, is more than sufficient to supply energy of activation. This is quite true but irrelevant, as this author has apparently failed to realize that chains cannot be propagated before they are initiated. It is the initiation of chains that is the problem in thermal reactions. In the case of benzaldehyde, if we accept for the moment Milas' inference that its energy of activation is 75 kg-cal. and if we rely upon the Maxwell-Boltzmann distribution of energy for the initiation of chains, we find, at room temperature, approximately 1 molecule in 10^{32} moles with the necessary energy. Actually, however, the situation may not be as bad as this, in view of the fact that there is some evidence (2, 3, 11, 18) indicating that chains may be initiated at the walls. Even if this is invariably true, it is difficult to conceive of a surface activation involving electronic excitation, although something akin to vibrational "stretching" is not difficult to picture. Now, if chains can be initiated without the intervention of electronic excitation, they ought to be capable of propagation through the agency of bonds which possess only vibrational energy. The writer, of course, does not intend to fly in the face of all the evidence against the so-called radiation hypothesis by assuming that infra-red radiation ought to be effective in such reactions. The decomposition of hydrogen peroxide, cited by Milas (7), is simply one of many cases in which radiation corresponding to, or in excess of, the known energy of activation is ineffective. It would be out of place to introduce here a discussion of this apparent anomaly.

In the above arguments the writer has attempted to confine himself to essentials in the conflict between his own viewpoint and that of the dative peroxide theory. A detailed discussion of all the minor points brought forward in the preceding paper would require an unjustifiably large amount of space; therefore such points must be left to the judgment of the reader. In conclusion, however, it seems desirable to expand slightly and, in one instance, to modify the viewpoint expressed earlier in the paper on "The Initial Act in Auto-oxidation" (14).

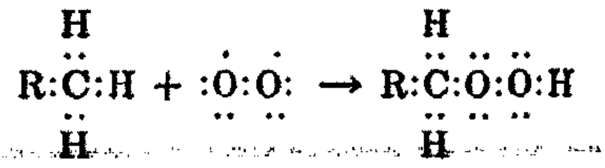
ADDITION OF OXYGEN TO A SINGLE BOND

The writer's interpretation of the auto-oxidation of the group V hydrides and their alkyl derivatives and of ethers, aldehydes, saturated hydrocarbons, etc., in which oxygen is represented as adding to a single bond, apparently does violence to the traditions of organic chemistry. According to these traditions addition reactions are characteristic of unsaturation, exhibited by multiple bonds or unpaired valence electrons. In order to reconcile this apparent conflict an analogy will be helpful. If we consider the action of, say, chlorine upon a saturated hydrocarbon,



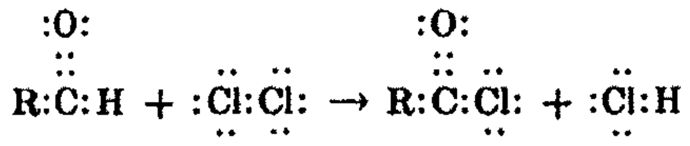
$$\mathrm{R{:}\underset{H}{\overset{H}{C}}{:}H + {:}\ddot{Cl}{:}\ddot{Cl}{:} \rightarrow R{:}\underset{H}{\overset{H}{C}}{:}\ddot{Cl}{:} + {:}\ddot{Cl}{:}H}$$

the sharing of pairs of electrons between chlorine and carbon and hydrogen, respectively, necessarily involves splitting of the chlorine molecule. In the parallel reaction of molecular oxygen, however, the two odd electrons of the latter may be shared without separation of the oxygen atoms.



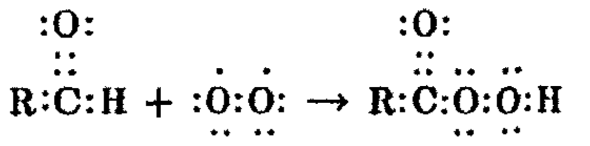
$$\mathrm{R{:}\underset{H}{\overset{H}{C}}{:}H + {:}\dot{O}{:}\dot{O}{:} \rightarrow R{:}\underset{H}{\overset{H}{C}}{:}\ddot{O}{:}\ddot{O}{:}H}$$

From the same point of view the action of oxygen on an aldehyde may be compared to the corresponding action of chlorine, which yields acid chlorides



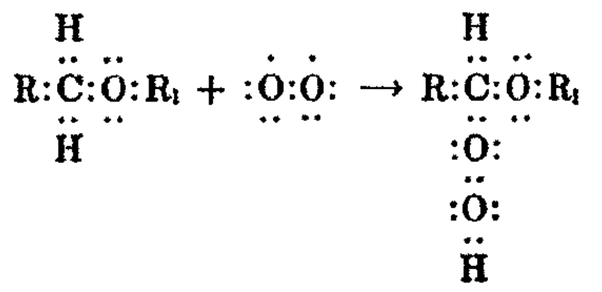
$$\mathrm{R{:}\overset{:O:}{C}{:}H + {:}\ddot{Cl}{:}\ddot{Cl}{:} \rightarrow R{:}\overset{:O:}{C}{:}\ddot{Cl}{:} + {:}\ddot{Cl}{:}H}$$

and



$$\mathrm{R{:}\overset{:O:}{C}{:}H + {:}\dot{O}{:}\dot{O}{:} \rightarrow R{:}\overset{:O:}{C}{:}\ddot{O}{:}\ddot{O}{:}H}$$

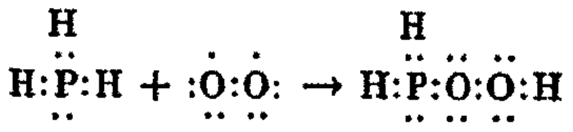
In the case of ethers the writer originally proposed the insertion of an oxygen molecule between the ether oxygen and one of the alkyl groups (17), but it now seems more probable that a C—H bond alpha to the oxygen is the point of attack.



$$\mathrm{R{:}\underset{H}{\overset{H}{C}}{:}\ddot{O}{:}R_1 + {:}\dot{O}{:}\dot{O}{:} \rightarrow R{:}\underset{\substack{:\ddot{O}: \\ :\ddot{O}: \\ H}}{\overset{H}{C}}{:}\ddot{O}{:}R_1}$$

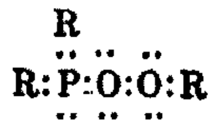
The reason for this modification is based upon the known predilection of oxygen for the α-carbon atom (13), which is parallel to the behavior of halogens (12). Chlorination of ethyl ether is known to produce the compound $CH_3CHClOCH_2CH_3$ as the primary product. In this latter case, as well as in the case of saturated hydrocarbons, cognizance is taken of the fact that thermal stability and reactivity toward a given reagent are not necessarily reciprocals of each other. If they were, we should expect halogenation of hydrocarbons to rupture a C—C linkage in preference to C—H, owing to the lower energy of the former bond. Similarly, ethers would be expected to split adjacent to the ether oxygen on halogenation.

To consider, finally, the hydrides of group V and their derivatives, it is known that chlorination of NH_3 yields NCl_3. Phosphine yields PCl_5, which probably is the inevitable addition product of chlorine with the primary PCl_3. Furthermore, there is evidence that intermediate compounds of the general formulas XH_2Cl and $XHCl_2$ are formed in the chlorination of NH_3, PH_3, and AsH_3 (19). These substitutions by chlorine may then be regarded as strictly comparable to those of the hydrocarbons. Now, if we carry further our analogy between chlorine and oxygen we should represent the first stage in the oxidation of, say, phosphine as follows:



$$H:\overset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{P}}}:H + :\dot{\underset{\cdot\cdot}{O}}:\dot{\underset{\cdot\cdot}{O}}: \rightarrow H:\overset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{P}}}:\ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{O}}:H$$

In this instance we have no evidence of such an intermediate, but in the case of triethylphosphine, as has been pointed out before, the formation of a diethyl phosphinic ester is strongly suggestive of the isomeric antecedent,



$$R:\overset{R}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{P}}}:\ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{O}}:R$$

It will be seen from the above considerations that the reactions of molecular oxygen may be placed in two categories, comparable to the addition and substitution reactions of the halogens. In both cases, however, the result is addition of oxygen; therefore unsaturation is not a necessary condition for such additions. On the contrary, the majority of additions of oxygen must be thought of as totally unrelated to unsaturation in the molecule to which the oxygen adds.

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ON THE RELATIONSHIP OF THE DISPERSION OF GOLD SOL TO THE INTENSITY OF REDUCTION AS INFLUENCED BY pH, AND A ONE-WAY EFFECT PRODUCED IN GOLD CHLORIDE BY CHANGES OF pH THROUGH CERTAIN RANGES

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That the production of gold sol is a procedure fraught with much uncertainty is admitted both by clinical pathologists, who are faced with the problem of production of colloidal gold for the Lange test, and by colloidal chemists. In a review of the many methods advanced for making gold sol, in which a great diversity of minutiae both as to technic and formulas are stressed, it was difficult to extract any generalizations that might lead to control of the process. The frequent inability of one laboratory to repeat the happy results of another would seem to indicate that we are lacking in knowledge of fundamental factors.

The following work is an attempt to uncover such fundamental factors. The work has been divided into four parts: (1) the study of the reducing agent with a constant amount of alkali; (2) and (3) the effect of variation in the amount of alkali upon reduction with the two agents commonly used by clinical pathologists, formalin and potassium oxalate; and (4) the study of an effect upon the reducibility of gold chloride immediately following alkalization, which I found at ranges below neutrality.

I. THE EFFECT OF VARIATION IN THE AMOUNT OF REDUCING AGENT UPON THE COLOR OF THE SOL, RATE OF REDUCTION, AND TEMPERATURE OF REDUCTION

Technic

In the work recorded in connection with this point, as well as in that subsequently given in this paper, a 0.01 per cent solution of chloroauric acid ($HAuCl_4 \cdot 4H_2O$), was reduced in Pyrex Erlenmeyer flasks. The stock solutions from which this dilution was obtained were made by dissolving a 1-g. ampule, as delivered by the manufacturer, in 100 cc. of distilled water, and this was assumed to be a 1 per cent solution. The secondary sodium phosphate used was "Baker's Analyzed" ($Na_2HPO_4 \cdot 12H_2O$). As the work has been carried on over a considerable length of time, the distilled water was not uniform throughout. Earlier in the work artesian well water, once distilled in a continuous block tin still, was used. Later, the water used was from the city mains, twice distilled from glass. Still later, the water was from a triple still run by steam, twice distilled from glass with permanganate (1). Under the optimum conditions each gave gold which rated as clear orange gold. Water which would not give this result was discarded. The water is undoubtedly one factor in the clarity of the sol and the criterion of a "clear orange sol" is not an absolute one. Many of the "clear orange sols" would probably not have matched one another by reflected light. The relative results, however, have been consistent.

In studying the effect of variation in the amount of reducing agent upon the color of the sol, the three reducing agents, formalin, potassium oxalate, and glucose, were used. The last reducing agent was included because it is reputed to give gold of an entirely different color from the others (6). The reducing agents were neutral and the amount of alkali used in each series was constant, but was not necessarily the same in different series. In the work recorded in table 1 the gold chloride was added to the boiling oxalate and alkali mixture; the formalin was added to the boiling gold chloride and alkali mixture; and in the series made with glucose, all reagents were mixed and then heated to boiling. With appropriate adjustment of the alkali content, however, the order in which the reagents are mixed can be varied. The series run with potassium oxalate contained 0.018 per cent of hydrated secondary sodium phosphate, that run with formalin contained 0.3 per cent, and that with glucose 0.08 per cent of phosphate. Colors of the gold sol were recorded as: blue, purple, blue-red, orange-blue (orange with a tinge of blue, especially noticeable at the angles of the flask, abbreviated to orange B), and orange. The orange-blue is darker than orange and might perhaps be called cardinal. The several

TABLE 1

Effect of variation in the amount of reducing agent used upon the color of colloidal gold

POTASSIUM OXALATE		GLUCOSE		FORMALIN	
1 per cent	Color	4 per cent	Color	1 per cent	Color
cc.		*cc.*		*cc.*	
0.50	Purple	0.0	Purple	0.05	Colorless
0.65	Orange	0.15	Orange B	0.1	Blue-red
1.0	Orange	0.2	Orange	0.2	Blue-red
2.0	Orange	0.6	Orange	0.3	Orange B
3.0	Orange B	1.0	Orange	0.4	Orange
4.0	Blue-red	3.0	Orange B	5.0	Brownish, blue-red
		5.0	Blue-red		
		7.0	Turbid blue-red		

series given in table 2 were not run simultaneously, but are a collection that have the common quality of 0.0375 per cent crystallized secondary sodium phosphate. The colors recorded are the result of comparison within the individual series. As a rule, the same run of distilled water was used in a series. The results recorded in table 3 were obtained by mixing the reagents and heating them simultaneously in a water bath.

TABLE 2

Showing that with a given degree of alkalinity there is an optimum range in the amount of reducing agent which will produce orange colloidal gold with regularity

OXALATE, 1 PER CENT	TRIAL				
	1	2	3	4	5
cc.					
0.50	Lavender	Blue	Blue	—	—
1.00	Purple	Purple	Purple	Blue-red	—
1.25	Blue-red	Blue-red	Blue-red	Blue-red	—
1.50	Blue-red	Blue-red	—	—	—
1.75	Orange	Blue-red	—	—	—
2.00	Orange	Blue-red	Orange B	Orange B	—
2.50	Orange	Orange	Orange	Orange	Orange
3.00	Orange	Orange	Orange	Orange	Orange
4.00	Orange	Orange	Orange B	Orange	Orange B
5.00	Purple	Orange B	Orange B	Orange	Orange B

TABLE 3

Temperature of formation of colloidal gold in relation to amount of reducing agent present

GLUCOSE	PHOSPHATE	GOLD CHLORIDE	TEMPERATURE
per cent	*per cent*	*per cent*	*degrees C.*
0.28	0.075	0.01	60 to 63
0.12	0.075	0.01	70 to 71
0.04	0.075	0.01	78 to 81
0.016	0.075	0.01	78 to 96
0.008	0.075	0.01	99 to 100

Results

It was found that at a suitable degree of alkalinity, if the quantity used of each of the three reducing agents is increased from an amount insufficient to reduce the gold chloride completely, a scale of colors in the gold sol may be obtained ranging through pale lavender, dark blue, purple, blue-red (due to incomplete reduction), to clear orange free from blue. With still further increase in the amount of reducing agent, the gold sol tends to be blue-red and finally, turbid. With respect to formalin this finding was early reported by Zsigmondy (15) and was recently repeated by Iwase (8). The line of demarcation between the amount of reducing agent necessary to produce clear orange sol and that which will only produce a blue-red is, for a given degree of alkalinity, well defined. The color at this limit may, however, come slowly, and repeated reheating of the medium may be required. A rather wide range exists over which orange gold sol is produced (table 1). From the work recorded in the tables and many other series not recorded, the generalization may be made that, contrary to the prevailing idea that the color of the sol is intrinsic to the reducing agent, each of the reducing agents may be made to produce the same quality of gold when appropriately handled. With each clear orange gold sols could be made, which showed less differences in color and clarity, one from another, than were produced by variation in the amount used of any one reducing agent.

~~It was found that orange gold sol was most consistently produced when~~ the amount of reducing agent approaches the minimum necessary for reduction (table 2).

These results were, on the whole, obtained with the use of secondary sodium phosphate as the reducing agent, which, because of its buffer value, gave more easily controlled results. Enough work was done with the substitution of sodium hydroxide and potassium carbonate, the two alkalizing substances heretofore used in making colloidal gold, to see that the relationship between the color of the gold sol produced and the amount of reducing agent used was independent of the alkalizing reagent.

With increase in the amount of reducing agent, the speed with which a clear orange was obtained increased and the temperature at which it could be obtained decreased (table 3).

II. THE RELATION OF ALKALINITY TO THE PRODUCTION OF GOLD SOL WITH FORMALIN

Euler and Lövgren (7) found that the velocity constant of the reaction $2HCHO \rightarrow HCOOH$ at 50°C. varies from 0.001 to 0.0929 through a range of pH 11.20 to 12.97. It would seem probable that the successful production of colloidal gold from gold chloride would be influenced by the effect of hydrogen-ion concentration upon the oxidation potential of formalin. A tabulation, incidentally introduced in an article by Wright and Kermack (14), shows that with a variation in the amount of formalin and potassium carbonate used in making colloidal gold, there was a central optimum area, as does a paper by another author who also does not relate his findings to pH. A comparison of the amounts of formalin and alkali recommended in some of the standard formulas for making colloidal gold (table 4), in which definite amounts of both reagents are stipulated, would not, however, suggest any definable relationship. Since it would appear from the preceding data that clear orange gold sol is obtained with the greatest regularity when the amount of reducing agent used is near to the least amount necessary for complete reduction of the gold chloride, a recognition of the relationship between the activity of the reducing agent and the degree of alkalinity of the medium in which reduction takes place would seem to be desirable. Following is a study of the effect of variations in the amount of alkali present upon reduction of chloroauric acid to colloidal gold by formalin using sodium hydroxide, potassium carbonate, and secondary sodium phosphate. The three alkalies were chosen in the hope that their use might shed some light upon the mechanism of the reaction, since one had no buffer value and the other two exerted their buffer effect in different ranges.

TABLE 4

Comparison of the relative amounts of formalin and potassium carbonate used in standard methods for making colloidal gold

Using 10 cc. of 1 per cent chloroauric acid in 1000 cc. of water

1 PER CENT K_2CO_3	1 PER CENT FORMALIN	TEMPERATURE OF REDUCTION	AUTHOR
cc.	*cc.*	*degrees C.*	
14 to 16	10	90 to 95	Lange
14	5	90	Levinson
14	10		Wright and Kermack
16	6	100	Cockrill
20	2.25	92 to 95	Stitt
20	10	75	Breuer

Technic

The pH determinations were made with indicators according to Clark except that double strengths of the dyes were used to avoid the masking effect of the color of the colloidal gold. The standard buffer solutions were obtained through the courtesy of Dr. Clark's laboratory. These were in intervals of 0.2. The readings were approximated to 0.1 by interpolation. All determinations of pH of gold chloride solutions were made at an interval of more than five minutes after the addition of the alkali. Samples of 50 or 100 cc. of the gold chloride solution with the alkali to be tested were brought to boiling, upon which the formalin was added with mixing by agitation. Where sodium hydroxide and secondary sodium phosphate were used, the differences between the pH of the mixtures of gold chloride and alkali at 100°C. and at room temperature were negligible. When potassium carbonate was used, however, the differences were considerable, owing to loss of carbon dioxide. Where more than a relative accuracy was desirable, as in the work recorded in table 8, the pH of the alkalized gold chloride solution was taken at boiling point. Since in the course of time, from twenty minutes to eighteen hours, gold chloride will change to orange sol with a smaller amount of formalin than is necessary to reduce it in a few minutes, a limit of five minutes was placed upon the time of reduction, in order to facilitate the work. In the more accurate work with secondary sodium phosphate, recorded in tables 7 and 8, the time interval was set between 4½ and 5 minutes. At each degree of alkalinity of the gold chloride chosen, trials were made with increasing amounts of reducing agent until a clear orange was obtained within the required time limit. This often involved a long series of determinations, especially at points of alkalinity at which the activity of the reducing agent was low. Only the greatest amount of reducing agent that did not produce orange sol, and the least amount tried that would produce it in the given time, are recorded, except in the case of data given in table 5. Other series than the ones given were run.

The amount of alkali used and the minimum amount of formalin required

Potassium carbonate. A series using potassium carbonate as the alkali is given in table 5.

It will be noted, first, that successful gold was not made by this method with 10 cc. of 1 per cent carbonate solution to 1000 cc. of 0.01 per cent chloroauric acid, which gave an initial pH of 6.0 to 6.2, nor with 20 cc., which gave, initially, a pH of 9.0. Secondly, that with 11, 12, and 15 cc. of carbonate, which with the gold chloride gave before boiling pH 6.8 to 8.4 and with which successful gold was produced, there was the same tendency, brought out in the first article in this series, to produce bluish-orange, purple, and turbid golds, as the optimum amount of reducing agent was exceeded. Thirdly, it will be noted that, as the amount of alkali was increased, the amount of formalin necessary to produce reduction in approximately five minutes decreased as follows: 11 cc. of 1 per cent carbonate to 7 cc. of 1 per cent formalin solution; 12 cc. of 1 per cent carbonate to 4 cc. of 1 per cent formalin solution; 15 cc. of carbonate to 2 cc. of 1 per cent formalin solution.

In comparing these results with the relative amounts of formalin and carbonate called for in the standard methods given in table 4 (3, 5, 9, 10, 11, 14), it is evident that considerably more formalin is stipulated in these than proved to be optimum in the above series. In the formulas which called for from 14 to 16 cc. of carbonate, the range of formalin added is 5 to 10 cc., whereas, with 15 cc. of carbonate, the optimum as given in table 5 would seem to be 2 to 2.4, 4 cc. being apparently more than the optimum as it gave a blue-orange. Of course, the temperature at which the reducing agent was added is lower in two of these formulas, being 90° to 95°C., which, as has been previously indicated, would require a greater amount of reducing agent. With 20 cc. of carbonate solution, which in the above series was unsatisfactory, Stitt (11) and Breuer (3) both succeeded in making colloidal gold. By Breuer's method the gold chloride is added to the carbonate at 75°C. immediately before reduction with formalin, and in the method given by Stitt, the gold and carbonate are added at 60°C. and are then brought up to 92° to 95°C., when the formalin is added. A decreased activity of the formalin at the lower temperatures used by Breuer and Stitt may account for their success in making colloidal gold with the larger amount of potassium carbonate.

TABLE 5

Effect of variation of potassium carbonate on amount of formalin necessary to produce colloidal gold within approximately five minutes

To 1000 cc. of 0.01 per cent chloroauric acid

1 PER CENT K_2CO_3	pH AFTER ADDING CARBONATE	1 PER CENT FORMALIN	QUALITY OF GOLD
cc.		*cc.*	
10	6.0-6.2	20	Purple
		40	Blue-red
		60	Blue-red
		100	Turbid purple
11	6.8	6	Orange in 6 minutes
		7	Orange in 7 minutes
		8	Orange in 2 minutes
		11	Orange in 2 minutes
		20	Blue-red
12	6.8	3	Did not turn in 5 minutes
		4	Orange in 5½ minutes
		5	Orange in 4 minutes
		6	Blue-red
		8	Orange in 3 minutes
		10	Blue-red
15	8.4	2	Orange in 5½ minutes
		2.4	Orange in 4 minutes
		4	Orange, slightly blue
20	9.0	1	Purple-red
		1.4	Purple-red
		3	Blue-red
		4	Blue-red

Sodium hydroxide. As sodium hydroxide is an alkaline substance of great strength and no buffer value, it is somewhat difficult to handle in such a series of reductions as the foregoing. Such series run with sodium hydroxide as the alkalizing agent showed a decrease in amount of formalin with an increase in the amount of hydroxide added. Owing, however, to the rapid increase in alkalinity caused by addition of sodium hydroxide, the range of amount of sodium hydroxide taken, through which colloidal gold could be made, was narrow. In the following, two amounts of formalin were used and the amounts of sodium hydroxide, necessary to add before reduction took place within five minutes, were determined with the initial and final pH. Results are given in table 6.

TABLE 6

Effect of variation in the amount of sodium hydroxide solution upon the activity of formalin in the reduction of chloroauric acid to colloidal gold within five minutes

To 1000 cc. of 0.01 per cent chloroauric acid

N/10 NaOH	INITIAL pH	COLLOIDAL GOLD pH	1 PER CENT FORMALIN	TIME
cc.			*cc.*	
14	8.2 to 8.4	6.6	1.4	Orange in 3¼ minutes
13.5	7.0		1.4	Did not turn in 5 minutes
12.5	7.0 to 6.8	5.6 to 5.4	4.0	Orange in 2 minutes
12.0	6.4		4.0	Did not turn in 5 minutes

TABLE 7

Showing variation in the amount of formalin required to produce colloidal gold in approximately five minutes at varying degrees of alkalinity produced by secondary sodium phosphate

To 1000 cc. of 0.01 per cent chloroauric acid

1 PER CENT $Na_2HPO_4 \cdot 12H_2O$	INITIAL pH	FINAL pH	AMOUNT OF 1 PER CENT FORMALIN ADDED	
			Did not give gold in 4½ min.	Gave gold sol in 5 minutes
cc.			*cc.*	*cc.*
300	8.2	8.2	1.5	1.6
160	7.5	7.2	1.8	2.0
120	7.3	7.0	2.4	2.5
80	7.0	6.8	5.0	5.5
70	7.0	5.4	5.0	5.5
60	6.9	5.4 to 4.8	7.0	8.0
50	6.8	5.4 to 4.8	10.0	11.0

Secondary sodium phosphate. By the use of secondary sodium phosphate, two of the difficulties which were met with the foregoing reagents were avoided; a considerable buffer value was introduced, which was not given by sodium hydroxide, and the apparent irregularities in result due to the loss of carbon dioxide from the carbonate radical were obviated. The results, given in table 7, again indicate an inverse relationship between the amount of alkali taken and the amount of formalin necessary for reduction of gold chloride to colloidal gold.

Relation between hydrogen-ion concentration and the activity of formalin in the reduction of gold chloride to colloidal gold

The foregoing data would seem to indicate clearly that with an increase in the amount of alkali used there is a decrease in the amount of formalin necessary to reduce the given solution of chloroauric acid to colloidal gold. It would seem to be a matter of interest to determine whether this increased efficiency is due to what Clark (4) calls the "quantity factor" of the alkali, or to the "intensity factor." In other words, is the hydrogen-ion concentration at some stage of the reaction the determining factor? When the results given in table 7 are plotted with respect to the initial and final pH and the amount of formalin used to effect reduction in five minutes (figure 1), the curve obtained for the initial pH is, within the errors of the technic used, a smooth one, while the graph for the final pH is irregular with re-

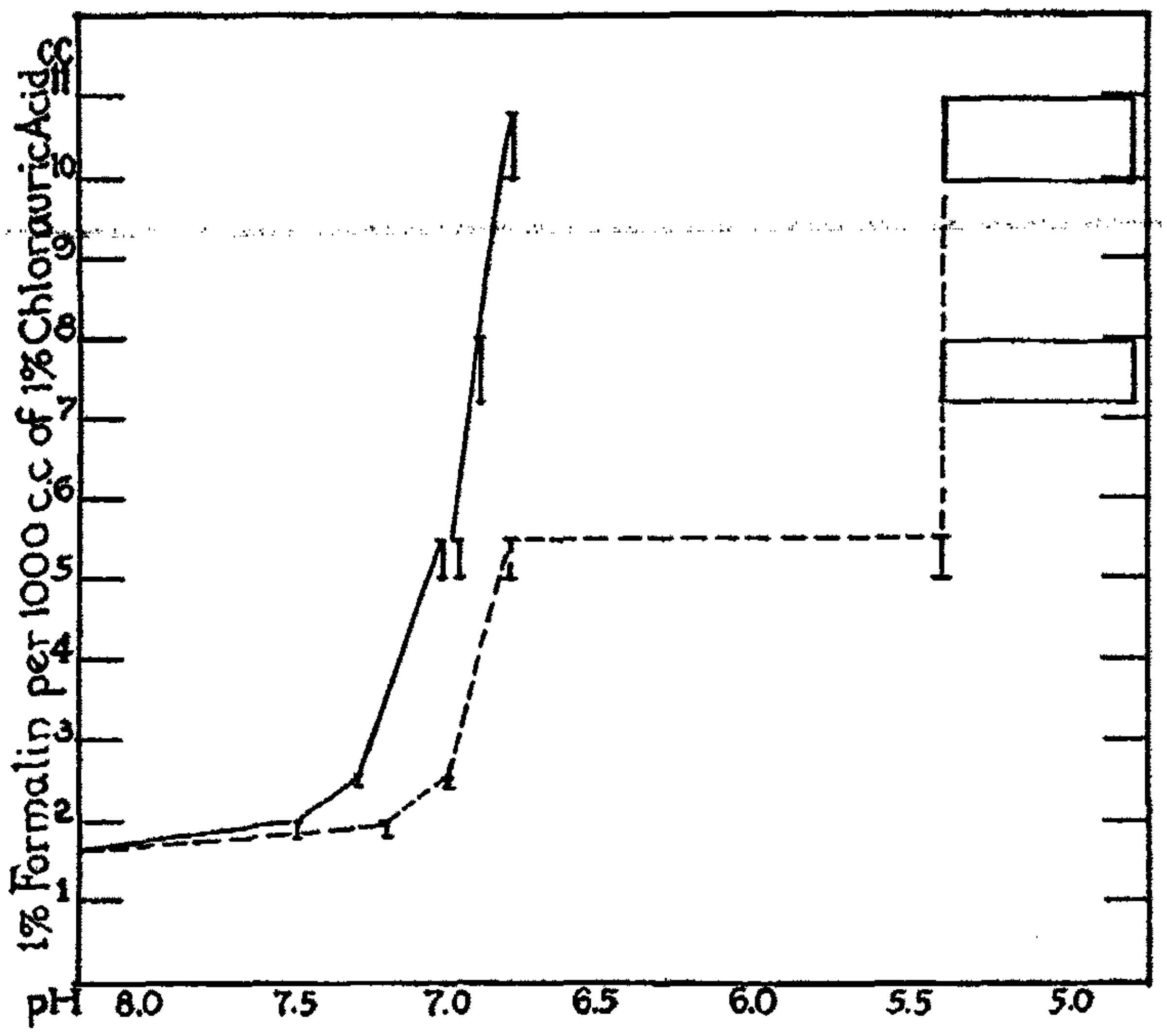

FIG. 1. THE AMOUNT OF FORMALIN PRODUCING COLLOIDAL GOLD IN FIVE MINUTES RELATED TO pH

spect to the amounts of formalin required. This suggestion, that the effective factor is the hydrogen-ion concentration at or near the beginning of the reaction, is supported when the curves obtained with secondary sodium phosphate are plotted in conjunction with the data obtained by the use of potassium carbonate and sodium hydroxide, an alkali with no buffer value, as is done in figure 2. To this graph were also added all other values obtained in which an approximate 5-minute period and 100°C. temperature was used, and in which the initial and final pH are determined. No high degree of accuracy is claimed for this comparison, as the determinations were made at wide intervals of time with unidentical solutions and the pH determinations in the case of the graph representing the results with potassium carbonate carry the inaccuracy due to loss of carbon dioxide. The points of the initial pH, however, do not fall more than pH 0.2 from their mean curve, except in one instance in which potassium carbonate was used. The points of final pH are widely scattered. If, on the other hand, the "normal" value of the three alkalies used is substituted for the pH value, curves are obtained which are independent of one another, but are situated parallel and related according to the strength of the alkali (figure 2).

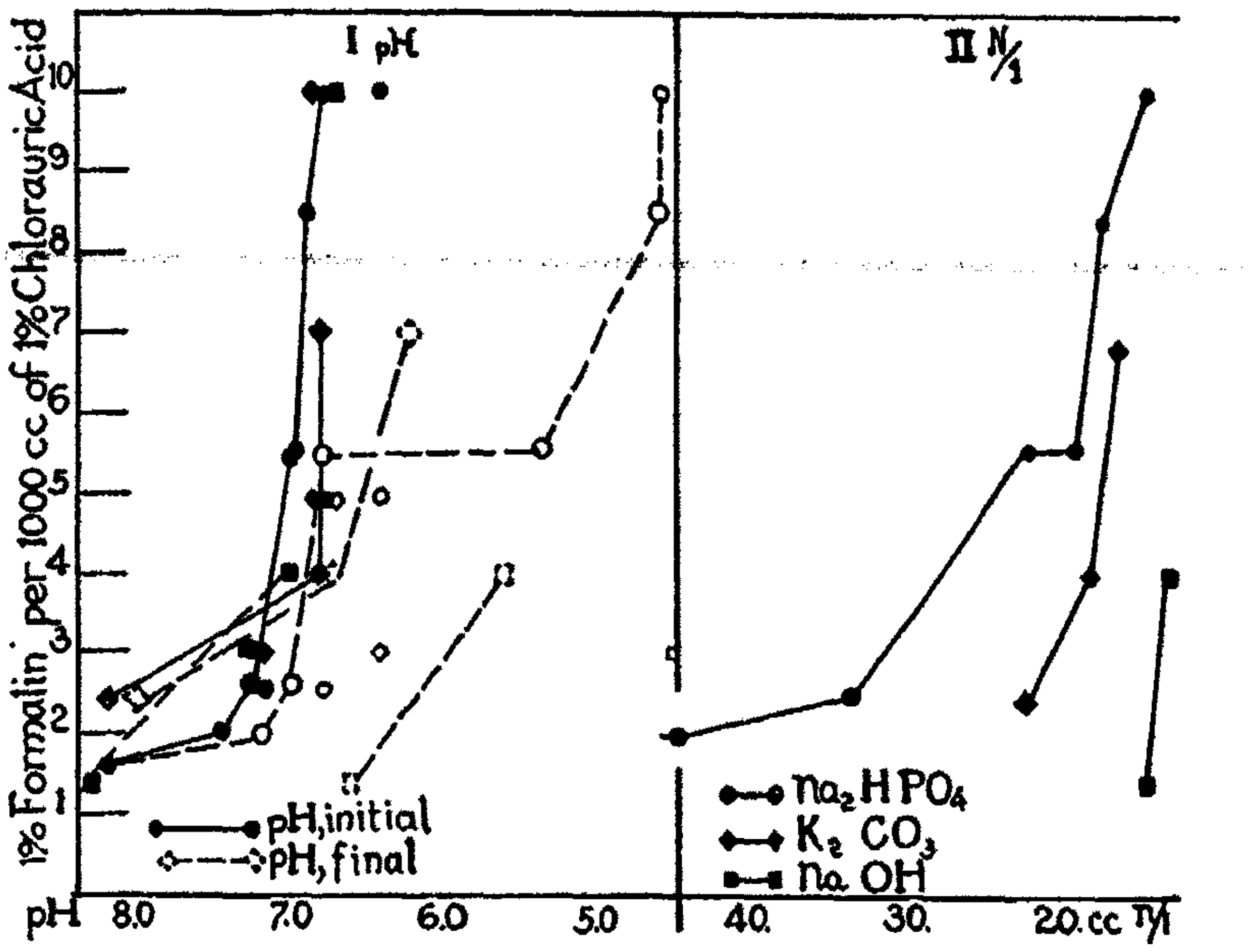

FIG. 2. THE AMOUNT OF FORMALIN PRODUCING COLLOIDAL GOLD RELATED RESPECTIVELY TO (I) THE INITIAL AND FINAL pH PRODUCED BY SECONDARY SODIUM PHOSPHATE, SODIUM HYDROXIDE, AND SODIUM CARBONATE, AND (II) THE AMOUNT OF ALKALI USED IN TERMS OF "NORMAL" VALUE

To check these results further, an attempt was made to find the minimum amount of each of the following three alkalies—sodium hydroxide, potassium carbonate, and secondary sodium phosphate—which would give orange sol with 0.14 cc., 0.3 cc., and 1.8 cc. of 1 per cent formalin to 100 cc. of gold chloride solution. With the given amount of formalin, the amount of alkali added to the gold chloride solution was increased until a clear orange sol was obtained in approximately five minutes. The pH of the gold chloride was determined at boiling point immediately before addition of the reducing agent. As NaH_2PO_4 gives a pH below the range dealt with in this series, it was held that the reaction $Na_2HPO_4 \rightarrow NaH_2PO_4$ only need be considered. A molar solution of Na_2HPO_4 has therefore been rated as a normal solution. Each of the three series was run with the same gold chloride and formalin solutions, but different solutions may have been used for different series, so the three series are only strictly comparable within themselves (table 8). These data, when taken in conjunction with those previously given, would seem to indicate that hydrogen-ion concen-

TABLE 8

Relationship of initial and final pH and combining value of alkali used to amount of formalin causing reduction in 100 cc. of 0.01 per cent chloroauric acid

AMOUNT OF 1 PER CENT FORMALIN	N/10 ALKALI		INITIAL pH	FINAL pH	TIME OF REDUCTION AND QUALITY OF GOLD
cc.		cc.			
0.14	NaOH	1.40 1.35	8.4 to 8.2 7.0	6.6	Orange gold in 3¼ minutes No reduction in 5 minutes
0.14	Na_2HPO_4	11.2 8.4	8.1 to 8.2 8.0	8.1	Orange gold in 6 minutes Orange gold in 7 minutes
0.3	NaOH	1.36 1.32	7.0 to 7.3 6.4	4.6 to 4.8	Orange Lavender
0.3	K_2CO_3	1.74 1.6	 6.6	6.8	Orange Blue-red
0.3	Na_2HPO_4	1.95 1.67	6.8 6.6	6.4	Orange Did not turn
1.0	NaOH	1.39 1.38	6.7 6.4	5.2−	Orange Blue-red
1.0	K_2CO_3	1.44 1.28	6.8 6.4	5.2−	Orange Blue-red
1.0	Na_2HPO_4	1.40 1.28	6 4 6.2	5.2−	Orange Did not turn

tration is the factor which determines the amount of formalin necessary to produce colloidal gold from gold chloride, and that it is the hydrogen-ion concentration at or near the beginning of the reaction which is the determinant.

III. RELATION OF ALKALINITY TO REDUCTION OF GOLD CHLORIDE TO COLLOIDAL GOLD BY OXALATE

What data we have on the optimum relationship between the amounts of oxalate and the alkalinity of the medium is derived from standard formulas devised for preparing gold sol for clinical use. A comparison of these indicates no relationship. According to Bacon (2), the oxalate radical increases its ability to be oxidized under the influence of sunlight with increase in acidity. As reduction with oxalate proceeds, the medium, of course, decreases in acidity, owing to destruction of the oxalic acid radical.

TABLE 9

Variation in the amount of oxalate required to reduce gold chloride to colloidal gold with variation in amount of sodium hydroxide used

N/10 NaOH	1 PER CENT POTASSIUM OXALATE	INITIAL pH	FINAL pH	QUALITY OF THE GOLD
cc.	cc.			
0.5	0.6	3.2	—	Blue-red
0.5	0.75	3.2	6.8	Brilliant orange
1.1	1.75	5.2	—	Blue-red
1.1	2.0	5.2	7.0	Brilliant orange

As the circumstances of oxalate reduction are probably the opposite of those with formalin, it seemed probable that the results with oxalate reduction would be a mirror image of those already obtained with formalin, provided that the gradient obtained with formalin was due to increase in the oxidation-reduction potential of the formalin under increased pH. Since the increase in alkalinity of the medium during oxidation of the oxalate would tend to check reduction, we would, as with formalin, expect to find a relationship between the amount of oxalate necessary for reduction in unit time and the initial pH of the medium. If, however, the gradient was due to an effect of alkalinity upon the gold chloride, it would be conceivable that results with oxalate would be similar to those obtained with formalin.

A short series run with sodium hydroxide and two with secondary sodium phosphate are given in tables 9, 10, 11. In the series given in table 10, the gold sol was made by adding the gold chloride to the boiling mixture of alkali and oxalate following the usual method. This necessitated determining the initial pH from a blank of the gold chloride and alkali. This determination probably gave the pH at which reduction commenced, since with the amounts of reducing agent used there was no evidence of reduction until after the gold salt had been added and mixed. The method, however, was considered unsatisfactory and in table 11 the oxalate was added to the hot gold chloride and phosphate mixture. With this modification the production of colloidal gold could not be carried down nearly so far into the acid side.

TABLE 10

Variation in the minimum amount of oxalate required to reduce 100 cc. of 0.01 per cent chloroauric acid to colloidal gold in approximately five minutes with variation in the amount of secondary sodium phosphate

Gold added last

1 PER CENT PHOSPHATE	1 PER CENT OXALATE	INITIAL pH	FINAL pH
cc.			
0	Did not give a clear gold	Less than 2.8	
0.5	0.7 cc. or less, more than 0.6 cc.	2.8 to 3.6	4.0
1.5	0.75 cc. or less, more than 0.7 cc.	2.8 to 3.6	6.8
2.0	0.75 cc. or less, more than 0.7 cc.	2.3 to 3.8	6.8
3.0	1.0 cc. or less, more than 0.75 cc.	5.6	6.9
4.0	1.3 cc. or less, more than 1.0 cc.	5.7	7.1
6.0	2.0 cc. or less, more than 1.8 cc.	6.8	7.3
8.0	3.0 cc. or less, more than 2.75 cc.	7.2	7.8
16.0	Did not give a clear gold	7.6	

TABLE 11

Variation in the amount of oxalate required to reduce 100 cc. of 0.01 per cent chloroauric acid to colloidal gold in approximately five minutes with variation in the amount of secondary sodium phosphate

Oxalate added last. (Series 3 in figure 3)

1 PER CENT PHOSPHATE	1 PER CENT OXALATE	INITIAL pH	FINAL pH
cc.			
4.5	1.5 cc. or less, more than 1.3 cc.	6.6	7.1
5.0	1.5 cc. or less, more than 1.3 cc.	6.6	7.2
6.0	2.0 cc. or less, more than 1.8 cc.	6.7	7.4
8.0	4.0 cc. or less, more than 3.8 cc.	7.1	7.5
12.0	5.3 cc. or less, more than 5.0 cc.	7.3	7.6
14.0	7 to 10 cc. gold purple, later changed to blue-red		

The first few series run indicated the relationship of an increase in effectiveness of the oxalate to produce gold sol with an increase in acidity of the medium. The expected relationship of the effective pH being somewhere near the beginning of the reaction, as was found to be the case with formalin, did not appear. Many series were run over a considerable length of time, during which fresh solutions had been made up with different batches of distilled water and with slight variations in technic, but apparently with discordant results. At last all series were plotted in terms of initial and final pH and the amount of oxalate which produced gold sol in 5 minutes. The amount which would not produce reduction in 5 minutes is indicated by a line attached to the initial pH, which is indicated with the solid circles. This is given in figure 3. This charting indicates that, instead of the initial pH, it is the final pH that is the uniform factor up to pH 7.3, more or less. After this the final pH is scattered and the initial pH shows a fair degree of alignment. The two points which are distinctly out of alignment belong to a series in which the technic was such that reduction began at a lower temperature and, therefore, form an exception.

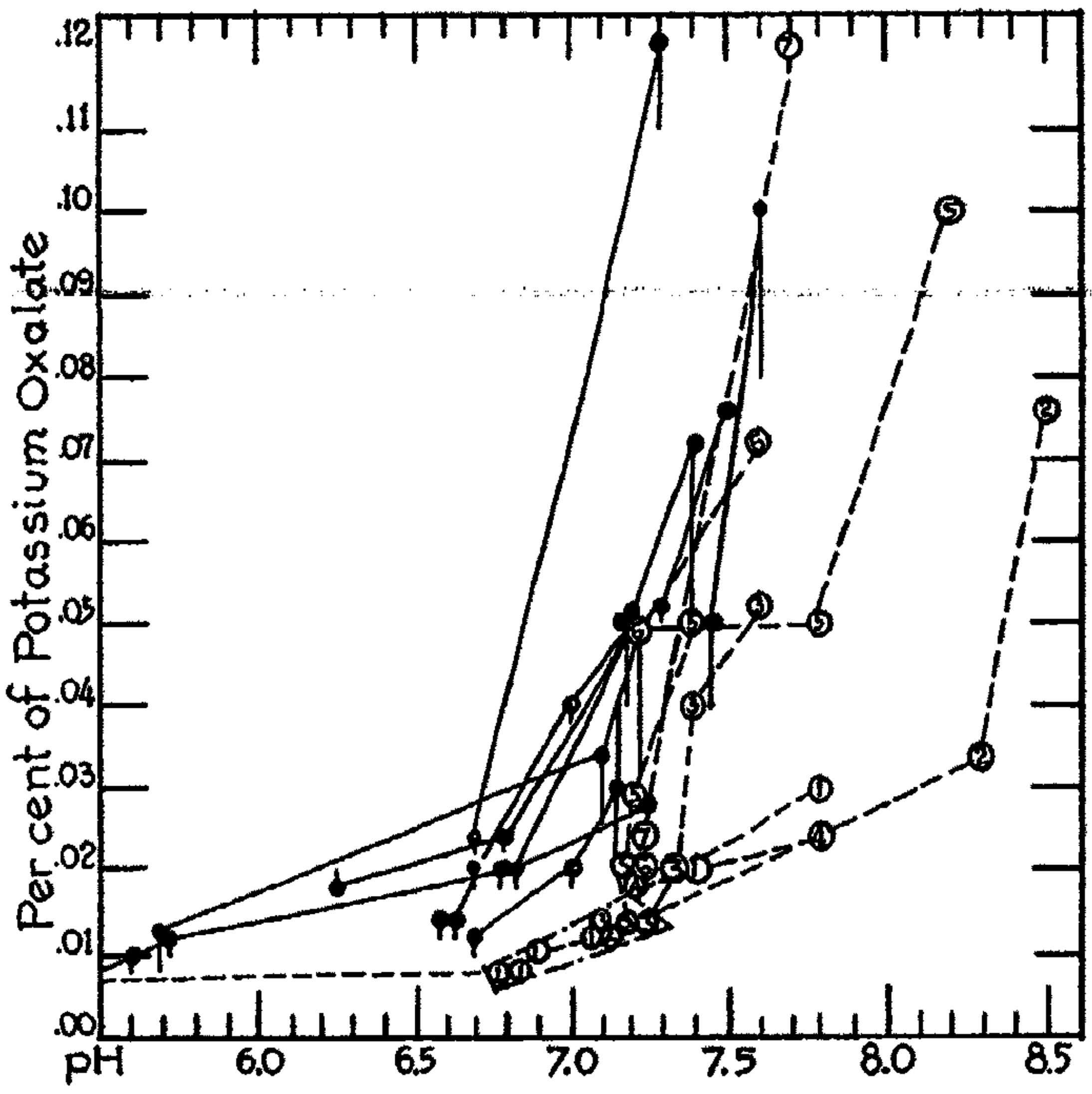

FIG. 3. SEVEN SERIES IN WHICH THE OXALATE REQUIRED FOR REDUCTION IS PLOTTED AGAINST THE INITIAL AND FINAL pH

As was done with formalin, a unit of oxalate was taken in this region in which the final pH seemed to be the determining factor; 1 cc. of 1 per cent to each 100 cc. of chloroauric acid was used, and the amount of the three alkalies—sodium hydroxide, potassium carbonate, and disodium hydrogen phosphate—was varied, until orange gold sol formed in 4½ to 5 minutes.

With phosphate, four determinations were made in which orange gold sol was formed in the required time. The amount of phosphate varied as much as 20 per cent. The initial pH was, respectively, 5.5, 5.8, 6.2, and 6.4. The final pH was in each instance pH 6.8 to 6.9. The mixtures which would not give orange gold in the required amount of time had a final pH of 7.0 or more. The results with sodium hydroxide and potassium carbonate were scattered. I do not believe that any of these pH determinations with oxalate as the reducing agent can be repeated, except with phosphate, since a certain amount of buffer value is necessary to damp the effect of loss of carbon dioxide which is formed during the reaction, and the buffer value of potassium carbonate over this range is low.

IV. A ONE-WAY EFFECT OF CHANGE OF HYDROGEN-ION CONCENTRATION UPON GOLD CHLORIDE

The rate of change of color of gold chloride upon acidification and alkalization

In the course of determining the pH of mixtures of gold chloride and secondary sodium phosphate, it was noted that there was a considerable time interval before the change of color, which occurs as acid gold chloride is made more alkaline, was finally established. This color change was studied with relation to change in alkalinity and acidity as follows.

If 2 cc. of normal hydrochloric acid are added to 100 cc. of approximately 0.01 per cent chloroauric acid, there is a well-defined increase in the depth of the yellow color which in a colorimeter shows approximately a relationship of 2:3 between the depth of the columns of acidified and unacidified fluids. When, on the other hand, alkali is added, the yellow color disappears and, finally, with the further addition of alkali, it is replaced by a bluish tinge which in turn disappears with the addition of acid, and with further addition of acid the yellow color reappears. The change in color when the solution is made alkaline is not instantaneous. There is a definite time element involved which is greater than that which would be necessary for the complete mixing of the ingredients. This is not true of the reverse color change upon the addition of acid.

To correlate the change of color and the pH, secondary sodium phosphate was added in varying amount to a 0.01 per cent solution of gold chloride. After 10 minutes, when the color change appeared to be established, a comparison was made of the resulting colors through a depth of three inches and the hydrogen-ion concentrations were read approximately with indicators. There was a gradual decrease in intensity of color with increase of pH from 3.4 to 6.4. The observer failed to discern any yellow at pH 6.6, although a faint trace was recorded for pH 6.4. When, however, the solution of gold salt was made eight times as strong, there was an appreciable amount of yellow remaining at pH 7.4. The apparent disappearance of the yellow color at the lower pH in the more dilute solution is probably real and due to a greater degree of hydrolyzation in the weaker solution under the influence of the same degree of alkalinity.

To make a rough measurement of the time taken to establish the color change, a solution was used containing 8 cc. of 1 per cent gold chloride per 100 cc. of water; to this secondary sodium phosphate was added, and the color was compared with a blank of the gold chloride solution to which no phosphate had been added. It was found that after 2 minutes the depth of color of the alkalized gold chloride was five-ninths of that of the blank, and after 3 minutes it was three-ninths of the blank. After 30 minutes there was no further change, indicating that a period between 2 and 3 minutes is required for the establishment of the change of color with an 0.08 per cent solution of gold chloride in the presence of insufficient alkali to change the color completely. This time element appeared to be of the same degree of magnitude for weaker solutions of gold chloride.

Upon attempting to see how soon the pH was established with these comparatively slow color changes, it was found that, when bromothymol blue was added to 0.08 per cent chloroauric acid solution immediately after alkalization, the color of the indicator was promptly destroyed, whereas, if a time interval of 5 minutes was allowed, the color of the indicator held for four hours or longer. As no color destruction was evident upon addition of the indicator to the gold chloride solution before adding the alkali, this destruction of the color of the indicator would seem to be due to some increased activity of the gold chloride in the process of changing from the acid to the alkaline state. This phenomenon was elicited with 0.5 cc. of the usual 0.04 per cent water solution of bromothymol blue, used in pH colorimetric determinations, to 5 cc. of the 0.08 per cent gold chloride solution, after the addition of enough phosphate solution to bring the reaction up to pH 6.8 to 7.4. It could also be demonstrated with the 0.01 per cent chloroauric acid solution, but it was necessary to use less indicator. The effect was masked by more than 0.1 cc. of indicator in 5 cc. of 0.01 per cent of gold chloride solution. Bromocresol purple, thymol blue, cresol red, and bromophenol blue were similarly destroyed, if added to the 0.08 per cent gold chloride solution immediately after alkalization. In the tubes in which the color was destroyed there gradually appeared faint pink or lavender coloration due to the formation of colloidal gold.

This retarded change of color with a concomitant instability of the salt solution upon alkalization did not occur upon acidification.

Effect of time interval after alkalization upon the formation of colloidal gold

This transitory period of sensitiveness of the gold salt to reduction after alkalization, observed in an attempt to use indicators, was studied with potassium oxalate as the reducing agent. It was examined with reference to range of pH and time interval after alkalization.

To study the range of acidity through which this effect might be demonstrated, a series of mixtures of secondary sodium phosphate and 0.01 per cent "gold chloride" was made and the solutions were allowed to stand for more than three minutes before bringing to the boiling point. At the boiling point 1 cc. of 1 per cent potassium oxalate per 100 cc. of solution was added to each. A second series was made containing the same proportions of phosphate, oxalate, and gold chloride, but in order that reduction might take place during this transitory effect of alkalization upon the gold chloride, the gold chloride was added last after the rest of the ingredients had come to the boiling point. These results are tabulated in the first part of table 12. In the course of reduction of gold chloride by potassium oxalate, the increase in alkalinity due to destruction of the oxalate radical also contributes to the alkalization of the unreduced gold chloride. The final pH, therefore, is the critical pH and it, rather than the initial pH, is given in the tabulation. In the series in which reduction took place, while, presumably, this transitory effect of the alkalization of the gold chloride held, a clear brilliant orange gold sol was produced. In the series in which there was a time interval allowed between alkalization and reduction with potassium oxalate, a clear gold solution was obtained when the final pH reached 6.8; but, as the final pH decreased, solutions of greater turbidity were obtained.

TABLE 12

Effect of the time interval after alkalization

1. With varying amount of alkali

$M/10$ Na_2HPO_4	FINAL pH	OXALATE ADDED LAST	GOLD ADDED LAST
1.2 cc. per 100	6.8	Clear orange	Clear orange
0.8 cc. per 100	6.7	Bluish red, slightly turbid	Clear orange
0.6 cc. per 100	6.5	Blue-red, turbid	Clear orange
0.4 cc. per 100	6.4	Precipitated	Clear orange

2. With variation of the time interval between addition of gold salt to alkali and reduction

TIME INTERVAL	QUALITY OF GOLD	FINAL pH
Gold added after oxalate	Clear orange	6.4
Oxalate added 5 seconds after gold	Clear orange	6.4
Oxalate added 15 seconds after gold	Slightly turbid blue-red	6.4
Oxalate added 15 seconds after gold	Blue-red, more turbid	6.4
Oxalate added 30 seconds after gold	Turbid purple	6.4
Oxalate added 1 minute after gold	Precipitated	6.4

The effect of the time interval was next tested, using the least amount of phosphate in the preceding series, 0.4 cc. of $M/10$ per 100 cc., which, when the oxalate was added to the gold salt already mixed with the phosphate, gave a heavy precipitate. The phosphate and water were brought to boiling, the gold chloride was added, and at varying intervals after the addition of the gold salt, the oxalate was added. The results are given in the second part of table 12. After an interval of 1 minute between the addition of the gold chloride and the reducing agent, the gold was heavily precipitated; after an interval of 30 seconds there was marked turbidity; with an interval of 15 seconds the turbidity was much less; and when there was approximately only a 5-second interval, a perfectly clear orange gold equal to the control was obtained.

These results cannot be attributed to inadequate mixing of the reagents, which might be a factor in causing the production of turbid gold, because the clear gold was produced after the shortest interval when the difficulties of adequate mixing were greatest. The production of the more turbid gold solution with the longer interval cannot be attributed to any effect of the alkali upon the gold chloride during the time that the mixture was kept at 100°C., as highly dispersed gold sol was produced under the same condition at a higher degree of alkalinity. The production of highly dispersed gold sol by means of potassium oxalate, when the final pH is less than 6.8, seems to be definitely associated with reduction during a short time interval after the alkalization of the gold salt.

In the series in which reduction took place after this time interval had elapsed, and in which turbid gold solution was formed, there was a distinct lag before any change of color indicating the beginning of reduction occurred, as compared with the series in which the reducing agent was added before or during this transitory effect following alkalization of the gold chloride and in which colloidal golds of high dispersion were obtained. An attempt was made to relate this effect to the surface of the container, but the results were negative.

DISCUSSION AND SUMMARY

By the introduction of the use of secondary sodium phosphate in place of sodium carbonate or sodium hydroxide, a greater degree of consistency has been developed in the production of gold sol by the methods of reduction of gold chloride with potassium oxalate and formalin. This finding would seem to be due to the greater effectiveness of secondary sodium phosphate in maintaining an optimum pH over the range through which these reducing agents function in the reduction of gold chloride to gold sol.

With the use of the three reducing agents, potassium oxalate, formalin, and glucose, it was found that, at appropriate degrees of alkalinity, colloidal orange golds of the same quality were produced, when the amount of reducing agent used did not greatly exceed the minimum amount required for reduction. With the use of an amount of reducing agent near to the minimum, consistent results were obtained. As this amount was exceeded, the sol tended to become blue-red and turbid. The color and quality of the sol would seem to depend upon the attainment of a certain intensity of reduction by the respective reducing agents and not upon the kind of reducing agent used, which is contrary to the prevailing idea (12).

By varying the amount of alkali and reducing agent it was found that the minimum amount of formalin that would give orange sol in approximately five minutes at 100°C. varied from 1.5 units to 10.0 units through a range of initial pH of 8.2 to 6.8, following a curve suggesting that obtained by Euler and Lövgren for the reaction rate of oxidation of formalin. The failure of big variations in the final pH, which occurred when sodium hydroxide and potassium carbonate were used in place of secondary sodium phosphate and through certain ranges of the phosphate alkalizer, to affect this relationship indicates that it is the pH somewhere near the beginning of the reaction which is effective.

With the use of oxalate as the reducing agent the same relation apparently holds from pH 7.6, where the effectiveness of potassium oxalate as a reducing agent begins to disappear, to approximately pH 7.2, after which some other factor appears which relates the amount of reducing agent required for reduction in a given time to the final pH of the medium. This factor would seem to be the effect of the increase in alkalinity, which the medium undergoes during the destruction of the oxalic acid radical, upon the reducibility of the gold chloride, as discussed below.

It was noted that the loss of color, which chloroauric acid undergoes when made neutral, involved a time element of approximately three minutes, while the appearance of the yellow color upon acidification was apparently instantaneous. It was found that indicator, added to the chloroauric acid immediately after adding alkali, was destroyed; whereas it was not destroyed when added after the change in color was complete, nor with the reverse process of acidifying the colorless gold chloride. It was further found that, if the gold salt is reduced with potassium oxalate immediately after the addition of alkali (secondary sodium phosphate), a highly dispersed colloidal gold can be made at a higher degree of acidity than is possible if the reducing agent is added after this transitory period of instability is passed. This entirely different behavior of the gold salt, when the reaction is changed from the acid to the alkaline side, to that which occurs when the reaction is changed from the alkaline to the acid side, is somewhat difficult to account for. I offer the following suggestion as a possible explanation of the phenomenon. I assume that the formation of $AuCl_4$ from $AuCl_3$ and HCl, or the reverse action, is a time-consuming, possibly non-ionic, process. Further, that the yellow color is produced by the presence of the radical $AuCl_3$, either as $AuCl_3$, or as part of the radical $AuCl_4$. The yellow color immediately disappears as $AuCl_3$ is hydrolyzed upon its formation with the addition of alkali, but as the formation of $AuCl_3$ from $AuCl_4$ is a time-consuming process, and, as we assume that $AuCl_3$, whether free or in the radical $AuCl_4$, produces yellow, the disappearance of the color involves appreciable time. With the reverse process of adding acid to the colorless gold salt solution, the ionization of $AuCl_3$ is suppressed by the acid with an immediate return of the yellow color, following which the slower formation of $AuCl_4$ takes place. If this were a fact, it would explain the slow loss of color upon alkalization, and the immediate return with acidification. To explain the temporary period of instability which occurs after alkalization to a pH approaching neutrality, and which does not occur after acidification, it might be assumed that in this shift involving the loss of chloride there is a readjustment of intramolecular tension, which leads to a greater sensitiveness to reduction. As $AuCl_4$ goes over into Cl and $AuCl_3$, there is a state of instability which does not occur when the reverse process takes place, and the forces are such that the radical is being built up.

The production of turbid colloidal solutions when certain optimum amounts of reducing agent are exceeded at any given degree of activity of the reducing agent as determined by the pH, and the production of turbid sols by oxalate when the activity of reduction is increased beyond a certain limit by increased acidity, and by formalin beyond a certain limit of alkalinity, would suggest some common factor. This could be expressed by Zsigmondy's hypothesis, that turbid sols result when the rate of reduction is excessive in relation to the rate of nuclei production, if we had some applicable concept of the mechanism of nuclei production.

If, for the various reasons that Weiser and Milligan (13) have advanced, von Weimarn's theory, that nuclei of gold sol result from the formation of particulate gold hydroxide, is untenable, the concept of nuclei derived from foreign particulate matter would seem to be equally ruled out by the above data. It is to me inconceivable that foreign particulate matter can explain the fact that, with the use of the same solutions and utensils, clear orange gold can consistently be made by adding potassium oxalate to the boiling solution of gold salt and phosphate when a final pH of 6.7 is attained, but that a very turbid sol is formed, presupposing few nuclei, when the phosphate is reduced so that the final pH is 6.4; while, if the same reagents are added in a different order, or with a different time relationship, a highly dispersed sol is again produced with the lesser amount of phosphate. It would seem that this phenomenon introduces the factor of the reducibility of the gold chloride into the question of nuclei formation, as there is evidence that the more highly dispersed gold was formed under conditions which produced decreased stability of the gold salt.

The finding of a relationship between the amount of formalin, or oxalate (except where the above phenomenon comes into play) required for reduction, and initial pH, together with the fact that as reduction proceeds the change of pH in the medium is such that the oxidation-reduction potential decreases, would suggest the possibility that nuclei formation is determined by the higher oxidation–reduction potential, and that, this initial reduction having taken place, more gold chloride is capable of being reduced, under the influence of the surface attraction of these nuclei, at the lower pressures of reduction produced by the less favorable degrees of alkalinity developed. The findings in the more acid ranges of oxalate reduction are not necessarily inimical to this hypothesis, but certain of my findings with other reducing agents, e.g., sodium tartrate, may be. But the above as a partial explanation will, I think, stand.

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STUDIES IN CELLULOSE DETERIORATION. I

THE AUTOXIDATION OF MANNITOL

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The deterioration of textiles has been shown by numerous investigations to be an atmospheric oxidation process, the speed of which is accelerated by light and influenced by positive and negative catalysts (3, 4, 15). None of the researches has been conducted with a view to establishing the mechanism of the oxidation process. If the proper steps to prevent the deterioration of textiles are to be taken, such knowledge of the reaction is essential. Now, in known oxidation process where prevention of the reaction by small quantities of an inhibitor is possible, the reaction has been shown to proceed by a chain mechanism. Effective inhibition can only be expected if textile deterioration be a reaction involving long chains. These principles of chain processes as applied to deterioration problems have been fully developed by Taylor (19), and will not be repeated here.

Cellulose possesses a molecule chemically similar to the molecules of carbohydrates and polyhydroxy alcohols, in that they all consist of a chain of carbon atoms with attached hydroxyl groups. Consequently, in most of its reactions cellulose behaves as a polyalcohol, a fact which is well recognized (5). Now, in the autoxidation of the analogous substances, inorganic materials exert positive accelerating effects, and Taylor has pointed out that attention should be paid to the influence of such agents in the deterioration of cellulose. The parallelism between the oxidation of cellulose and of related substances in reality seems to be very close. For example, Traube (22) showed originally that mannitol is oxidized by air in the presence of copper salt, and more recently that ferric chloride and alkali cause a great increase in the amount of oxygen absorbed by the solution (24). The oxidation of sugars by air in the presence of sodium ferropyrophosphate has been demonstrated by Spoehr (17, 18). Dhar and his collaborators (14) have many instances of induced oxidations of carbohydrates and alcohols by such inductors as ferrous hydroxide, stannous hydroxide, and sodium sulfite. With cellulose, the atmospheric oxidation proceeds slowly, but can be considerably accelerated by light. Alkali-cellulose,

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however, shows very appreciable absorption of oxygen (26), and Davidson's (6) recent extensive investigation shows the great effect of heavy metals as positive catalysts for the oxygen up-take. Apparently, also, sodium bisulfite present in pressed alkali-cellulose induces the aging of the substrate (25), much as sodium sulfite is able to induce the oxidation of carbohydrates.

The polyhydroxy alcohol, mannitol, has been chosen as typical of a complex molecule related to cellulose, and its autoxidation in the presence of various agents has been studied. The primary purpose has been to determine whether or not the oxidation proceeds by a chain mechanism, for if the oxidation of this simpler molecule proved not to be a chain reaction, then it seemed unlikely that the oxidation of cellulose and other related substances could be a chain process. Reaction rates have been measured by determining the rate of absorption of oxygen from the gas phase, and the usual criteria of chain reactions have been employed to test the character of the oxidation.

EXPERIMENTAL

Apparatus

Two types of apparatus have been used to determine the oxygen absorption rate, a shaker machine and a bubbler apparatus. The former has been described elsewhere (1). Its main parts are a Hulett gas buret (20) connected by a short length of pressure tubing to a reaction vessel which is clamped securely to a shaker device. The latter, operated by a motor-driven eccentric, makes about 260 oscillations per minute. The reaction vessel and shaker device are completely immersed in a large thermostat. To facilitate photochemical work, a hole was cut in the side of the thermostat and covered with a quartz window.

The bubbler apparatus was a modification of one used by Egerton (7); its general principles also have been incorporated in a somewhat similar apparatus by Long and Chataway (13). Its main features are a pump to circulate gas around a closed system, a reaction cell to contain the oxidizable liquid, and a gas buret to indicate the volume of oxygen absorbed.

For circulating the gases, the double action pump described by Spence and Kistiakowsky (16) was employed, with, however, the ordinary type of ground glass valves to control the direction of gas flow. The pump operated at atmospheric pressure to give a flow of about 650 cc. of gas per minute.

The reaction cell was designed to insure complete saturation of the liquid by the gas. As shown in the sketch, figure 1, a Pyrex tube, 3 × 16 cm., closed at one end, was fitted by a ground joint to a glass cap. Attached to the cap was an outlet tube, and also a tube serving for the introduction of liquids into the cell. Likewise, ring-sealed through the center of the cap, a 7-mm. Pyrex tube projected downward. At the end of this down-tube, a porous alundum plate ("A" in the sketch) was sealed through a hole drilled in its center. A hemispherical cup of Pyrex was sealed around the porous plate. The cell was attached to the apparatus so the circulating gas entered through the down-tube and was broken into fine bubbles as it was forced through the porous alundum.

The bubbler apparatus has certain advantages over the shaker machine, especially in event of gaseous oxidation products, for suitable absorbents for these can be placed in the circulating system. It is superior, also, for photochemical experiments. A vertical type mercury arc is conveniently mounted directly in front of the reaction cell, and for quantum yield work with the uranyl oxalate actinometer, the necessary auxilliary vessel is easily held in position in rear of the reaction vessel. Thus the position of the arc, reaction cell, and auxiliary vessel is readily and definitely fixed, a troublesome problem with a shaker device. The chief defect of the present bubbler apparatus was the difficulty of accurate pressure adjustment during an experiment. Such trouble was due to the rather large total volume of the system, but mainly to the pressure fluctuations resulting from the pressure head built up by the circulating pump.

FIG. 1. THE REACTION CELL

Materials

The mannite was prepared by recrystallization of a Kahlbaum's product. The solutions were made up by accurately weighing out the desired quantities and dissolving in the necessary amounts of distilled water. The sodium hydroxide solutions were prepared from a saturated solution of Merck's C. P. sodium hydroxide by diluting to the desired strengths. A solution of ferric chloride was made up to approximately 0.5 molar, and its strength determined by the iodometric method. Portions of this solution were diluted to the desired concentrations as the occasion demanded.

Procedure

In measuring the rate of oxygen up-take with the shaker machine, the general procedure was the following. The apparatus was first filled with tank oxygen, and the solutions were then added to the reaction vessel from calibrated pipettes. These solutions previously had been made up to such concentrations that, when added in the correct amounts to the reaction vessel, the final concentrations of the various components were those desired for the particular experiment. The final total volume was 25 cc. in every case. After adjustment of the pressure in the system to atmospheric, the shaker was started and volume readings, always at atmospheric pressure, taken at suitable time intervals.

With the bubbler system the procedure was necessarily different. The clean dry reaction vessel was first attached to the apparatus by its greased ground joint, and a small thermostat then raised up to immerse the vessel. By means of a Cenco Hyvac pump, the system was evacuated, and then was immediately filled with tank oxygen. The solutions were run into the cell through the attached calibrated burets, a final volume of 25 cc. being employed as with the shaker machine. After adjusting the pressure to atmospheric, the circulating pump was started. The decrease in volume at atmospheric pressure with time gave the rate of oxidation.

RESULTS

The dark reaction

Preliminary experiments showed that no oxygen was taken up by pure aqueous mannitol solutions, but that on the addition of both ferric chloride and sodium hydroxide to the mannitol, absorption of oxygen occurred at an appreciable rate. Under these conditions, no precipitation of ferric hydroxide resulted, because, as Traube and Kuhbier (23) showed, a complex ferrimannite compound formed. The research consequently resolved itself into an investigation of the effect of these inorganic materials on the oxidation rate. As pointed out in the introduction, the deterioration of cellulose is most rapid after treatment with these same agents.

The oxidation by gaseous oxygen of mannitol in the presence of ferric salt and alkali is an auto-accelerating reaction. A typical rate curve is shown in figure 2, in which cubic centimeters of oxygen (at N. T. P.) are plotted against time in minutes. The reaction rate increases with time until a fairly constant value is reached. Record may be made of the fact that when ferrous sulfate was substituted for ferric chloride, oxygen was taken up immediately on starting the shaking machine, forming a small amount of precipitate in the process. The amount of gas absorbed was about that necessary to oxidize the ferrous iron to ferric. The reaction then proceeded as in those cases where ferric salt was added originally, the same kind of slowly accelerating rate becoming apparent.

In a good many runs, especially at the lower iron and alkali concentrations, there existed an induction period, varying anywhere from ten to sixty minutes in length. During this time no absorption of oxygen was observable. The duration of the period was not the same under any given set of conditions, and consequently duplicate runs were not exactly reproducible. However, the final constant value for the rate of reaction could be checked within about 10 per cent, and therefore in comparing oxidation rates under different conditions of concentration, etc., this constant value was used as a measure.

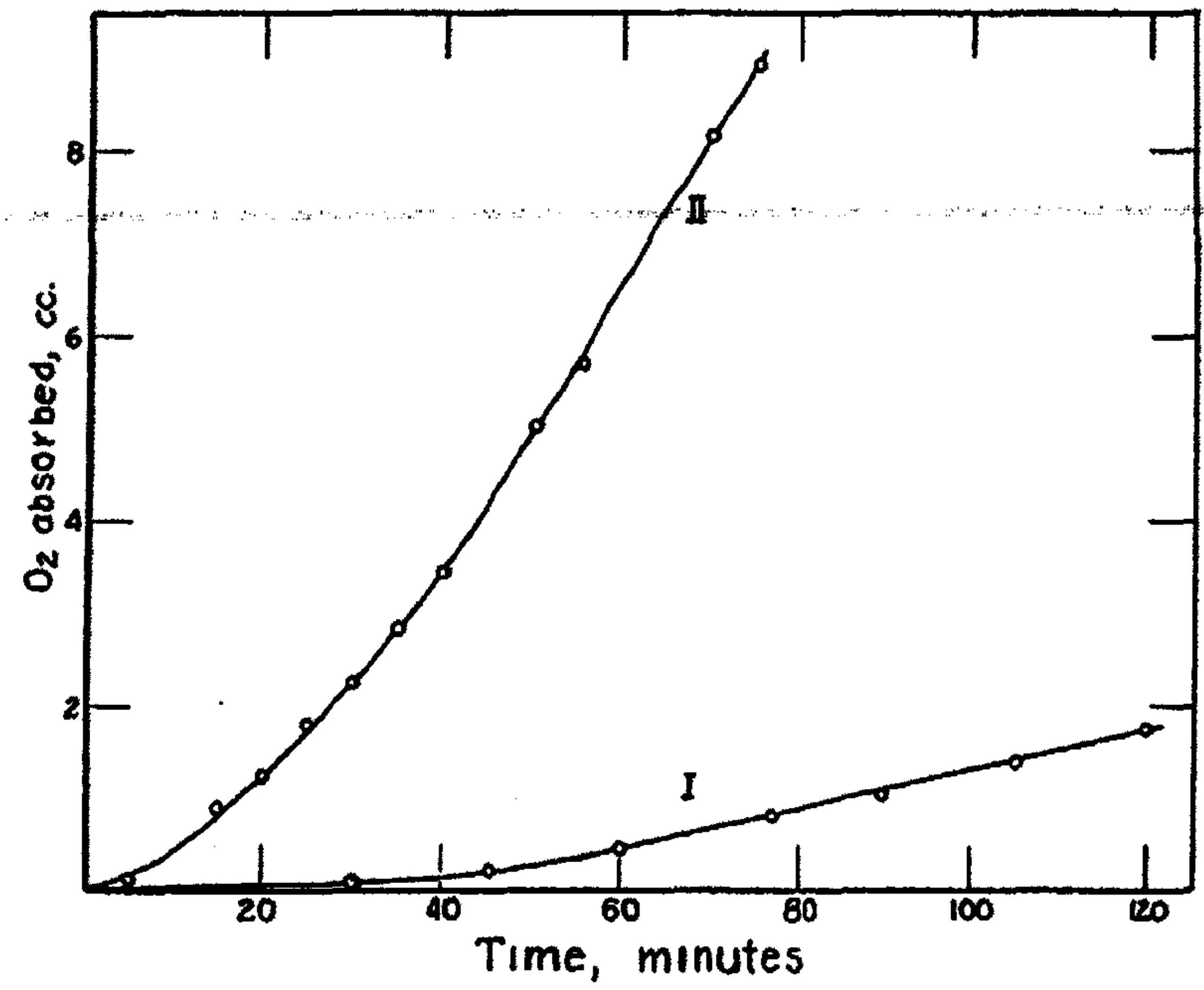

FIG. 2. TYPICAL RATE CURVE
I, The dark reaction; II, the photochemical reaction

Runs have been made to determine the effect of concentration of mannite, of sodium hydroxide, and of ferric chloride on the rate of oxidation for the dark reaction. The data are all summarized in table 1, in which are given the initial concentrations in millimoles per cubic centimeter, the type of apparatus in which the experiments were performed, the temperature of the reaction correct to ±0.05°C. and the reaction rate in cubic centimeters of oxygen (at N. T. P.) absorbed per minute by a 25-cc. sample of solution.

An examination of the data shows that with constant initial iron and alkali amounts, the oxidation rate is roughly proportional to the mannite concentration, up to about 0.1 molar; higher concentrations of mannite result in but a small increase in the rate. At constant iron and mannite but varying sodium hydroxide, the rates increase with the amounts of alkali added; at low alkali concentration they are less than to be expected for direct proportionality. This behavior very likely arises from the considerable decrease in hydroxyl ion concentration which must result with smaller initially added amounts of sodium hydroxide.

TABLE 1

The dependence of rate on concentration and temperature

MANNITE	$FeCl_3$	NaOH	APPARATUS	TEMPERATURE	REACTION RATE
millimoles per cc.	*millimoles per cc.*	*millimoles per cc.*		*degrees C.*	*cc. O_2 per minute*
0.050	0.050	1.00	Bubbler	25	0.012
0.075	0.050	1.00	Bubbler	25	0.018
0.100	0.050	1.00	Bubbler	25	0.031
0.250	0.050	1.00	Bubbler	25	0.038
0.100	0.001	1.00	Bubbler	25	0.011
0.100	0.001	1.00	Shaker	25	0.012
0.100	0.003	1.00	Bubbler	25	0.014
0.100	0.010	1.00	Bubbler	25	0.022
0.100	0.010	1.00	Shaker	25	0.023
0.100	0.020	1.00	Bubbler	25	0.028
0.100	0.050	1.00	Shaker	25	0.034
0.100	0.001	1.00	Shaker	35	0.047
0.100	0.005	1.00	Shaker	35	0.112
0.100	0.010	1.00	Shaker	35	0.131
0.100	0.050	1.00	Shaker	35	0.146
0.100	0.050	0.20	Shaker	35	0.006
0.100	0.050	0.50	Shaker	35	0.064
0.100	0.050	2.10	Shaker	35	0.220

The data depicting the variation of reaction rate with added ferric chloride, other concentrations held constant, are shown graphically in figure 3. The crossed circles represent the data obtained with the shaker machine. The effectiveness of ferric salt in increasing the reaction rate falls off abov- concentrations of about 0.005 millimole per cubic centimeter. Since come paratively large amounts of ferric salt are necessary to cause even a rather slow oxidation rate, the reaction is evidently not one in which long chains are started by a positive catalyst.

From the data given in table 1, the temperature coefficient, k_{35}/k_{25}, can be calculated at the different iron concentrations. The values vary considerably, being respectively, 4.4, 5.5, 5.4, and 4.6 for 0.001, 0.005, 0.01, and 0.05 millimoles per cubic centimeter of added ferric salt. The very high values obtained are peculiar, but their explanation is probably to be found in the temperature effect on the complex equilibria which apparently govern the oxidation.

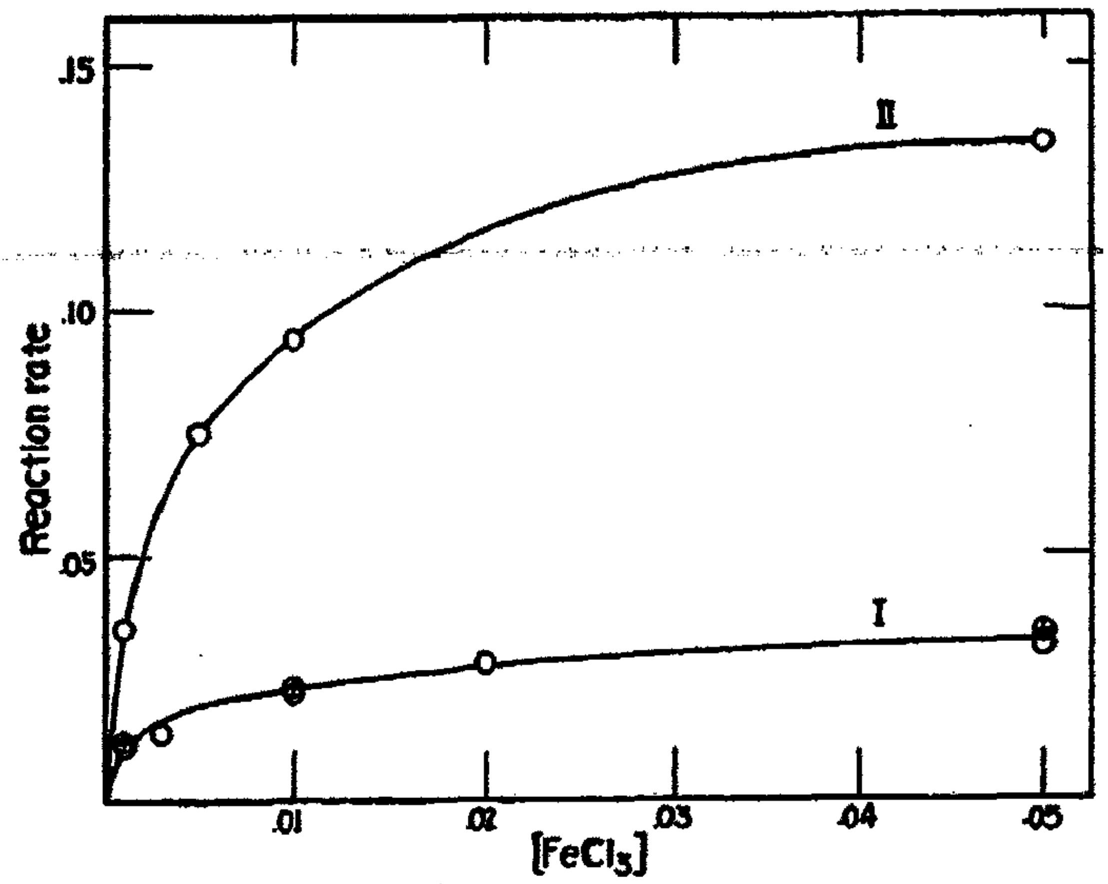

FIG. 3. THE DEPENDENCE OF REACTION RATE ON FERRIC CHLORIDE CONCENTRATION

I, the dark reaction; II, the true photochemical reaction.

Concentration rate in millimoles per cubic centimeter; reaction rate in cubic centimeters of oxygen absorbed per minute.

The photochemical reaction

The oxidation of mannitol in the presence of ferric chloride and sodium hydroxide was found to be accelerated by light. A series of photochemical experiments were carried out, using a vertical type Cooper-Hewitt mercury arc operated hot at 80 ± 1 volts and 3.0 ± 0.1 amperes as a light source. The lamp was mounted beside the reaction cell of the bubbler apparatus, but outside of the thermostat; a quartz window in the latter transmitted the light.

At the light intensity employed, the rate of the photoöxidation was increased some four or five times over the dark reaction. However, as the example plotted in figure 2 shows, the typical rate curve possessed no different features, and therefore the reaction rate was determined as in the dark oxidation.

A series of runs were made at different iron concentrations, with sodium hydroxide and mannitol concentrations held constant. The results are recorded in table 2.

In figure 3, the true photochemical rate obtained by subtracting the dark rate from the light rate, is plotted against the added ferric salt content. The type of curve obtained is approximately that which results from increased light absorption with increased solution concentration. This is borne out by absorption spectra pictures of the solutions, which show the usual shift of absorption edge to the longer wave lengths as the concentration is raised. Thus for a layer of solution 8 mm. in depth, with mannitol and sodium hydroxide at 0.10 and 1.00 millimole per cubic centimeter, respectively, complete absorption for a ferric chloride solution of 0.001 millimole per cubic centimeter begins at about 3000 A.U. and extends to shorter wave lengths. The absorption edge then shifts to longer wave lengths, lying at approximately 3950 A.U. and 4500 A.U., for 0.01 and 0.05 molar ferric chloride, respectively.

TABLE 2

The dependence of photoöxidation rate on ferric chloride concentration

NaOH, 1.00 millimole per cc.; mannitol, 0.10 millimole per cc. Arc, 80 volts, 3.0 amperes. Temperature, 25.0 ± 0.10°C.

$FeCl_3$	"LIGHT" RATE	"DARK" RATE	"TRUE LIGHT" RATE
millimoles per cc.	*cc. O_2 per minute*	*cc. O_2 per minute*	*cc. O_2 per minute*
0.001	0.046	0.011	0.035
0.005	0.095	0.020	0.075
0.010	0.117	0.023	0.094
0.050	0.167	0.033	0.134

It may be pointed out here that the absorption pictures show clearly the formation of a ferri-mannite complex in the presence of alkali. The absorption edge lies at approximately the same point for ferric chloride alone and ferric chloride with mannitol, but on addition of sodium hydroxide, the absorption commenced at a much longer wave length. Now, although a slow rate of photoöxidation was observed for mannitol and ferric chloride in the absence of alkali, the rate was much accelerated in the presence of alkali. This suggests that the ferri-mannite complexes are chiefly responsible for the increased light absorption and the consequent increased photooxidation.

Since a test of the chain character of a reaction is given by its quantum yield, a determination of this quantity was undertaken for this photochemical oxidation. Use was made of the uranyl oxalate actinometer described by Leighton and Forbes (12), a form of their "compound actinometer" being adapted. An auxiliary cell was placed behind the reaction cell of the bubbler apparatus. When both of these were filled with actinometer solution, they corresponded to cells 1 and 2 of Leighton and Forbes; when the reaction cell was filled with mannite-iron-alkali solution and the auxiliary cell with actinometer solution, they corresponded to cells 3 and 4. Calculation of the unknown quantum yield, ϕ', is given by

$$\phi' = \phi \frac{(m_3)}{(m_1)} \frac{(m_1 - m_2)}{(m_1 - m_4)}$$

where ϕ is the quantum yield of the uranyl oxalate photolysis, m_1, m_2, and m_4, the moles of oxalate photolyzed, and m_3 the moles of unknown reacting. Determination of the decrease in titer of cells 1 and 2 gave m_1 and m_2, and later, a determination of the amount of oxygen taken up and the decrease in titer of the auxiliary cell gave m_3 and m_4.

The absorption spectra pictures showed that for the depth of liquid obtaining in the cell, a solution with 0.01 millimole per cubic centimeter of ferric chloride (mannitol and sodium hydroxide concentrations as usual), commenced to absorb at about the same limit as the actinometer solution; consequently the quantum yield determination was made at this one concentration of ferric chloride. Also, since the operations were carried out in Pyrex vessels, the effective light must lie approximately between 3100 A. U. and 4800 A. U. For this region of the spectrum then, the average quantum yield of the actinometer photolysis was taken as 0.535. A sample calculation of the yield, molecules of oxygen reacting per quantum, is given:

$$\begin{array}{lclcl} \text{Light reaction} & - & \text{dark reaction} & = & \text{True reaction} \\ 0.118 & - & 0.023 & = & 0.095 \text{ cc. } O_2 \text{ per minute.} \end{array}$$

$$m_3 = \frac{0.095}{22.4} = 0.00424 \text{ millimoles } O_2 \text{ per minute.}$$

Cell 1 decreased 12.35 cc. of 0.0871 *N* $KMnO_4$ in 10 minutes.
m_1 = 0.0537 millimole per minute.

Cell 2 decreased 0.59 cc. of 0.0871 *N* $KMnO_4$ in 10 minutes.
m_2 = 0.0025 millimole per minute.

Cell 4 decreased 0.60 cc. of 0.0871 *N* $KMnO_4$ in 70 minutes.
m_4 = 0.0037 millimole per minute.

$$\phi' = 0.535 \frac{(0.00424)}{(0.0537)} \frac{(0.0537 - 0.0025)}{(0.0537 - 0.0004)}$$

$$\phi' = 0.040$$

An average value of 0.037 was found for the quantum yield. Thus, only one molecule of oxygen reacts for every 25 or 30 quanta of light absorbed by the solution. This low efficiency of the process shows that the oxidation does not occur by a chain mechanism.

The effect of inhibitors

The effect of small quantities of organic substance in slowing down or inhibiting a reaction also serves to indicate the chain character of a process. Such effect was sought in the present autoxidation, using known effective inhibitors of oxidation reactions (2). In no instance was any inhibition observed, as shown by the data collected in table 3. Such results are in complete accord with the quantum yield determination, and indicate more strongly the absence of chains in the oxidation process.

Hydroquinone acts as an excellent inhibitor of oxidation processes (2) under some conditions, but in the present reaction it was a marked accelerator. On the addition of freshly prepared hydroquinone solution to the ordinary reaction mixture, a very rapid up-take of oxygen occurred in the first few minutes of shaking. The rate gradually fell off, to proceed eventually at a constant value which, however, was greater than ordinarily attained. Undoubtedly, in this alkaline medium the hydroquinone is itself rapidly oxidized, and in the process induces the oxidation of the mannitol.

TABLE 3

The effect of inhibitors on the oxidation rate

INHIBITOR	INHIBITOR CONCENTRATION	$FeCl_3$	TEMPERATURE	REACTION RATE
	millimoles per cc.	*millimoles per cc.*	*degrees C.*	*cc. O_2 per minute*
Blank	—	0.01	25	0.023
Ethylamine	0.01	0.01	25	0.026
Phenol	0.01	0.01	25	0.022
Blank	—	0.05	35	0.145
Benzylamine	0.01	0.05	35	0.145
Ethylamine	0.01	0.05	35	0.148
Blank*	—	0.01	25	0.064
Ethylamine*	0.01	0.01	25	0.060

* Photochemical experiments.

The accelerating action of hydrogen peroxide

On the addition of hydrogen peroxide to the usual alkaline solution of mannitol and ferric chloride, the rate of absorption of oxygen by the solution was much enhanced over the usual dark rate. At the same time, the peroxide was destroyed. Thus, not only was the oxygen from the decomposing peroxide used up by the mannitol, but additional oxygen was simultaneously absorbed from the gas phase. Figure 4 shows the type of oxygen absorption-time curve obtained in the presence of peroxide; the millimoles of atmospheric oxygen absorbed are plotted against time. Also included in the figure is a plot of the millimoles of peroxide decomposed with time. This latter curve was obtained by determining the peroxide concentration existing at the end of definite time intervals, the determinations being made by the iodometric method. Since this depends on the titration with thiosulfate of the iodine liberated from potassium iodide by the peroxide, and since the ferric iron present also liberates iodine, the proper correction for the ferric iron had to be previously determined. Blank runs on iron–peroxide mixtures showed that reasonably reliable results could be obtained in this manner.

More extended runs with peroxide present showed that after twenty-five to thirty minutes of shaking the oxidation rate slowed down to continue at a constant value. This rate was about 70 per cent faster than the final value attained in the dark under the usual conditions without peroxide. Furthermore, qualitative tests showed that no peroxide existed at the end of such runs.

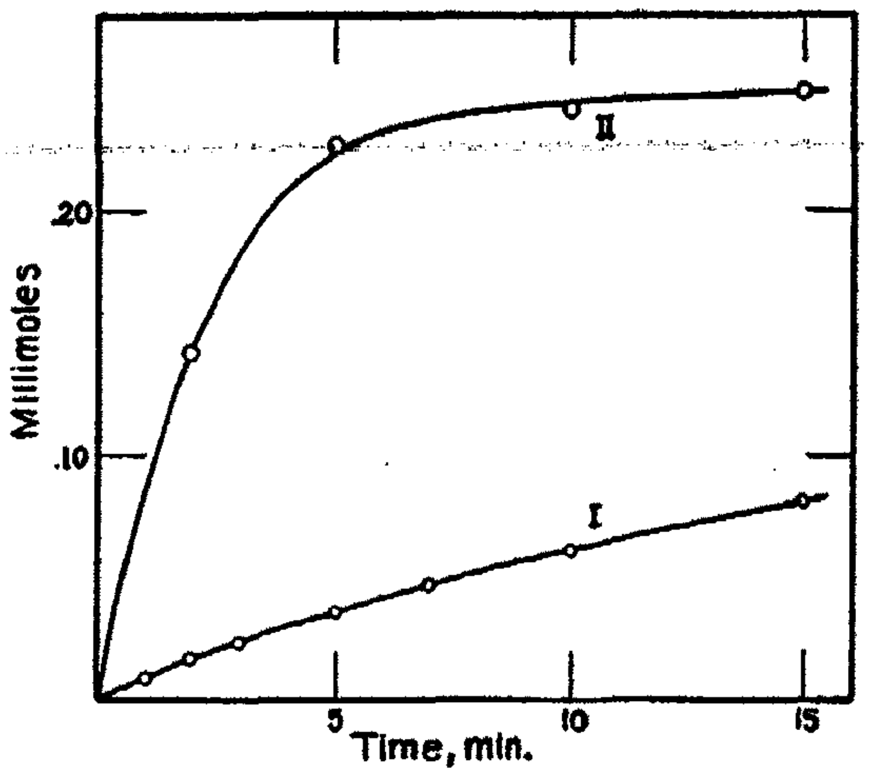

FIG. 4. RATE CURVES FOR THE OXIDATION ACCELERATED BY HYDROGEN PEROXIDE

I, millimoles of oxygen absorbed; II, millimoles of hydrogen peroxide decomposed

The initial rates of oxygen up-take in the presence of peroxide depended on the concentration of ferric chloride, as did the final rates attained after the peroxide had all disappeared. For both these rates, the plot of the dependence of rate on ferric salt concentration gave a curve of practically the same form as shown in figure 3 for the unaccelerated autoxidation. With no ferric chloride present, however, oxygen was evolved, although not quantitatively. The initial rate of oxidation was also shown to be dependent on the initial peroxide concentration, and an approximate temperature coefficient determination gave a value of 2.6 for k_{35}/k_{25}.

DISCUSSION

The experimental evidence on the oxidation of mannitol in the presence of alkali and ferric salt indicates clearly that the oxidation is not a chain reaction. The low quantum yield, the absence of inhibitory effect by added organic substances, and the evidence that the ferric salt does not function as a trace catalyst, all point to the fact that a chain process is not operative.

As to the actual mechanism of the autoxidation, but little can be said since the data are not readily amenable to kinetic treatment. The auto-accelerating type of rate curve observed cannot result from preliminary oxidation of impurities acting as inhibitors, for such an explanation holds only in event of a chain process. The auto-acceleration is explicable, however, on the assumption that products are formed during the oxidation which themselves are more easily oxidized than the original substance. On the other hand, Spoehr (17, 18) has demonstrated that glucose, and mannitol also, in the absence of oxygen were capable of reducing his sodium ferripyrophosphate catalyst to the ferrous compound, and he considered that the induction period found in the reduction reaction accounted for the induction period of the oxidation.

The dependence of the reaction rate on iron salt concentration in the manner shown in figure 3 would suggest that the oxidation process is very complicated and that complex equilibria regulate the speed of reaction. Certainly these data show definitely that the concentration of ferri-mannite complexes is not the rate controlling factor, since their concentration must be very nearly directly proportional to the amount of ferric salt initially added.

The acceleration of the oxidation by hydrogen peroxide may furnish evidence of some importance. Haber and Willstätter (9) have proposed a chain mechanism for the enzymotic oxidation of alcohols and aldehydes. They have suggested that free hydroxyl radicals served as active links in the chain, operating to produce organic radicals which were then oxidized by atmospheric oxygen. Now, the decomposition of hydrogen peroxide supposedly proceeds through a chain also involving hydroxyl radicals, and Haber and Weiss (8) have recently indicated how the chain can be started in catalytic peroxide decomposition by iron salt. Consequently, in the presence of a high concentration of hydroxyl chain propagators furnished by decomposing hydrogen peroxide, an alcohol might be expected to show increased up-take of oxygen from the gas phase. Taylor and Gould (21) have demonstrated that such is the case for the interaction of ethyl alcohol and oxygen in the presence of photodissociated peroxide. Figure 4 amply demonstrates a parallel behavior for mannitol and thermally decomposed peroxide. Now, the evidence on the autoxidation of mannitol in the presence of iron and alkali indicates that any chain theory for the oxidation of polyalcohols at least is untenable. Furthermore, whereas the Haber-Willstätter chain theory would require the up-take of at least one oxygen molecule for every hydrogen peroxide molecule decomposed, a comparison of the rates of peroxide decomposition and oxygen absorption given in figure 4 shows that initially about eight peroxide molecules decompose for every one of oxygen absorbed; only when nearly all the peroxide has disappeared is a one to one ratio approached. Thus, although a chain process for the oxidation cannot be presumed, some sort of an oxidation mechanism involving free radicals may be operative in both the accelerated and the normal oxidation. Qualitative evidence obtained from the fact that hydroquinone is an activator lends support to this view, because the oxidation of such a substance falls into the Haber-Willstätter scheme. In the present instance, the hydroquinone can operate as an accelerator by supplying an increased concentration of hydroxyl.

Turning to the deterioration of cellulose, the close parallelism which exists between the oxidation of alkali-cellulose and of alkaline mannitol solutions by atmospheric oxygen is brought out by a comparison of the experimental results reported by Davidson (6) and those presented above. The same auto-accelerating type of curve is obtained for both oxidation processes, and the dependence of the oxidation rate on iron concentration is very similar. Since the oxidation of mannitol in the presence of iron and alkali is not a chain process, this suggests that the oxidation of cellulose or alkali-cellulose does not involve a chain. Attempts to prevent the deterioration of cellulose by addition of inhibitors, which works so effectively in the retardation of the aging of rubber for example, would most probably be ineffective with cellulose. Methods which involve removing positive catalysts or the prevention of any catalytic activity by such would be more likely to yield desirable results.

Certain empirical observations are closely analogous to the acceleration of oxygen up-take caused by hydrogen peroxide in the oxidation of the alkaline mannite–iron mixtures. It is well-known, of course, that fabrics are tendered in peroxide or chlorite bleach liquors, the more rapidly if first impregnated with heavy metal (10). Likewise, the aging of alkali-cellulose is accelerated manyfold by the addition of small quantities of iron and peroxide (27). Chemical evidence cited by Kauffmann (11) indicates that in the decomposition of chlorite bleaches and in the accompanying dye bleaching, a chain mechanism might operate. Thus in the presence of activators, notably hydrogen peroxide, the chlorite bleach showed a much increased oxidation activity for dyes and other substrates such as cellulose. Presumably the peroxide served to maintain a high concentration of the chain carrier, the hydroxyl radical. However, the evidence presented in the case of the mannitol oxidation accelerated by peroxide would indicate that the oxidation of a comparable substrate such as cellulose would not be a chain process, although it could be considerably accelerated by the presence of the peroxide.

SUMMARY

1. The effect of inorganic substances, ferric chloride and sodium hydroxide, on the autoxidation of mannitol has been investigated for both the dark and the photochemical oxidations.

2. The oxidation is auto-accelerating in nature.

3. The oxidation is not a chain process. This is shown by the low quantum yield of the photo-reaction, and by the absence of any inhibition by known effective oxidation inhibitors.

4. A considerable acceleration of the rate of absorption of oxygen from the gas phase by mannitol solutions is produced by thermally decomposing hydrogen peroxide.

5. The application of the results obtained in the autoxidation of mannitol to problems of oxidation of related substances, particularly to the deterioration of cellulose and to bleaching processes, is indicated.

The author wishes to express his sincere thanks to Professor Hugh S. Taylor, who suggested this line of work, and who served for the Textile Foundation as director of the research. Without his continued aid and interest the problem could not have been carried through to its present stage of development.

Grateful acknowledgment is made to the Textile Foundation for the fellowship under which this work was carried out.

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THE OXIDATION OF MANNITOL BY OXYGEN PHOTOSENSITIZED BY HYDROGEN PEROXIDE

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In a previous paper (3) on the autoxidation of mannitol in the presence of ferric chloride and sodium hydroxide, evidence was presented to show that the oxidation was not a chain process. The importance of this finding to problems of oxidation of related substances, particularly in connection with the deterioration of cellulose, was indicated. Furthermore, its bearing on the Haber-Willstätter (2) chain theory of alcohol and aldehyde oxidation was emphasized. It was pointed out that, although in the case of polyalcohols a chain theory was unnecessary, experiments in which the rate of oxygen up-take was markedly accelerated by thermally decomposing hydrogen peroxide suggested that a mechanism of the Haber-Willstätter type might be applicable.

Taylor and Gould (4) have recently shown that ethyl alcohol interacts with gaseous oxygen when photosensitized by hydrogen peroxide. The induction of oxidation in this manner is convenient and efficient, as compared with methods involving thermal peroxide decomposition, and should yield results of a quantitative nature.

For their particular oxidation, Taylor and Gould established the existence of short chains, and concluded that the experimental results were compatible with the ideas of Haber and Willstätter. The photosensitization may be formulated in the following manner:

$$\mathrm{H_2O_2} + h\nu = 2\mathrm{OH} \qquad \text{(a)}$$

$$\mathrm{OH} + \mathrm{RCH_2OH} = \mathrm{R}\overset{\cdot\,/}{\mathrm{C}}\mathrm{H(OH)} + \mathrm{H_2O} \qquad \text{(b)}$$

$$\mathrm{RCH_2OH} + \mathrm{R}\overset{/}{\mathrm{C}}\mathrm{H(OH)} + \mathrm{O_2} = 2\mathrm{RCHO} + \mathrm{OH} + \mathrm{H_2O} \qquad \text{(c)}$$

On the basis of the above scheme, each hydrogen peroxide molecule decomposed by light should cause the absorption of not less than two oxygen molecules. Many more will react if a long chain follows the initial step. A comparison of the simultaneous rates of peroxide decomposition and

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oxygen absorption therefore should give some idea as to the chain length involved in the reaction. Only at the higher concentrations of the alcohol will approach be made to the true chain length, as then the probability is greatest that each hydroxyl radical will start an oxidation step. In such a range, the observed reaction rates should be independent of the alcohol concentration. With these considerations in mind, an examination of the oxidation of aqueous mannitol solutions photosensitized by hydrogen peroxide has been made over a range of both peroxide and mannitol concentration.

EXPERIMENTAL

The shaking machine used previously in the autoxidation of mannitol, and also used by Taylor and Gould, was employed in these experiments. A quartz reaction vessel was available, and a quartz window was fitted in the thermostat in which the shaker device carrying the reaction vessel was immersed. The thermostat was regulated at 25°C. ± 0.05°C. Two vertical type Cooper-Hewitt mercury arcs placed side by side in front of the quartz window served as the source of light. They were each operated at 70 ± 1 volts and 4.0 ± 0.1 amperes.

The mannitol solutions were made up by accurately weighing out samples of a recrystallized Eastman product and dissolving in the required amounts of distilled water. The hydrogen peroxide solutions were obtained by diluting Merck's Superoxol to the desired concentrations.

In carrying out a run, the general procedure was to fill the apparatus with oxygen, and then introduce the solutions from calibrated pipettes. The added solutions were of such concentrations that the sample in the reaction vessel possessed the concentrations desired for the particular experiment, and also totaled 25 cc. in final volume in all cases. After a 10-minute period of shaking in the dark, the reaction was initiated by removing a shutter from before the window. Runs of ten minutes in length were made in most cases. The rate of oxygen absorption was followed by observing the decrease in oxygen volume at constant pressure.

At the end of the run, determination of the acid produced was made by titration of the total contents of the reaction vessel with 0.1 *N* sodium hydroxide with phenolphthalein indicator. This titration was carried out as rapidly as possible, and the hydrogen peroxide was then determined by the iodometric method. Appropriate control analyses were made in all cases.

RESULTS

Preliminary experiments showed that on illumination with a mercury arc, an aqueous solution of mannitol and hydrogen peroxide absorbed oxygen from the gas phase. No reaction whatever was observed when the mixture was shaken in the dark for periods of ten to thirty minutes, and, also, no oxygen absorption persisted in the dark after cutting off the light. Mannitol alone did not take up observable amounts of oxygen when rayed ten to thirty minutes under existing conditions. Such behavior is to be expected from the fact that absorption spectra pictures of aqueous mannitol solutions indicated that even weak absorption did not take place for light of wave length longer than about 2300 A.U.

A series of runs was made to determine the variation of both the oxygen absorption and the peroxide decomposition with change in mannitol concentration. This was done for each of three initial peroxide concentrations. Also, the rate of photolysis of pure aqueous hydrogen peroxide solutions was followed by measuring the production of oxygen. This was possible because the apparatus is equally well adapted for observing oxygen absorption or evolution.

Hydrogen peroxide photolysis

In a given experiment, the rate of photolysis of pure aqueous hydrogen peroxide solutions did not quite follow the equation of a first order reaction. When approximately 50 per cent of the peroxide had disappeared, the calculated constant had drifted to a value about 20 per cent greater than the initial. The decomposition rate was thus not exactly directly proportional to the initial peroxide concentration.

The value chosen for the rate of peroxide photolysis was that given by the oxygen evolution (at N. T. P.) observed during the first two minutes, at the end of which time the concentration was still about 85 per cent of the original. The rate so obtained was expressed in millimoles of peroxide decomposed per minute for 25 cc. of solution. In view of the fact that duplicate runs agreed only within 15 per cent, this method of choosing the initial rate of reaction provided a value within the limit of accuracy of the experiments.

Photosensitized mannitol oxidation

For a typical experiment in which oxygen was taken up by an illuminated mannitol-peroxide mixture, a plot of the cubic centimeters of oxygen absorbed against time gave an exact straight line. Although most of the individual experiments were but ten minutes long, tests indicated that this linear relationship extended for thirty minutes or more in almost every case. The slope of the straight line obtained from the graph was taken as the rate of reaction, and expressed as cubic centimeters (at N. T. P.) of oxygen absorbed per minute for a 25-cc. sample.

The rate of photodecomposition of hydrogen peroxide in the presence of mannitol was obtained simply by determining the amount disappearing in a 10-minute run, dividing this by ten, and expressing the result as millimoles of peroxide decomposed per minute. This procedure is justified by the fact that in every case, the peroxide concentration at the end of ten minutes was still over 78 per cent of the initial, so the rate can be taken essentially as linear for such a period. In fact, determinations at the higher mannitol concentrations showed that this linear behavior held over a period as long as thirty minutes.

TABLE 1

The dependence of reaction rate on concentration

HYDROGEN PEROXIDE	MANNITOL	I/I_0	RATE OF REACTION				RATIO OF RATE OF O_2 ABSORBED TO H_2O_2 DECOMPOSED
			O_2 absorption		H_2O_2 decomposition	Acid formation	
millimoles per cc.	*millimoles per cc.*		*cc. per minute*	*millimoles per minute*	*millimoles per minute*	*millimoles per minute*	
0.0110	0.0	1.09	0.250*	0.0114*	0.0227	—	—
0.0110	0.001	1.09	0.052	0.0023	0.0059	0.0043	0.4
0.0110	0.005	1.09	0.082	0.0037	0.0044	0.0037	0.8
0.0110	0.010	1.09	0.092	0.0041	0.0042	0.0034	1.0
0.0110	0.10	1.09	0.111	0.0049	0.0025	0.0021	1.9
0.0108	0.10	1.09	0.110	0.0049	0.0021	0.0024	2.2
0.0256	0.00	1.07	0.500*	0.0223*	0.0447	—	—
0.0269	0.00	1.07	—	—	0.0410	—	—
0.0266	0.001	1.07	0.042	0.0019	0.0120	0.0068	0.1
0.0271	0.005	1.07	0.141	0.0063	0.0096	0.0071	0.7
0.0266	0.010	1.07	0.162	0.0072	0.0075	0.0064	1.0
0.0271	0.050	1.07	0.208	0.0093	0.0052	0.0054	1.8
0.0266	0.10	1.07	0.208	0.0093	0.0050	0.0053	1.9
0.0271	0.10	1.07	0.208	0.0093	0.0045	0.0051	2.0
0.0522	0.00	1.00	—	—	0.0974	—	—
0.0529	0.00	1.00	1.015*	0.0453*	0.0907	—	—
0.0525	0.001	1.00	0.125*	0.0055*	0.0234	0.0076	—
0.0514	0.005	1.00	0.151	0.0067	0.0166	0.0127	0.4
0.0527	0.010	1.00	0.213	0.0095	0.0154	0.0117	0.6
0.0515	0.050	1.00	0.293	0.0131	0.0100	0.0094	1.3
0.0496	0.10	1.09	0.298	0.0133	0.0087	0.0084	1.5
0.0521	0.10	1.07	0.302	0.0135	0.0088	0.0086	1.5
0.0527	0.10	1.00	0.302	0.0135	0.0095	0.0089	1.6
0.0518	0.10	1.00	0.296	0.0132	0.0082	0.0087	1.6

* In these experiments, oxygen was evolved at this rate.

The rate of formation of acid was also taken as linear for a 10-minute period. The amount resulting in that time was ascertained and the rate was determined as millimoles formed per minute. In longer runs the acid was produced in amounts greater than a linear rate would provide.

The reproducibility of the rates of oxygen up-take was good, check runs agreeing within 2 to 3 per cent. The rates of peroxide decomposition and acid formation were not so readily checked, however, variations of 10 per cent occurring between duplicates.

In order to check the light intensity for each series of runs at a given peroxide concentration, a reference run was always made under the standard conditions of 0.052 millimole per cubic centimeter of peroxide and 0.10 millimole per cubic centimeter of mannitol. The runs of the several series could then be related. Variations in the light intensity amounted to no more than 10 per cent.

The rates of reaction as determined according to the methods outlined above are recorded in table 1, and the other pertinent data are also given. (The figures in the column I/I_0 are the factors obtained from the reference runs made to check the light intensity. The rates actually observed have been divided by these factors, and the quotients so obtained are the values recorded in the table as rates of reaction.)

DISCUSSION

Examination of the data of the table indicates that at a constant initial peroxide concentration, variation of the mannitol concentration causes an increase in the rate of absorption of oxygen and a simultaneous decrease in the rate of decomposition of peroxide. As a case in point, the data obtained with a peroxide concentration of 0.027 millimole per cubic centimeter are plotted in figure 1. This graph shows the dependence of both the oxygen absorption rate and the peroxide decomposition rate, respectively, on the initial mannite concentration. At zero mannite content, oxygen is evolved in amount equivalent to the peroxide decomposed; then, at comparatively low mannitol concentrations, oxygen absorption commences while peroxide destruction is inhibited. In some cases, as much as eight- or nine-fold inhibition is observed. The graph also makes apparent the important fact that at sufficiently high mannite concentrations the rates of both the peroxide decomposition and oxygen absorption are independent of the mannite concentration.

This behavior is practically repeated with the two other peroxide concentrations used. Taking the values obtained with the mannite concentration of 0.10 millimole per cubic centimeter, a plot is made in figure 2 of the dependence of the oxygen absorption rate and the peroxide decomposition rate on the initial peroxide content. The rate of disappearance of peroxide appears as directly proportional to the amount of peroxide initially present. The same is not true, however, for the rate of oxygen absorption, as the oxygen up-take at the higher peroxide concentrations is less than that necessary for direct proportionality. Such conduct can be explained on the basis that at sufficiently high peroxide content the peroxide is not completely efficient in sensitizing the oxidation. Some of the peroxide may be decomposed with evolution of oxygen, thereby causing an apparently slower rate of oxygen up-take.

Emphasis has been laid on the important fact that at sufficiently high mannite content, the rates of peroxide decomposition and oxygen absorption become independent of the mannitol concentration. As pointed out in the introductory paragraphs, the existence of such a range suggests that very nearly every photodecomposed peroxide molecule starts off an oxidation process, and therefore comparison of the two rates of reaction obtaining in this region of mannite concentration should serve as a measure of the chain length. The figures for the ratio of the rates of oxygen absorption to peroxide decomposition have been calculated over the whole range and are recorded in table 1. These bring out the fact that a maximum of two oxygen molecules is absorbed for each peroxide molecule decomposed, this maximum being attained under the most favorable conditions.

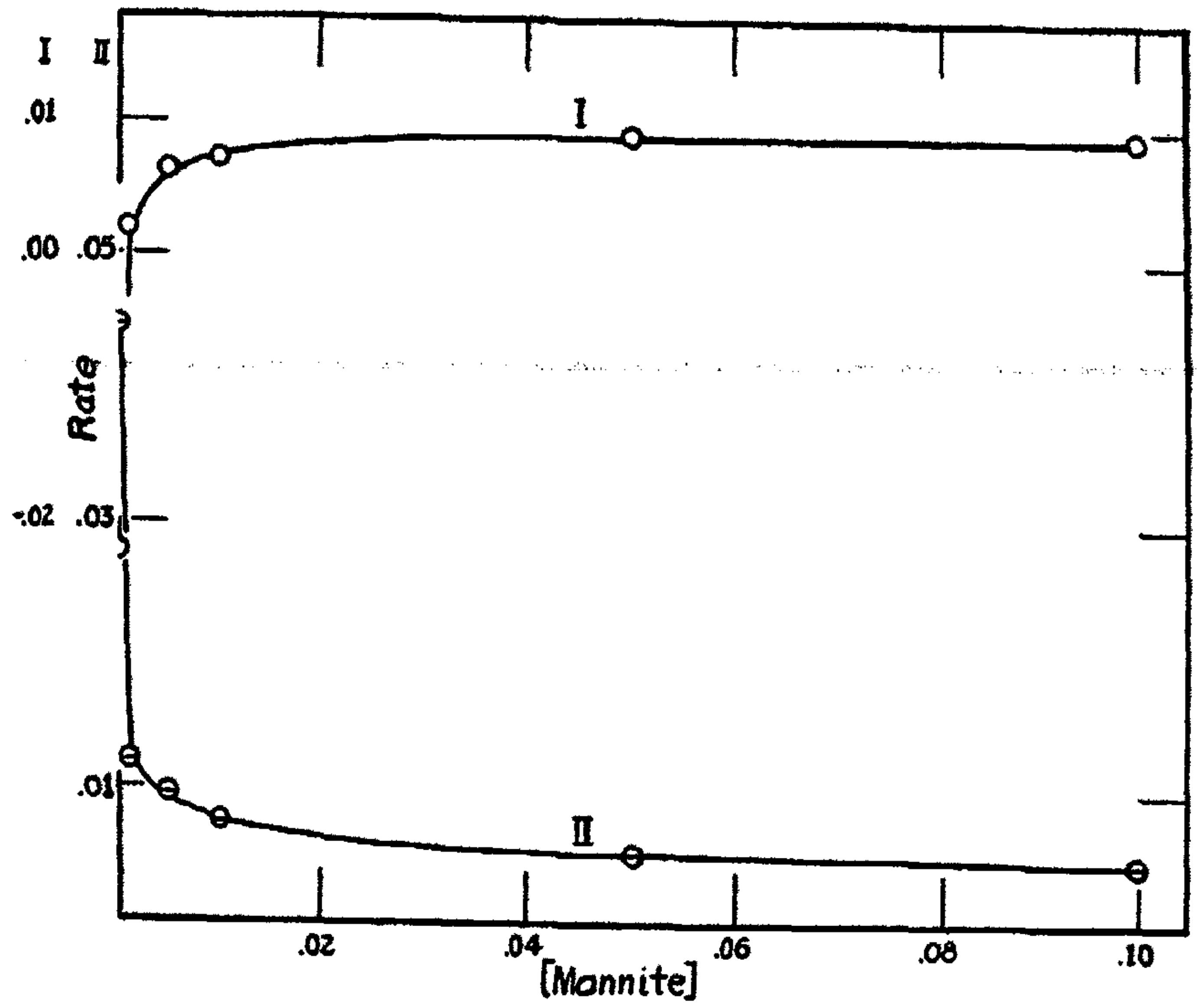

FIG. 1. THE DEPENDENCE OF REACTION RATE ON MANNITE CONCENTRATION

Concentration in millimoles per cubic centimeter; reaction rates in millimoles per minute.

I. Oxygen absorption. The negative coördinates indicate oxygen evolution.

II. Hydrogen peroxide decomposition.

The optimum ratio of two oxygen molecules absorbed for each peroxide molecule decomposed indicates that chains are not set up in the oxidation process. On the accepted basis (5) that photodissociation of a peroxide molecule results in two hydroxyl radicals, each hydroxyl must induce the absorption of but one oxygen molecule. The scheme previously given in the introduction would indicate at least a one to one ratio of hydroxyl produced to oxygen absorbed, and suggests that a much higher ratio is possible. The magnitude of the ratio will depend, of course, on the relative efficiencies of the chain propagating process to the various possible chain breaking reactions, and low ratios are not impossible. Therefore, although the evidence indicates that for the oxidation of polyalcohols a chain mechanism is unnecessary, the original scheme for the photosensitization cannot be excluded. The fact that photodissociation of peroxide causes absorption of oxygen is explicable on a mechanism of the Haber-Willstätter type involving hydroxyl.

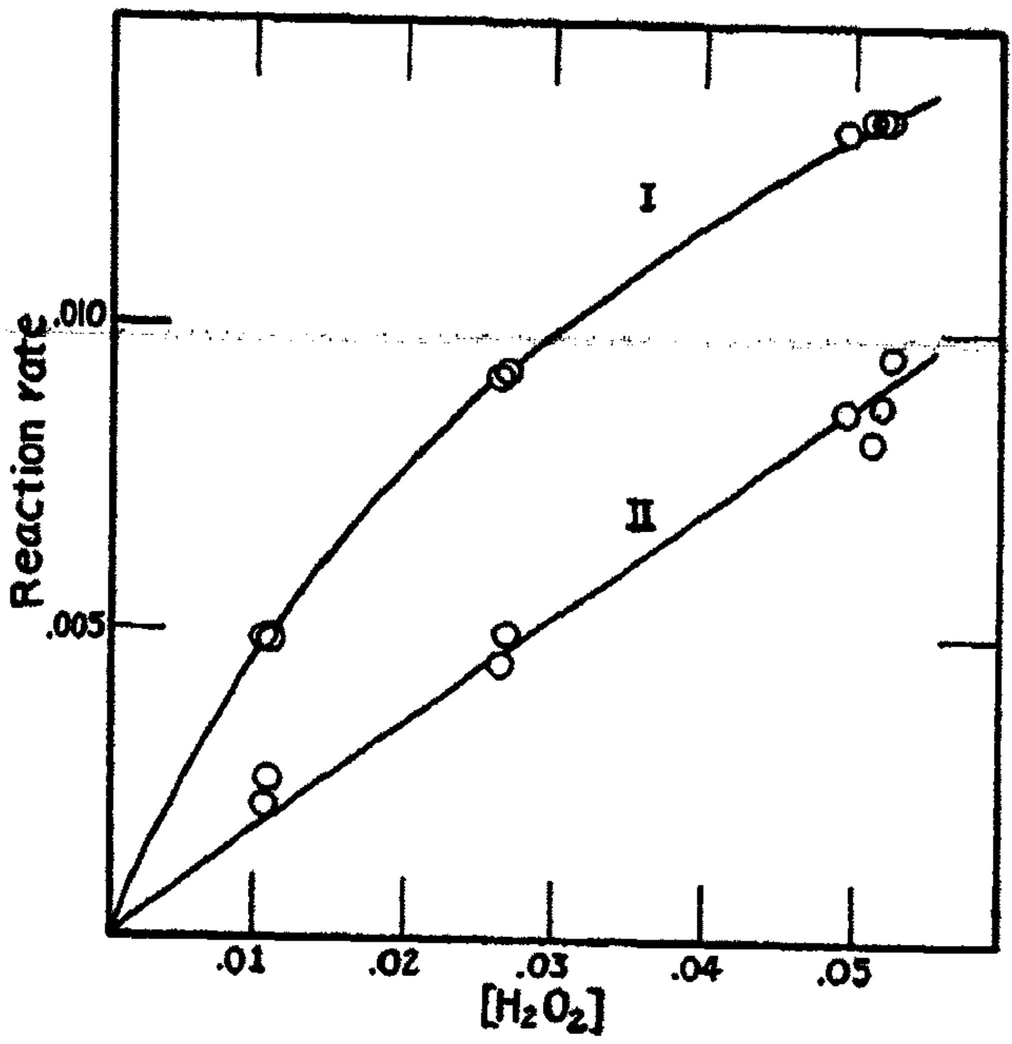

FIG. 2. THE DEPENDENCE OF REACTION RATE ON HYDROGEN PEROXIDE CONCENTRATION

Concentration in millimoles per cubic centimeter; reaction rates in millimoles per minute.

I. Oxygen absorption. II. Hydrogen peroxide decomposition.

The formation of acid during the oxidation of the mannitol occurs in a reasonable manner. At the low mannite concentrations, very nearly all of the oxygen and peroxide used up appears as acid formed. Furthermore, the indications are that oxidation of both primary alcohol groups of the mannite molecule takes place, for slightly less than two moles of acid are formed for each mole of polyalcohol originally present. In the high mannitol concentration range, the amount of oxygen used up cannot be accounted for quantitatively as acid. Only partial oxidation to an aldehyde stage must occur in such cases. This is to be expected, as the concentration relationships favor the probability of oxidation of a new polyalcohol molecule rather than of one already partially oxidized. However, the fact that some acid is formed, as well as the observations at low mannite concentration, indicate that the specific oxidation rate of the first reaction product is greater than that of the mannitol itself.

The fact that oxidation proceeds to an acid does not affect in any way the conclusion drawn concerning the chain length in the reaction. The aldehyde oxidation to the acid stage was supposed by Haber and Willstätter to proceed in the same manner as the alcohol oxidation, and the important point is that each peroxide molecule induces the absorption of only two oxygen molecules, whether these go to oxidize aldehyde or alcohol.

Several runs were made in an attempt to determine the effect of an inhibitor on the photosensitized oxygen absorption. Ethylamine was the only substance tried; it has been shown to be a very efficient inhibitor for the photolysis of peroxide (1) and at the same time exhibits no "internal light filter" effects. Experiments were performed with hydrogen peroxide and mannitol concentrations of 0.052 and 0.10 millimole per cubic centimeter, respectively.

At an ethylamine concentration of 0.01 millimole per cubic centimeter, the oxygen absorption rate was decreased, for example, from the normal value of 0.302 cc. per minute to 0.254 cc. per minute; at the same time the peroxide decomposition rate was increased from 0.0092 millimole per minute to 0.180 millimole per minute. These figures represent a 16 per cent decrease and almost a 100 per cent increase, respectively. Similar results, but of lesser magnitude, were obtained at an ethylamine concentration of about 0.002 millimole per cubic centimeter.

The reason for the acceleration in the peroxide decomposition rate is not clear. The fact is known that ethylamine increases the thermal decomposition, probably because the solution is rendered alkaline, and a similar effect may enter here. In any event, this acceleration does not result in efficient sensitization of the mannitol to oxygen absorption. In fact, destruction of the peroxide with partial evolution of oxygen must occur, rendering an apparently slower oxygen absorption rate. These effects with ethylamine as an inhibitor do not, therefore, influence the previous result, namely, that reaction chains are not present in the oxidation.

SUMMARY

1. The oxidation of aqueous mannitol solutions by oxygen, photosensitized by hydrogen peroxide, has been investigated over a range of mannitol and peroxide concentrations.

2. At sufficiently high mannite concentrations, the rates of both the oxygen absorption and peroxide decomposition become independent of the mannite concentration.

3. In such a concentration range, but two oxygen molecules are absorbed by the mannitol solution for each peroxide molecule disappearing.

4. It follows that the photosensitized oxidation is not a chain process.

5. The bearing of the observations on the Haber-Willstätter theory of alcohol and aldehyde oxidation is discussed.

The author wishes to express his sincere thanks to Professor Hugh S. Taylor for his assistance and interest during this work.

Grateful acknowledgment is made to the Textile Foundation for the fellowship under which this research was carried out.

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II. THE ADSORPTION OF CALCIUM AND COPPER FROM AMMONIACAL MEDIUM BY SILICA GEL[1]

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A detailed study has been made of the adsorption of calcium hydroxide alone and of copper hydroxide and of calcium hydroxide in the presence of ammonia and ammonium salts by silica gel with the purpose of finding out in what forms the cations are held at the surface of the gel.

The gel used and the general procedure followed are described in previous communications (5, 6).

ANALYTICAL

The amount adsorbed was determined by analysis of the supernatant liquid and of the solution obtained after extraction of the washed gel with a known volume of standard acid. Calcium was determined by the oxalate procedure, ammonia in the absence of copper volumetrically by oxidation with calcium hypochlorite, and copper iodometrically. It was found that ammoniacal copper solutions on standing give rise to the formation of nitrite, which interferes badly with the volumetric determination. The interference was eliminated by removing the nitrite by evaporation with sulfuric acid. If the presence of nitrite is ignored, deviating results may be obtained from the direct iodometric analysis. A solution originally 0.0522 molar in copper, 0.02 molar in ammonium chloride, and 1.1 molar in ammonia gave an iodometric titer of 0.0522 after three days, 0.0538 after seven days, 0.0568 after twelve days, 0.0588 after nineteen days. After seven months the results of the titration were inconsistent, but at least 20 per cent high.

ADSORPTION OF CALCIUM HYDROXIDE

Although the solubility of the silica gel in calcium hydroxide solutions was very small, no adsorption equilibrium could be attained even after long periods of shaking. This is clearly shown by the curves in figures 1 and 2.

In the former case 0.5 g. of gel and in the latter 0.2 g. of gel was shaken

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[1] From a thesis submitted by Vernon A. Stenger, J. T. Baker Fellow in Analytical Chemistry, 1932–1933, to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1933.

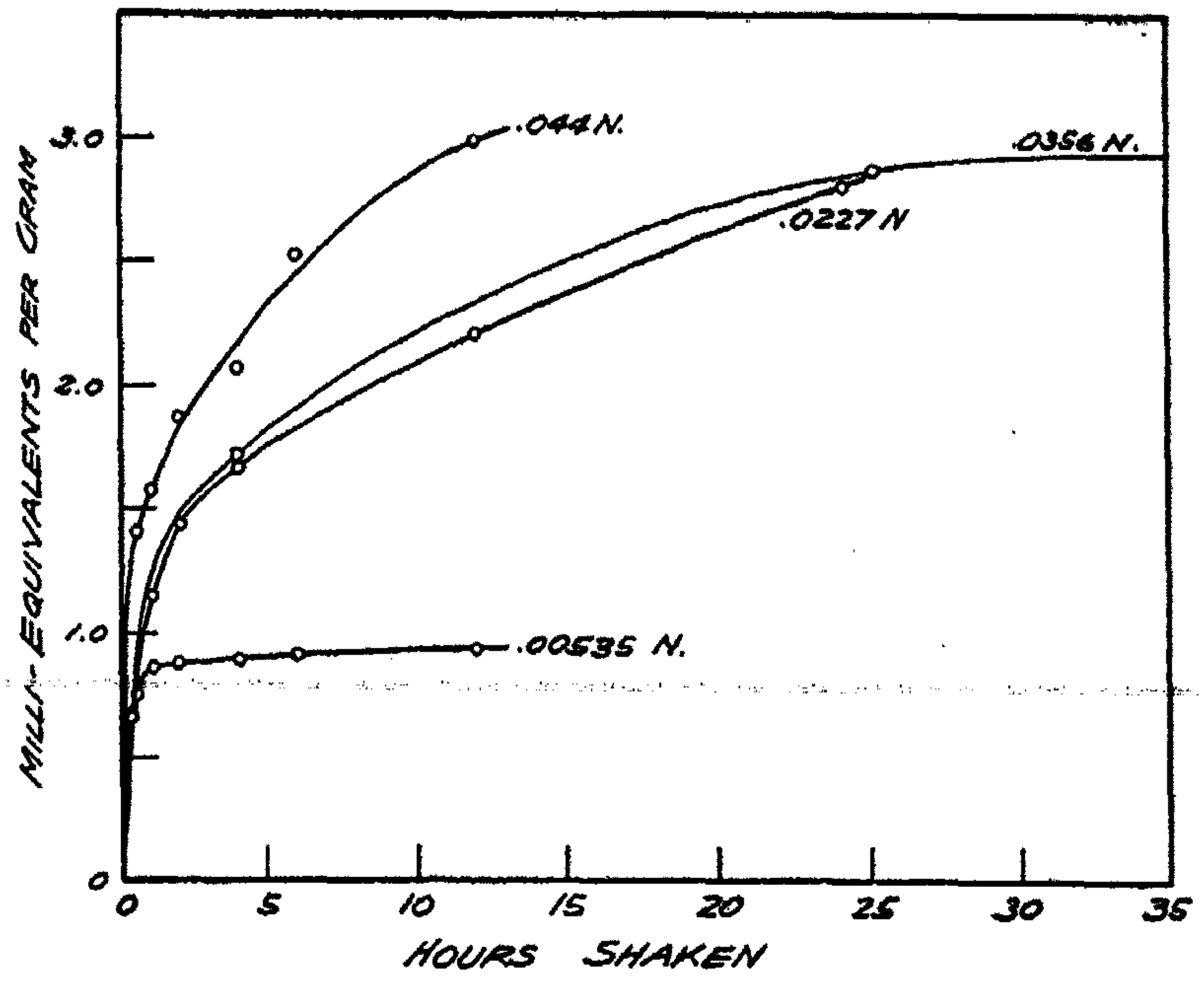

FIG. 1. TIME EFFECT. ADSORPTION OF CALCIUM HYDROXIDE

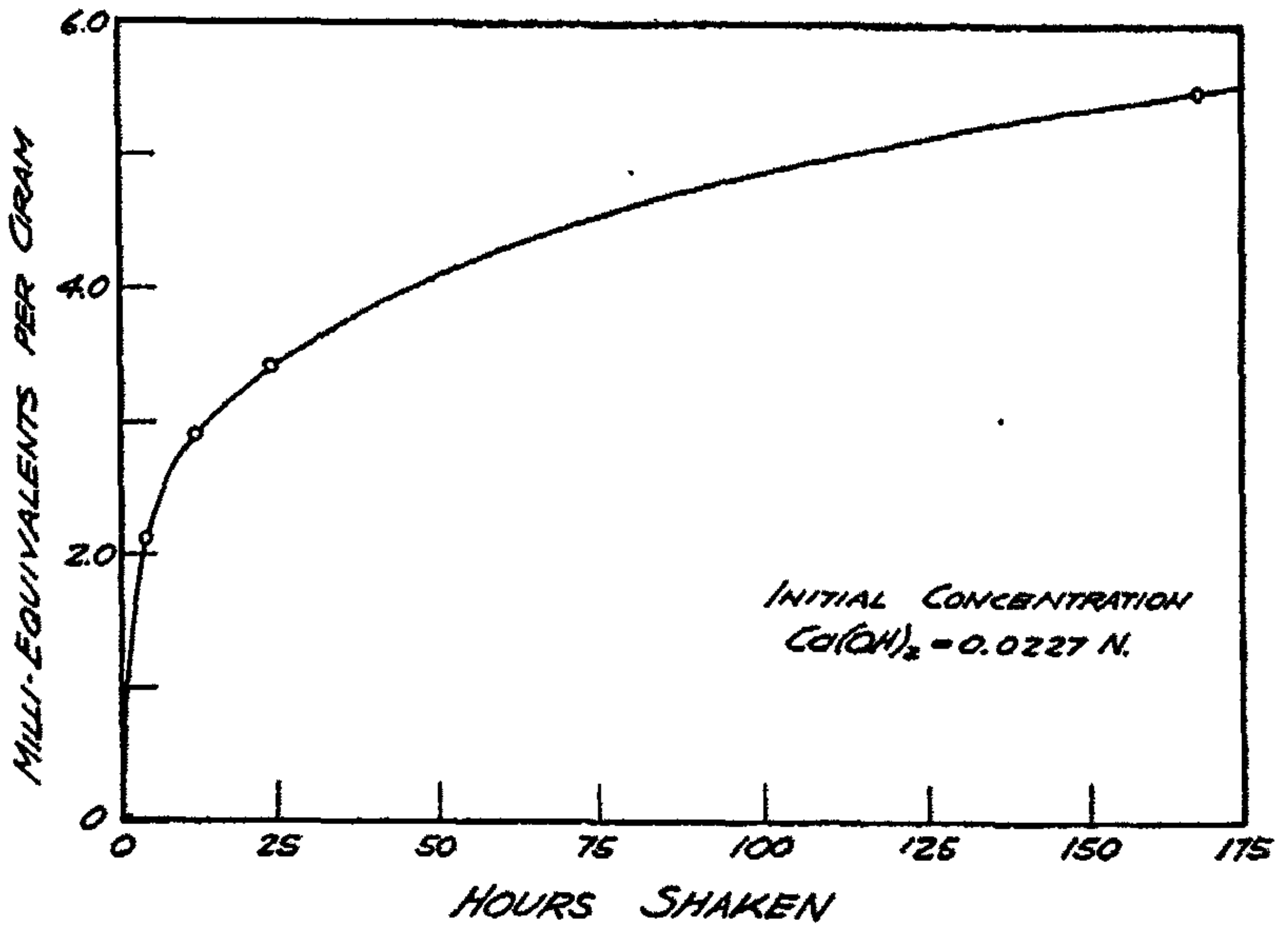

FIG. 2. TIME EFFECT. ADSORPTION OF CALCIUM HYDROXIDE

with 100 cc. of solution. The calcium hydroxide is strongly adsorbed by the gel; however, since the calcium silicate formed is insoluble, the adsorbed base obstructs the capillaries and inhibits or prevents the diffusion of more base into the interior of the gel.

In order to compare the adsorption of calcium hydroxide with that of alkali hydroxides, experiments were made in which 0.5 g. of gel was shaken for four hours with hydroxide solutions. The results are plotted in figure 3 of the previous paper (6) and given here in table 1.

MIXTURES OF CALCIUM HYDROXIDE AND AMMONIA

The adsorption of calcium and ammonium hydroxides was determined after various periods of shaking. Even after seven days of continuous shaking, no adsorption equilibrium was attained, as can be seen from the curves in figures 3 and 4.

TABLE 1

Adsorption of calcium hydroxide

0.5 g. of gel; 4 hours of shaking

CONCENTRATION OF $Ca(OH)_2$		GEL DISSOLVED	$Ca(OH)_2$ ADSORBED	
Initial	Final		Analysis solution	Analysis extract
N	*N*	*per cent*	*milliequiv. per gram*	*milliequiv. per gram*
0.00535	0.0012	4.07	0.87	0.93
0.0111	0.0033	4.34	1.64	1.64
0.0221	0.0138	0.86	1.68	1.69
0.0227*	0.0186	2.66	2.10	2.12
0.0356	0.0271	1.16	1.72	1.71
0.0443	0.0339	1.47	2.10	2.03

* 0.2 g. of gel used.

The points of the curves in figure 3 were obtained by shaking 0.5 g. of gel with 100 cc. of 0.022 *N* calcium hydroxide in 0.0375 *N* and in 0.75 *N* ammonia, respectively. The points in figure 4 were obtained by shaking 0.2 g. of gel with the same solutions. The molar ratio of ammonia to calcium hydroxide adsorbed decreases with the time of shaking. For comparison with the adsorption of the ammino copper complex, it is of interest to report some results. This is done in table 2.

The adsorption of calcium hydroxide, or more probably its speed of adsorption, increases with increasing concentrations of ammonia in the solution. A maximum is reached in about 0.3 *N* ammonia, and with increasing concentration of the latter, the adsorption of calcium hydroxide decreases (see figure 5). This is easily seen from some results reported in table 3 after a shaking period of four hours.

In order to be able to compare the adsorption of calcium with that of copper from ammoniacal medium, experiments have been made with

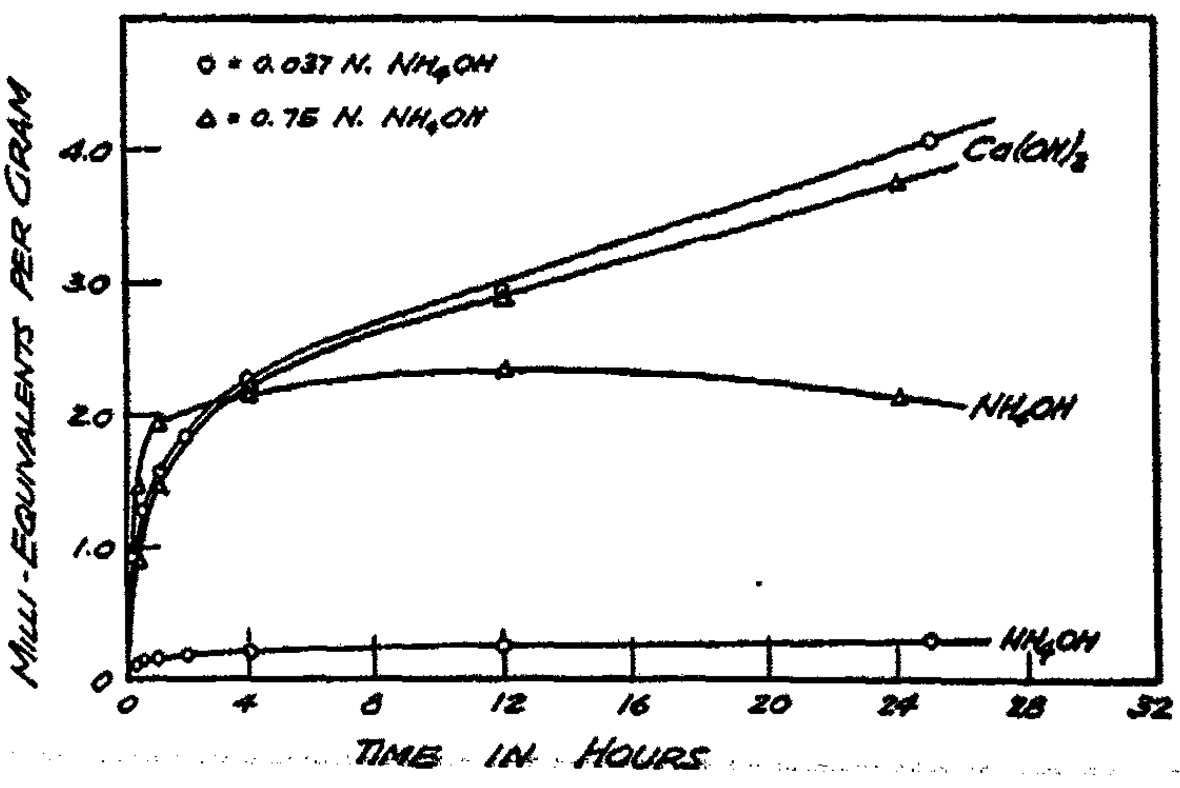

FIG. 3. TIME EFFECT. ADSORPTION FROM CALCIUM HYDROXIDE-AMMONIUM HYDROXIDE MIXTURES

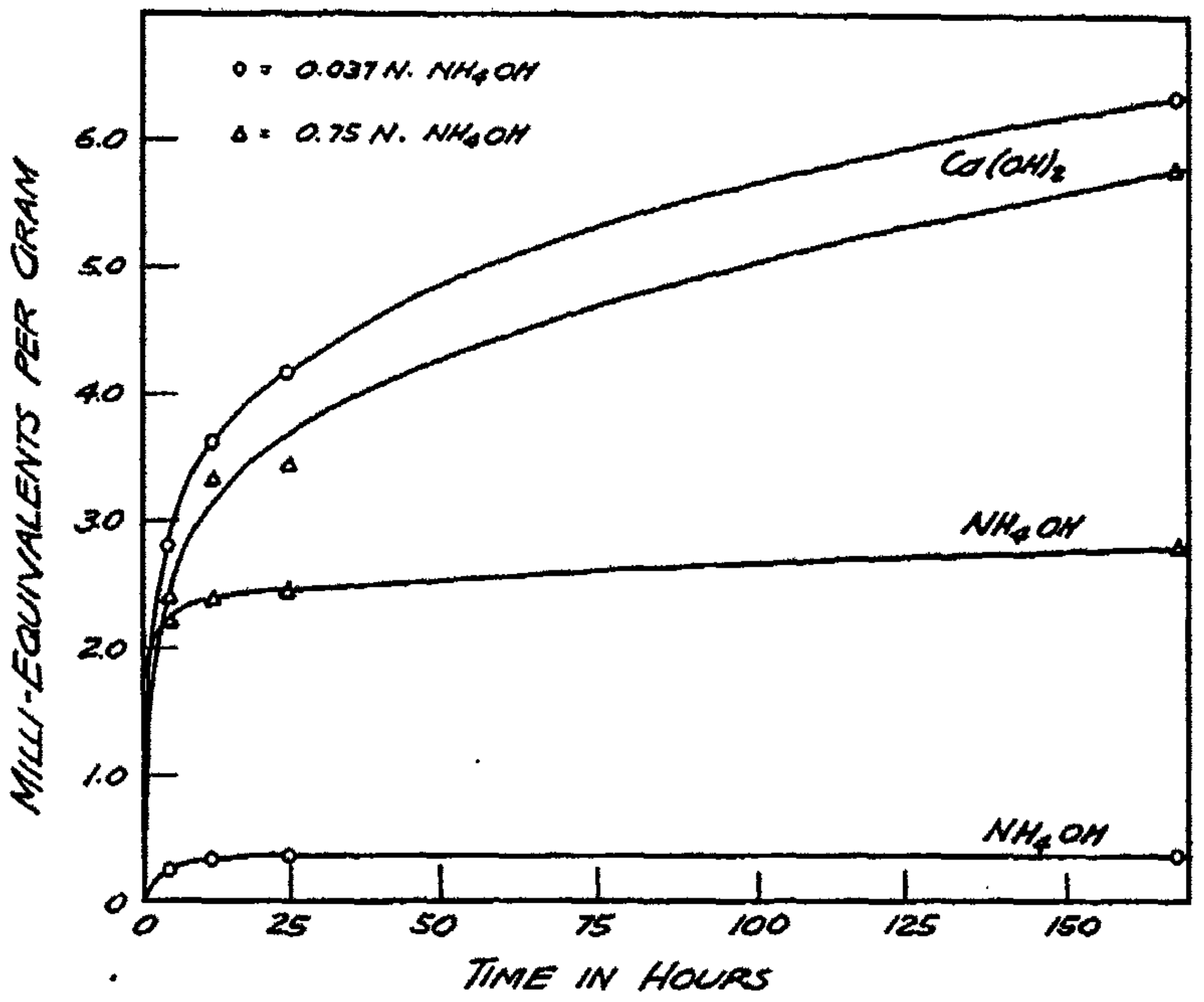

FIG. 4. TIME EFFECT. ADSORPTION FROM CALCIUM HYDROXIDE-AMMONIUM HYDROXIDE MIXTURES

TABLE 2

Adsorption of calcium hydroxide and ammonia (time-adsorption)

0.2 g. of gel; concentration of $Ca(OH)_2$, 0.0227 *N*

TIME OF SHAKING	FINAL NORMALITY		GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM			MOLAR RATIO NH_3: $Ca(OH)_2$ ADSORBED
	$Ca(OH)_2$	NH_4OH		Total base	$Ca(OH)_2$	NH_3	
Initial concentration of NH_3 = 0.037 *N*							
hours	*N*	*N*	*per cent*				
4	0.0172	0.0368	2.5	3.08	2.81	0.27	0.19
12	0.0156	0.0366	3.1	3.97	3.63	0.34	0.19
24	0.0146	0.0364	3.3	4.53	4.17	0.36	0.17
168	0.0102	0.0364	4.7	6.75	6.37	0.38	0.12
Initial concentration of NH_3 = 0.75 *N*							
4	0.0178	—	2.3	4.63	2.41	2.22	1.84
12	0.0163	—	2.8	5.72	3.32	2.40	1.45
24	0.0158	—	2.8	5.87	3.45	2.42	1.40
168	0.0114	—	4.9	8.66	5.83	2.83	0.97

TABLE 3

Adsorption of calcium hydroxide and ammonia (influence of concentration of ammonia

0.5 g. of gel; 100 cc. of solution; 4 hours of shaking

INITIAL NORMALITY		FINAL NORMALITY		GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM			MOLAR RATIO NH_3: $Ca(OH)_2$ ADSORBED
$Ca(OH)_2$	NH_3	$Ca(OH)_2$	NH_3		Total	$Ca(OH)_2$	NH_3	
N	*N*	*N*	*N*	*per cent*				
0.0111	0	0.0033	0	4.3	1.64	1.64	—	—
0.0109	0.0185	0.0023	0.0179	5.6	1.97	1.80	0.17	0.19
0.0109	0.0376	0.0018	0.0363	5.7	2.24	1.94	0.30	0.31
0.0221	0	0.0138	0	0.9	1.69	1.69	—	—
0.0222	0.0183	0.0119	0.0178	1.3	2.19	2.05	0.14	0.14
0.0222	0.0374	0.0108	0.0365	1.1	2.52	2.28	0.24	0.21
0.0217	0.0750	0.0086	0.0731	1.0	3.06	2.62	0.44	0.34
0.0180	0.250	0.0030	0.25	2.3	4.06	3.01	1.05	0.70
0.0180	0.50	0.0038	0.50	2.0	4.48	2.86	1.62	1.1
0.0180	1.00	0.0066	1.0	1.1	4.65	2.25	2.40	2.1

mixtures of calcium chloride and ammonia, some in the presence of ammonium chloride. The results are given in table 4.

The tremendous inhibiting effect of the excess of ammonium salt upon the adsorption of calcium hydroxide is clearly demonstrated by the curves in figure 6.

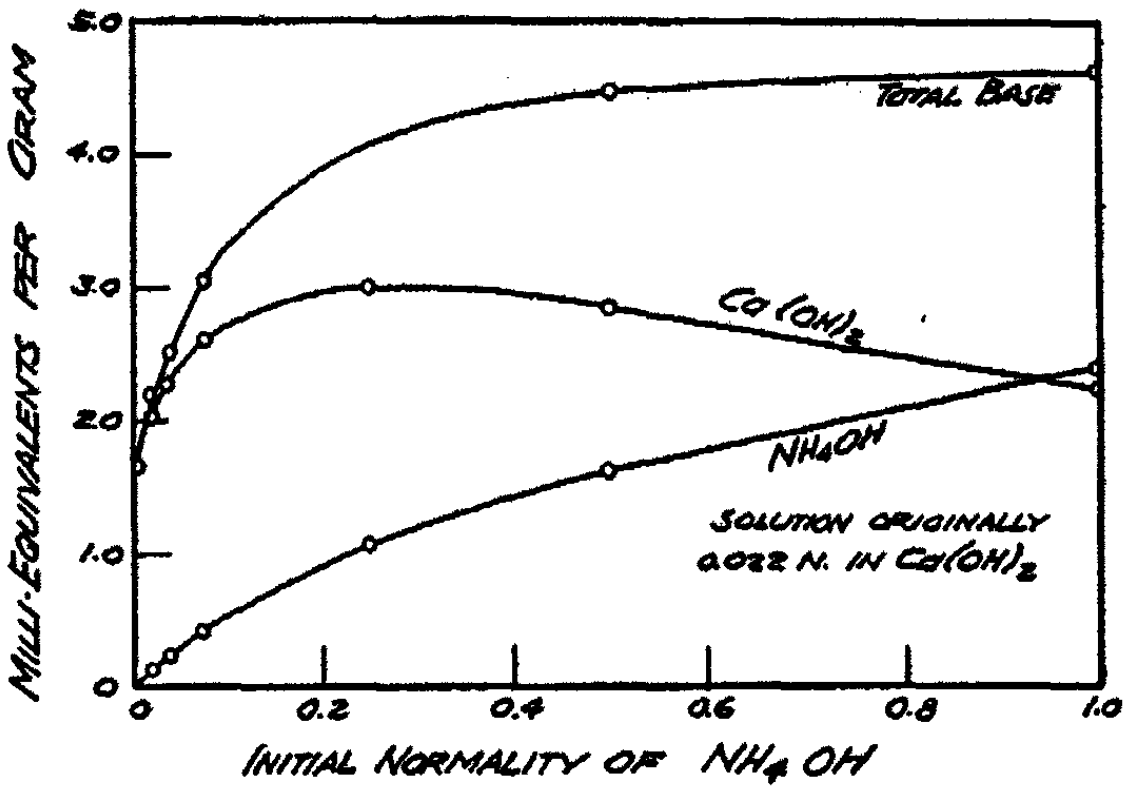

FIG. 5. FOUR-HOUR ADSORPTION FROM AMMONIUM HYDROXIDE–CALCIUM HYDROXIDE SOLUTIONS

TABLE 4

Adsorption of calcium hydroxide and ammonia from mixtures of 0.0829 N calcium chloride, ammonia, and ammonium chloride

0.2 g. of gel and 100 cc. of solution

TIME SHAKEN	FINAL NORMALITY		GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM			MOLAR RATIO NH_3: $Ca(OH)_2$ ADSORBED
	Ca	NH_3		Total	$Ca(OH)_2$	NH_3	
Concentration of NH_3 = 0.0373 *N*							
hours	*N*	*N*	*per cent*				
4	0.0189	0.0335	9.1	2.61	2.27	0.34	0.30
12	0.0175	0.0315	12.1	3.46	3.10	0.36	0.23
24	0.0175	0.0312	11.7	3.57	3.21	0.36	0.22
168	0.0161	0.0298	11.8	4.36	3.97	0.39	0.20
Concentration of NH_3 = 0.75 *N*							
4	0.0173		5.3	5.06	3.07	1.99	1.30
24	0.0155		6.5	6.26	4.07	2.19	1.08
335	0.0139		9.0	8.31	4.99	3.32	1.33
Concentration of NH_3 = 0.75 *N*; of NH_4Cl = 0.75 *N*							
4	0.0220		10.1	3.04	0.63	2.41	7.65
12	0.0217		11.7	3.44	0.84	2.60	6.20
24	0.0216		12.1	3.58	0.91	2.67	5.86
168	0.0214		11.7	3.85	0.99	2.86	5.78
335	0.0214		14.3	5.15	0.92	4.23	9.20

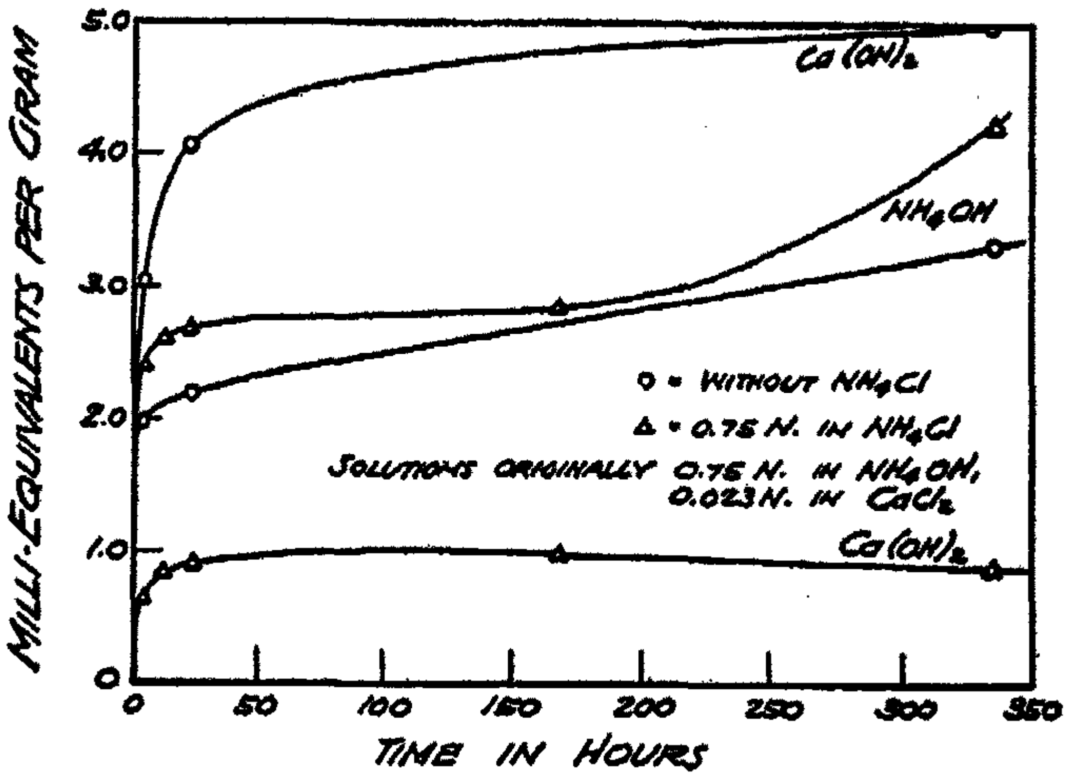

FIG. 6. TIME EFFECT. ADSORPTION FROM CALCIUM CHLORIDE-AMMONIUM HYDROXIDE-AMMONIUM CHLORIDE SOLUTIONS

TABLE 5

Adsorption of copper and ammonia (time effect)

0.2 g. of gel and 100 cc. of solution containing 0.025 *M* $Cu(NH_3)_4SO_4$ and excess of ammonia and ammonium chloride

TIME OF SHAKING	INITIAL NORMALITY		FINAL COPPER MOLARITY	GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM OF GEL			MOLAR RATIO NH_3:Cu ADSORBED
	NH_3	NH_4Cl			NH_3	$Cu(OH)_2$	Total	
hours	*N*	*N*	*M*	*per cent*				
4	0.10	0	0.0229	4.7	2.94	2.28	5.22	2.6
24	0.1	0	0.0220	4.5	3.76	3.14	6.90	2.4
168	0.1	0	0.0183	9.5	4.65	7.52	12.17	1.2
672	0.1	0	0.0171	8.6	4.71	8.70	13.41	1.1
4	0.1	0.50	0.0240	5.7	2.58	1.12	3.70	4.6
24	0.1	0.50	0.0236	10.1	3.20	1.72	4.92	3.7
168	0.1	0.50	0.0235	10.1	3.26	1.80	5.06	3.6
672	0.1	0.50	0.0234	9.0	3.01	1.81	4.82	3.3
4	0.75	0	0.0223	12.7	5.15	3.18	8.33	3.2
24	0.75	0	.00218	26.0	6.55	4.22	10.77	3.1
168	0.75	0	0.0190	27.8	7.29	8.40	15.69	1.7
672	0.75	0	0.0184	29.0	8.41	9.34	17.75	1.8
4	0.75	0.50	0.0243	6.8	3.52	0.80	4.32	8.8
24	0.75	0.50	0.0239	14.6	4.38	1.30	5.68	6.7
168	0.75	0.50	0.0240	13.1	4.46	1.24	5.70	7.2
672	0.75	0.50	0.0240	13.6	5.74	1.18	6.92	9.7

Finally a set of experiments was carried out with mixtures of calcium and sodium hydroxide. Both bases were adsorbed, the adsorption of each of them being decreased by the presence of the other.

ADSORPTION OF COPPER FROM AMMONIACAL SOLUTION

The adsorption of the copper and total ammonia (as complex copper ion and free base) depends upon the time of shaking, and the concentration of copper, ammonia, and ammonium salt in the solution. From the results

TABLE 6

Adsorption of copper and ammonia from mixtures with various concentrations of ammonium chloride

0.5 g. of gel with 100 cc. of solution 0.025 *M* in $Cu(NH_3)_4SO_4$; 4 hours of shaking

INITIAL CONCENTRATIONS		FINAL Cu	GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM OF GEL			MOLAR RATIO NH_3: $Cu(OH)_2$ ADSORBED
NH_3	NH_4Cl			NH_3	$Cu(OH)_2$	Total	
N	*N*	*M*	*per cent*				
0.1	0	0.0197	1.7	2.75	2.18	4.93	2.5
0.1	0.1	0.0195	3.6	2.68	2.23	4.91	2.4
0.1	0.5	0.0221	4.3	2.30	1.25	3.55	3.7
0.1	1.0	0.0232	4.3	2.15	0.75	2.90	5.7
0.4	0	0.0177	5.9	3.70	3.28	6.98	2.3
0.4	0.5	0.0222	4.8	2.92	1.10	4.02	5.3
0.4	1.0	0.0235	4.2	2.57	0.54	3.11	9.5
0.75	0	0.0189	10.8	4.62	3.02	7.64	3.1
0.75*	0	0.0223	12.7	5.15	3.18	8.33	3.2
0.75*	0.5	0.0243	6.8	3.52	0.80	4.32	8.8
1.0	0	0.0192	14.1	4.90	3.00	7.90	3.3
1.0	0.5	0.0227	6.7	3.50	0.94	4.44	7.4
1.0	1.0	0.0238	6.2	3.11	0.46	3.57	13.5

* 0.2 g. of gel taken.

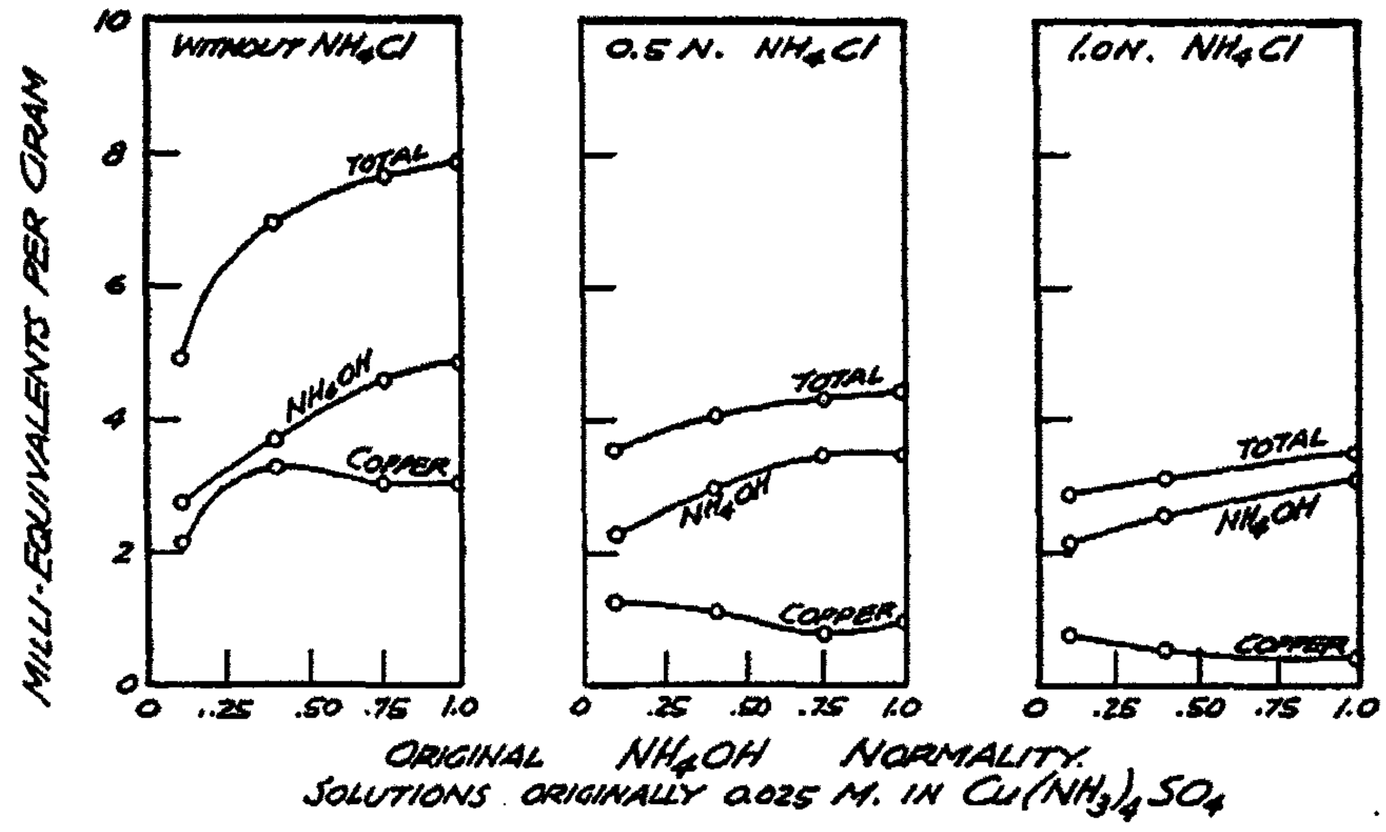

FIG. 7. FOUR-HOUR ADSORPTION FROM $Cu(NH_3)_4SO_4$–NH_4OH–NH_4Cl SOLUTIONS

in table 5 it is evident that no adsorption equilibrium is attained even after a long period of shaking. The molar ratio of ammonia to copper adsorbed decreases continuously with the time of shaking.

Ammonium chloride decreases the adsorption of copper and of the total base very strongly. This is clearly demonstrated by the figures in table 6 and the curves plotted in figure 7.

DISCUSSION OF THE RESULTS

1. Calcium hydroxide is much more strongly adsorbed by silica gel than the alkali hydroxides are. This could be expected, since the calcium silicate formed at the surface is very slightly soluble. From the investigations of Michaelis (8), Kühl and Wang Tao (7), and especially of Baylis (1), and of van der Burgh (9) there is no doubt that silica and lime react in a chemical way. The last author found that if enough calcium hydroxide is supplied to the lime a compound is formed with a molecular ratio of SiO_2 to CaO of 1:1, which is in equilibrium with a solution of 0.003 to 0.004 N calcium hydroxide. This compound can take up more lime (final molecular ratio, 1.4 CaO: 1 SiO_2). In our experiments there was always a large excess of silica, and the final concentration of the calcium hydroxide was often found to be smaller than 0.001 N. Therefore the concentration of calcium hydroxide in equilibrium with the solid phases, silica and calcium silicate, must be much smaller than that given by van der Burgh. In our experiments with calcium hydroxide alone and with mixtures containing ammonia, equilibrium was not attained even after ten days of shaking. This can be explained by the formation of insoluble calcium silicate in the pores of the gel resulting in a much slower rate of diffusion of the electrolyte in the interior of the gel.

2. Addition of ammonia promotes the adsorption of calcium hydroxide. At a concentration of ammonia of about 0.3 N, the lime adsorption reaches a maximum. At such high concentrations of ammonia the latter exerts a replacing effect upon the adsorbed calcium hydroxide, similar to that discussed in a previous paper (6).

Charriou (4) found the same effect of ammonia upon the coprecipitation of calcium with hydrous ferric oxide. The amount of calcium coprecipitated first increases, then reaches a maximum, and finally decreases with increasing ammonia concentration in the solution. He attributes the decrease to the formation of a complex compound between ammonia and calcium. However, from a special study to be reported later, it could be concluded that calcium hydroxide does not form complex compounds with ammonia even if the concentration of the latter is 2 N in the solution. It remains to be explained then why ammonia in smaller concentrations favors the adsorption of calcium hydroxide by silica gel. In the first place, it has to be considered that ammonia is much faster adsorbed than calcium hydroxide. It also exerts a dissolving effect and thus widens the pores of the gel. In order to prove this assumption, experiments were made in which the gel was shaken two hours with 0.1 *N* ammonia and then quickly washed with dilute acid and water. By such a process the adsorbent properties of the gel for calcium hydroxide had markedly increased, but not enough to account for the large effect noticed in the experiments described in table 3. Therefore, we have to assume that the adsorbed ammonia favors the chemical reaction between silica and lime. A solution of silica in dilute ammonia yields a white flocculent precipitate of calcium silicate upon the addition of calcium hydroxide. Such a precipitate is not noticed outside of the gel in the experiments with mixtures of calcium hydroxide and dilute ammonia. However, this reaction takes place in the interior of the gel, the adsorbed ammonia forming ammonium silicate, which has a tendency to diffuse out. On its way it meets the calcium hydroxide and forms the insoluble silicate in the interior of the gel. In many cases the gel becomes opaque by the calcium silicate formed. Summarizing then, the ammonia by its dissolving effect upon the gel widens the pores, and the ammonium silicate formed reacts in a chemical way with the calcium hydroxide in the interior of the gel.

3. Addition of ammonium salts decreases the pH and increases the solubility of the calcium silicate very markedly. Consequently, the adsorption of calcium hydroxide is strongly decreased by addition of ammonium chloride to a mixture of calcium chloride and ammonia. In a previous paper (6) a similar effect has been described of the influence of ammonium salts upon the adsorption of potassium hydroxide from a mixture of potassium chloride and ammonia.

4. The molecular ratio of ammonia to copper adsorbed is much greater than that formed under comparable conditions with ammonia and calcium. This and the dark blue color of the gel indicate clearly that the copper is first adsorbed as ammino complex. It is hard to say which complex of copper is adsorbed, since the ratio of NH_3 to Cu decreases with the time of shaking, whereas certainly part of the ammonia is adsorbed as such (compare with the adsorption of ammonia in the mixtures containing calcium). Berthon (2) claims that the copper is adsorbed as diammino complex by silica gel. As he made experiments after twenty-four hours of shaking only, it was quite accidental that he found a molecular ratio of ammonia to copper adsorbed of 2 to 1. Since part of the ammonia is certainly adsorbed as such, the ammonia content of his complex must have been less than two molecules per one copper. Experiments have been made in 0.1 *N* ammonia as reported in table 5, but in which the analyses were made after 15 minutes, 1 hour, and 2 hours of shaking. The molar ratios of ammonia to copper adsorbed were 3.6, 3.0, and 2.7. After one month of shaking the ratio decreased to 1.1. With higher concentrations of ammonia higher

ratios are found; here, however, the amount of uncombined ammonia adsorbed becomes much greater. From the figures in table 5 and by comparison with those in table 3 one may infer that at small ammonia concentration the copper is originally adsorbed as tri- or di-ammino complex. On further shaking this complex loses ammonia and finally approaches the composition of the monoammino complex. J. Bjerrum (3) from an extensive study concluded that various complex copper ammino ions exist, of the general formula

$$Cu(NH_3)_x(H_2O)_{4-x}^{++}$$

in which x may vary from 0 to 4. Upon prolonged electrodialysis practically all the ammonia could be removed from the gel, whereas all the copper remained behind.[2] The color of the gel during this process changed from blue to green. Originally all the copper in the solution was present as ammino complex. Therefore, first of all it had to be adsorbed as $Cu(NH_3)_x(H_2O)_{4-x}(OH)_2$ or more likely as $Cu(NH_3)_x(H_2O)_{4-x}SiO_3$, in which x had a value of approximately 2. This silicate is not in equilibrium with the solution, and on standing is transformed into $Cu(NH_3)(H_2O)_3SiO_3$. A different equilibrium therefore exists at the interface than in the solution. On electrodialysis the complex is forced to give off its last molecule of ammonia and the least soluble compound, aquo copper silicate, remains behind. The fact that the copper originally is adsorbed as ammino complex is also quite evident from the influence of ammonium chloride. The latter decreases not only the adsorption of the copper but also that of the ammonia very markedly (table 6), whereas in the case of calcium, which does not form a complex, the adsorption of ammonia is slightly increased (table 4).

5. The adsorption of calcium from ammoniacal solution is strictly comparable with that of copper, with the understanding that the former is primarily adsorbed as aquo ion and the latter as ammino ion which on standing returns ammonia to the solution.

SUMMARY

1. It has been explained why ammonia up to concentrations of 0.3 *N* promotes the adsorption of calcium hydroxide by silica gel.

2. The adsorption of calcium and copper is greatly decreased by the addition of much ammonium salt.

3. Copper from dilute ammoniacal solution is adsorbed as a complex ammino ion. At the surface it forms a silicate $Cu(NH_3)_2(H_2O)_2SiO_3$, which on standing is transformed into $Cu(NH_3)(H_2O)_3SiO_3$. Upon electrodialysis in water it loses its last molecule of ammonia.

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[2] Experiments performed by Dr. W. G. Mitchell.

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ON THE ORIGIN OF THE ACTINIUM SERIES OF RADIOACTIVE ELEMENTS. II[1]

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We have recently discussed the origin of the actinum series in the light of F. W. Aston's mass spectrum analysis of uranium leads and our own measurements of the protoactinium: uranium ratio (12).

In the meantime, F. W. Aston has communicated new results at the Chicago meeting of the American Association for the Advancement of Science and has just published them (4). His results give fresh support to the actino-uranium theory and its discussion is warranted, especially since at the same meeting other views on the actinium series and their bearing on geological time measurements were expressed and our conclusions were far from being accepted.

I. THE ACTINO-URANIUM THEORY AND DISCUSSION OF LATEST RESULTS OF F. W. ASTON

The actino-uranium theory can be summarized as follows: The actinium series is independent of the uranium–radium series and is derived from actino-uranium (Ac-U), an isotope of uranium, which has a period equal to 4.0×10^8 years and which occurs in all the uranium minerals in a constant ratio to uranium I (U-I), independent of their age. The ratio of disintegrating atoms of actino-uranium to uranium I at our present geological epoch equals 4.0:100.

Aston's recent results on uranium leads, the chemical analysis of the minerals from which they were extracted, and other data pertaining to these minerals are given in table 1, which is also a continuation of table 1 from a preceding paper (Paper I, see reference 12).

The results with the Morogoro lead (column 4) are in complete agreement with the predictions of the actino-uranium theory, and the percentage of actinium D atoms found in this lead (7.4) is exactly the one to be expected from its age. (See figure 1, Paper I.)

The analysis of this lead is especially valuable because it is, like the Katanga lead, free from ordinary lead (as seen from the absence of the Pb^{208}

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[1] Reported in part at the Chicago meeting of the American Association for the Advancement of Science, June, 1933.

TABLE 1

	4	6	7	8
1. Mineral	Pitchblende	Thorite	Broeggerite	Uraninite
2. Geographical origin	Morogoro, East Africa	Langesundfjord, Norway	Karlshus, Raade, Norway	Great Bear Lake, LaBine Point, Canada
3. Chemical analysis:				
Uranium, per cent	70.45¶	0.45†	61.16§	52.14**
Thorium, per cent	0.2 ¶	30.10†	4.38§	0.0
Lead, per cent	8.30¶	0.35†	8.02§	10.50**
4. Isotopic constitution of lead:				
Pb^{206}	93.1	4.6	86.8	89.8
Pb^{207}	6.9	1.3	7.3±0.2	7.9
Pb^{208}	0	94.1	3.7	2.3
			(a) (b)	
5. Percentage of RaG	93.1		85.5 86.3	88.5
AcD	6.9		6.4±0.2 6.9±0.2	7.0
ThD	0*		1.5 2.8	0.0
6. Chemical atomic weight of lead		207.90‡		close to 206 ††,**
7. Mean mass number	206.069	207.895		206.125
8. Ratio of lead to uranium	0.1178			0.201**
9. Ratio of radium G to uranium I	0.1093		0.1129	
10. Age in years	748 × 10^6		769 × 10^6	
11. Number of disintegrating protoactinium atoms for 100 decaying uranium I atoms	4.0 ±0.1¶			
12. Number of actinium D atoms for 100 atoms of radium G in uranium lead	7.4		7.5–8.0	

(a) Corrections made assuming $\lambda_{Th} = 4.0 \times 10^{-11} a^{-1}$, value of International Radium Standard Committee, 1931.

(b) Corrections made assuming $\lambda_{Th} = 6.0 \times 10^{-11} a^{-1}$, value of Geiger and Rutherford, corrected for $Z_{Ra} = 3.72 \cdot 10^{10}\ \alpha$/sec. & gr.

¶ A. V. Grosse and I. D. Kurbatov.

* The theoretical thorium D percentage calculated from the thorium content and using $\lambda_{Th} = 6 \times 10^{-11} a^{-1}$ = 0.09 per cent.

† Fajans K.: Sitzber. Heidelberg. Akad. Wiss. 1918, A, Abh. 3; Z. Electrochem. **24**, 164 (1918).

‡ Hönigschmid, O.: Z. Elektrochem. **25**, 91 (1919).

§ Analysis by C. N. Fenner and C. S. Piggot: Nature **123**, 793 (1929).

†† Report of the Committee on the measurement of geologic time of the National Research Council, p. 3 (1932).

** Private information from Dr. J. P. Marble for the same uraninite sample, from which the lead chloride used by us for the preparation of lead methyl was derived.

line), and therefore, the total amount of Pb^{207} found can be attributed, without any corrections, to actinium D.

The analysis of the Thorite lead (column 6), kindly supplied by K. Fajans, allowed F. W. Aston (5) to determine the "hydride effect," i.e., the contamination of a Pb^n with the $Pb^{n-1}H^1$ line. The effect was found to be 2.3 per cent of the line intensity and this correction has to be made for all his measurements.

We can also apply this correction to the Broeggerite lead, the first uranium lead to be analyzed by Aston (2), where the rather high values led A.

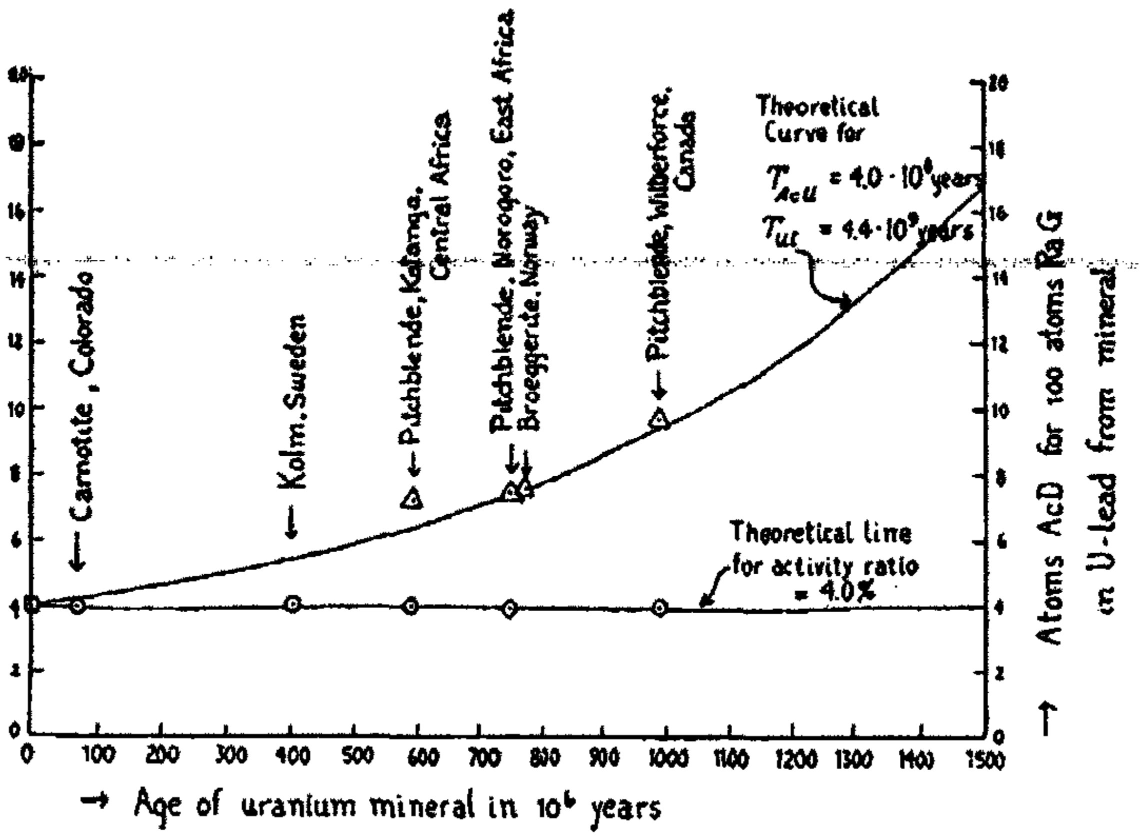

FIG. 1. THE ACTIVITY AND ACTINIUM D TO RADIUM G RATIOS AS A FUNCTION OF A MINERAL'S AGE

△ = ratio of actinium D to radium G in uranium lead determined directly by F. W. Aston with mass spectrograph.

⊙ = ratio of protoactinium to uranium I disintegrating atoms or activity ratio determined by A. V. Grosse and I. D. Kurbatov.

Holmes (13) to object to the actino-uranium theory. The corrected figures are given in column 7. From these the concentrations of radium G and actinium D are derived in the following way: We calculate the amount of thorium D from the thorium-content and approximate age of the mineral, and by subtracting it from the percentage of Pb^{208} we obtain the amounts due to isotopes of ordinary lead. Correcting Aston's values for these, we obtain the real percentages of radium G and actinium D. They are given in two columns corresponding to the two still disputable values of the disintegration constant of thorium, i.e., $\lambda_{Th} = 4.0 \times 10^{-11}a^{-1}$ or $6.0 \times 10^{-11} a^{-1}$.

The mean value for actinium D (7.7) again lies on the theoretical curve at the point corresponding to its age, which we derive in the most exact possible way from the radium G: uranium I ratio.

These results, combined with data of our previous paper are shown in figure 1. The agreement is far better than one could expect. The experimental results supplied by the mass spectrograph and the protoactinium: uranium activity ratio determinations can be explained satisfactorily only by the actino-uranium theory.

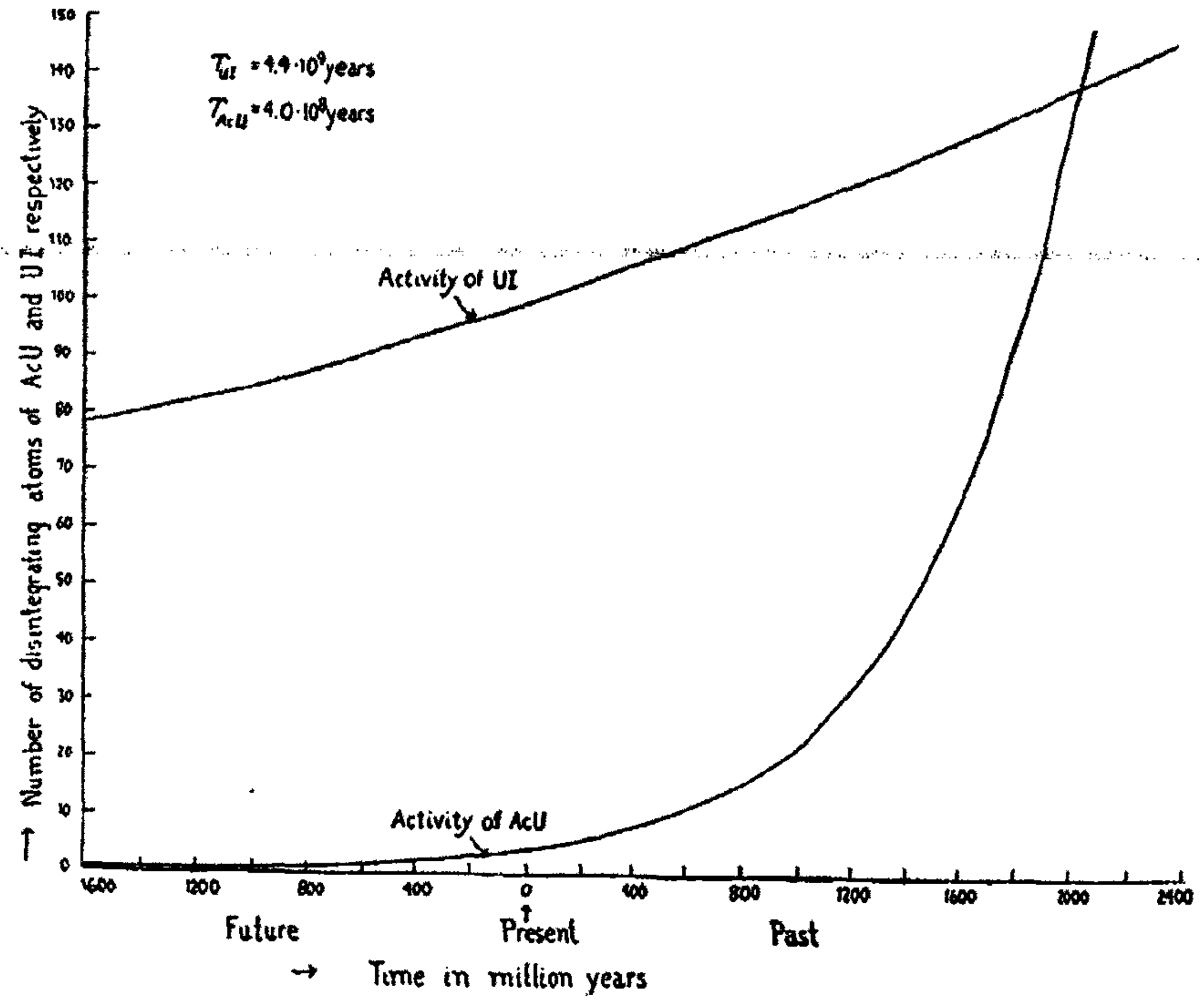

FIG. 2. ACTIVITY DUE TO ACTINO-URANIUM AND URANIUM I AS A FUNCTION OF TIME $T_{\mu I} = 4.4 \cdot 10^9$ years; value of International Radium Standard Committee, 1931

Figure 2 shows the activity due to actino-uranium and uranium I, respectively, as a function of time, and illustrates the actino-uranium theory in a simple way. We see how rapidly the actino-uranium activity increases as we go into the past; for instance, at the time of formation of Wilberforce uraninite (987 × 10^6 years ago) about twenty-two atoms of actino-uranium disintegrated for every one hundred and eighteen atoms of uranium I, whereas now it has dropped to four per hundred; this high initial quantity of actino-uranium in an old mineral of course now manifests itself in the large amount of accumulated actinium D in the uranium lead.

Figure 2 is also instructive in another respect. The energy and heat evolution by members of the two series is directly proportional to the activity of the mother element, and we see how important a part the actinium series played in the heat balance and geological processes of the earth's crust in the early days of its history. The theories of J. Joly, H. Jeffreys, and A. Holmes will have to be reconsidered from this angle.

DISCUSSION OF OTHER THEORIES

We take this opportunity to discuss two theories which arose from other investigations.

1. A. Kovarik's theory (14) that the relative amounts of actino-uranium to uranium I and uranium II are initially the same, in all uranium-bearing minerals, is inconsistent with our protoactinium: uranium I ratio determinations; besides, it implies the unnatural idea that if an old uranium mineral, in which the actino-uranium has already decayed, goes into solution and a new uranium mineral forms from it, the actino-uranium will again be present in the initial ratio, appearing, so to speak, spontaneously.

2. E. R. Bishop (6, 8) and C. S. Piggot (16), interpreting the minima obtained from radioactive elements (1, 7, 10), using the magneto-optic method of F. Allison, have suggested schemes of four radioactive families, with eight isotopes of uranium, and Piggot (16) has discussed the significance of these findings in geological age determinations.

The radioactive schemes proposed contradict many well-established facts of radioactivity.

The *interpretation* of the minima is open to many objections and we think a clarification of the problem can best be accomplished by the use of definite radioactive elements as indicators.

The validity of the family schemes themselves can be easily checked with protoactinium. Contrary to the statement of E. Bishop (6) that no member of the actinium series has been isolated, pure protoactinium is available in centigram quantities (11) and since, according to E. Bishop (6) and C. S. Piggot(16) four isotopes of protoactinium exist, all of which gave birth to isotopes of the new elements "virginium" and "alabamine," their appearance in protoactinium preparations could be easily verified.

Even if the correctness of the family schemes suggested will be proven, which we doubt, the concentration and order of abundance of the individual isotopes still remain undecided. The statements concerning the last point are unclear and contradictory. The order of abundance of bismuth and thallium isotopes is absolutely against the mass spectrographic and chemical atomic weight facts.[2] The following is another example: Piggot (16) assigns a magneto-optic minimum to radium B or Pb^{214}, presumably formed from traces of uranium, which he states are always present in lead salts; a simple calculation shows that from these uranium traces only a *fraction of an atom* of radium B can be formed in the whole apparatus, which we doubt even the magneto-optic method will be able to detect.

Under these circumstances, we consider the discussion of magneto-optic data premature. Even if they prove to be correct they would in no way affect the reliability of age determinations based on the experimental radium G:uranium I ratio.

THE GREAT BEAR LAKE PITCHBLENDE AND THE ACTINO-URANIUM THEORY'S CRITERION OF ALTERATION AND LEACHING

The only apparent exception to the actino-uranium theory is the Great Bear Lake pitchblende. It is reported (17) that this pitchblende has an age of about 1400×10^8 years and belongs to the oldest known; it is further reported (15) that it has a chemical atomic weight close to 206, suggesting an unusually small content of actinium D in uranium lead in contradiction to the demands of the actino-uranium theory.

On the other hand, this pitchblende shows definite signs of alterations; the mineral is tremendously brittle and traversed all over by veins, the larger ones seen with the unaided eye. Further, the lead:uranium ratio varies very much from sample to sample, i.e., from about 0.19 to 0.21, and in some cases reaches the limits 0.11 and 0.27 (17).

Aston's analysis (3) shows that the amount of actinium D is similar to the Morogoro and Broeggerite lead, indicating an error in the chemical atomic weight determination. Nevertheless the actual actinium D content is smaller than one would expect from the actino-uranium theory on the basis of its age, as given by the lead: uranium ratio. The theory demands, however, a relationship as expressed by formula 2 of Paper I *only* for *unaltered* minerals. Since the demands of the theory have been, as far as we see, sufficiently proven by experimental evidence, we can safely conclude that the lead: uranium ratio ($\simeq 0.20$) does not give the real age of Great Bear mineral and some of the lead or uranium, or both, have been leached. We infer generally that if (in the age range up to 1×10^9 years) the age does not check with the actinium D: radium G ratio, leaching or alterations of some kind have taken place.

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[2] Magneto-optic data indicate Bi^{211} and Bi^{210} to be the most abundant isotopes, whereas Bi^{209} is so far the only one found by Aston, in complete agreement with the chemical atomic weight 209.00; also the most abundant minimum of thallium is attributed to 207, whereas Aston (Proc. Roy. Soc. London **134A**, 577 (1932)) and also H. Schüler and J. E. Keyston (Naturwissenschaften **19**, 320 (1931)) found only 205 and 203, in agreement with the chemical atomic weight 204.39.

A safe estimate of the age of a leached mineral from this ratio alone is not possible, as the lead might be leached out to different extents at different times in the mineral's history; besides, there is always a possibility of infiltration of ordinary lead. This seems to be the case here as Pb^{208} is present (= 2.3 per cent), which can not be thorium D, since thorium is reported absent in the mineral (17). Summing up, the Great Bear Lake lead, because of alteration, cannot be used as evidence against the actino-uranium theory; instead, we have in the experimental actinium D:radium G ratio, a new check for alteration in uranium minerals.

FUTURE INVESTIGATIONS AND CONCLUSIONS

It is very important to continue the mass spectrographic investigations of uranium and thorium leads so successfully started by F. W. Aston. The mass analysis of the lead halides, instead of lead methyl,[3] would be desirable to avoid completely the correction due to hydride effect and to increase precision.

Data on the oldest obtainable uranium leads from minerals unaltered as far as possible are especially desirable, to test the applicability of the actinium D: radium G ratio formula beyond a billion years. (The Manitoba uraninite, for instance, discovered by H. V. Ellsworth (9), with a lead/uranium = 0.27 should prove worth while). They might also be interesting in another respect: In case the experimental curve should deviate in that range from our theoretical it might indicate the existence of a second actino-uranium isotope (still a possibility as we mentioned in paper I), not yet in equilibrium with our present isotope. The Rutherford-Soddy disintegration theory allows one to calculate in a simple way the ratio of actinium D to radium G for different possible cases; it would be, however, premature to discuss these points at the present time.

Besides supplying data for the development of the actino-uranium theory, the mass analysis allows one to determine, besides the isotopic constitution of the lead, the radium G: uranium I ratio, the exact age of the mineral and the atomic weight of the lead in a much shorter time and with greater reliability and accuracy than a chemical atomic weight determination.

SUMMARY

The latest mass spectrographic results of F. W. Aston with radiogenic leads are discussed and found to support completely the Piccard-Rutherford actino-uranium theory.

It is pointed out that the interpretation of magneto-optic minima by E.

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[3] Perhaps the rapid advance in the Washburn method of concentrating H. Urey's H^2 will soon allow the preparation of $Pb(CH^2_3)_4$, where the hydride effect will of course not interfere in any way with the measurement of actinium D.

Bishop and C. Piggot and their schemes of radioactive families contradict well-established facts of radioactivity.

The anomaly of the Great Bear Lake pitchblende is traced back to alterations.

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ADHESION TENSION OF LIQUIDS AGAINST STRONGLY HYDROPHILIC SOLIDS

A Series of Liquids Against Barite

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The object of the present investigation was to improve and simplify the pressure of displacement method for measuring adhesion tension (1, 3, 4, 6, 11, 12), to adapt it for use with softer and less rigid materials than had previously been employed, and to obtain additional adhesion tension data with hydrophilic solid systems. It had been found that maximum pressure values obtained with receding liquid columns were more reproducible and more readily obtained than those determined with advancing liquid columns (8, 9). Accordingly pressures were measured which were just sufficient to cause the liquid column in the compressed powder membrane to recede.

APPARATUS

Since it had been found that the original hydraulic press method of packing cells caused crushing or cleaving of solid materials such as barite, new methods of packing the compressed powder membrane were studied. A tamping method of packing was finally adopted. Reproducible results were obtained by tamping even when the tamping plunger was operated by hand. Identical volumes were obtained by tamping the powder wet or dry. Hand tamping had the disadvantage that the force of impact of the packing plunger could not be measured in definite units, hence one investigator had difficulty in reproducing the results of another. A mechanical tamping machine was constructed which could be regulated so as to give definite and reproducible degrees of packing.

The cell to be packed was placed on a base, mounted on a stiff coil spring, which vibrated with each impact of the plunger. A packing guide directed the packing plunger as it fell into the cell. The plunger was raised by a small chain which passed through a pulley mounted above the cell. The pulley was adjustable and its position determined the distance of fall of the plunger. A rachet device attached to the chain released the packing plunger, which fell freely with each revolution of a hand-turned crank shaft. It was necessary to determine the weight of the packing plunger and the distance of fall advisable for each solid. For the measurements with barite reported herein, a plunger weighing 360 g. was dropped 20 mm. fifty times with each added increment. About five 1-g. increments were used in the preparation of the membrane. A circular disc of linen cloth was placed in the cell before packing and a second disc was placed over the powder

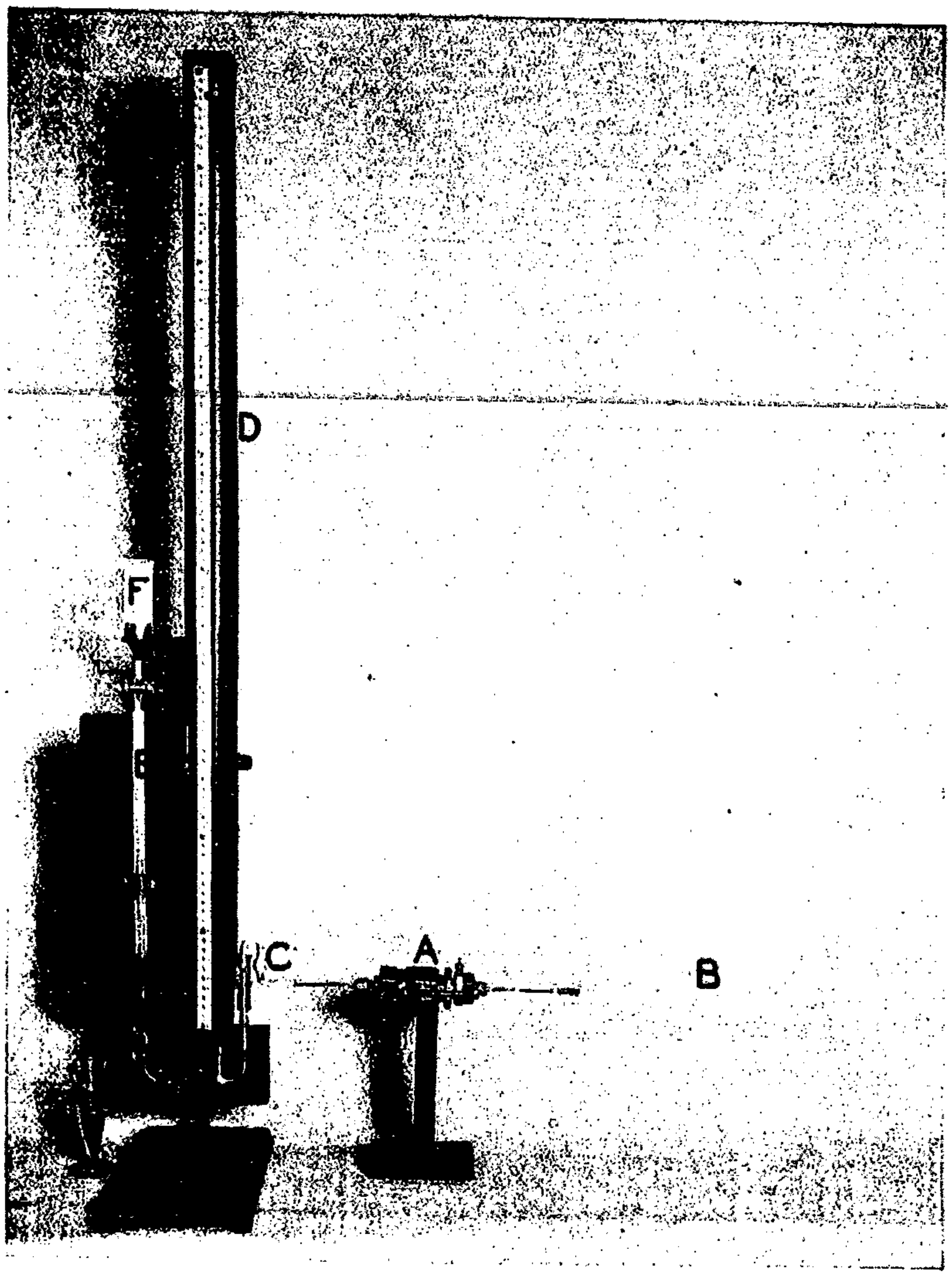

Fig. 1. Cell and Manometer Assembly

A, displacement cell; B, indicator tube; C, bulb, intermediate section; D, manometer tube; E, auxiliary tube; F, mercury reservoir and drop control.

during the tamping process and was left in place after the last tamping. The tamping method of packing eliminated almost entirely difficulties previously encountered which were traceable to improperly packed cells.

The displacement cell assembly used in this investigation is shown in figure 1. This apparatus is similar to that used by Bartell and Whitney (8). All measurements were made in a constant temperature thermostat held at 25°C. ± 0.1°C.

MATERIALS

The liquids used in this investigation were acetylene tetrabromide, benzene, carbon tetrachloride, heptane, butyl acetate and water. The liquids were all purified before use. In general, the purification was not rigorous, but was sufficient to give a reasonably pure product. The surface and interfacial tension values were determined for all the liquids.

The solid used was mineral barite, which contained less than one per cent of silicious material. The barite was heated in an electric oven for two hours at 400°C. and then ground in a ball mill. It was then washed with acetone (the very fine material was removed by decantation), dried for three hours at 110°C., and finally sifted through a series of screens to give definite particle size, 200 to 300 mesh.

METHOD OF MEASUREMENT

The graded powder was packed dry into the cell by tamping. The cell plunger was put in place and securely fastened. The liquid to be used was then drawn into the cell by suction until the powder was completely wetted, and the liquid column was caused to extend from the cell into the capillary indicator tube. For the pressure of displacement measurement of liquid-air systems the pressure was slowly built up by very fine drops of mercury which were caused to fall into the auxiliary arm E of the manometer D (see figure 1). As soon as the movement of liquid outward in the indicator tube was definite and constant, the auxiliary arm of the manometer was closed, leaving the manometer directly connected to the cell. The pressure in the manometer now continued to decrease as the liquid-air interface continued to move outward. Finally movement of the liquid column ceased and the pressure remained constant. This pressure was readily reproducible and was taken to represent the equilibrium pressure. The most consistent results were obtained when the interface was caused to come to rest near the middle of the membrane.

Measurements with liquid-liquid systems were carried out in a similar manner. The membrane was first wetted with the displacing liquid (for hydrophilic solids, water). In this case the indicator tube, B, was left full of liquid. The second liquid (organic liquid) was put into the glass bulb, C, which formed the intermediate section between the cell and manometer.

It was necessary to eliminate air completely from the liquid–liquid interface. This was accomplished by making a connection to the end of the indicator tube and applying enough pressure to cause the liquid in the cell to move through the small metal tube leading to the intermediate section. This section containing the organic liquid was tilted so as to bring the two liquids together and the interface, now free from air, was forced back into the membrane. Final connections to the manometer were made by means of ground glass joints and the procedure from this point was exactly the same as described for liquid–air systems.

TABLE 1

Adhesion tension measurements with barite

Air–organic liquid–barite

$r = 1.43 \times 10^{-3}$ cm.

LIQUID	P	cos Θ_{12}	Θ_{12}	S_2	A_{12}
	grams per cm².				
Acetylene tetrabromide	57.7	0.822	34°	49.07	40.5
α-bromonaphthalene	56.9	0.909	25°	44.00	39.9

P = Displacement pressure.
Θ_{12} = Contact angle solid–organic liquid–air.
Θ_{23} = Contact angle solid–organic liquid–water.
S_2 = Surface tension organic liquid.
S_{23} = Interfacial tension organic liquid against water.
A_{12} = Adhesion tension organic liquid against solid.
A_{13} = Adhesion tension water against solid.

TABLE 2

*Adhesion tension measurements with barite**

Water–organic liquid–barite

LIQUID	P	cos Θ_{23}	Θ_{23}	S_{23}	A_{12}	A_{13}
	grams per cm².					
Acetylene tetrabromide	50.7	0.928	22°	38.32		76.1
α-Bromonaphthalene	52.3	0.883	27°	41.57		76.6
Benzene	45.7	0.935	21°	34.31	44.3	
Heptane	61.8	0.877	28°	49.40	33.1	
Butyl acetate	16.8	0.896	26°	13.17	64.6	

* See footnote to table 1.

DISCUSSION OF RESULTS

A summary of the adhesion tension values obtained for the different liquids against barite is given in tables 1 and 2. Each of the values is the average of several separate determinations. The equations used and methods of calculating results have been presented in previous articles from this laboratory. The three liquids, benzene, carbon tetrachloride, and water were used to determine the pore radius (*r*). The radii as determined with these liquids showed excellent agreement. The adhesion tension values obtained for the series of liquids against barite were of the same order of magnitude as those which had been obtained for these liquids against silica (8) and against aluminum oxide (7). Table 3 gives the adhesion tension values obtained with five different liquids against these three different solids. In checking the data obtained in two hundred thirty-three different measurements made with these three different solids by the receding contact angle method, it was found that the largest average deviation in any one system was less than 1.5 per cent.

TABLE 3

Comparison of adhesion tension values for hydrophilic solids

SOLIDS	α-BROMONAPHTHALENE	ACETYLENE TETRABROMIDE	BENZENE	BUTYL ACETATE	WATER
Barite	39.9	40.5	44.3	64.6	76.4
Aluminum oxide (7)	40.1	43.0	45.0	64.5	76.7
Silica (8)	39.6	42.8	44.1	64.5	76.7
Silica (2) (Single capillary method)	41.1	43.3	45.4	66.6	75.9
Calcium fluoride (1)	43.0	—	50.1	65.2	76.5

The fact that these hydrophilic solids tend toward similar adhesion tension values indicates that they possess free surface energy values of the same order of magnitude.[1] It has been noted also that these solids exhibit similar behavior in settling experiments. With a series of liquids the degree of packing of the powders of these different solids on settling is always in the same order and usually of the same magnitude. It would be unreasonable to assume that all the solids per se possess the same free surface energy values. It would be more reasonable to assume that their surfaces when exposed to atmospheric conditions become altered. Probably water vapor

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[1] Bartell and Osterhof (5) have pointed out that the adhesion tension values which they obtained for different liquids against Tripoli, based on a water–Tripoli value of 81.5 dynes, are about 6 dynes higher than the values obtained with the same liquids against other silicas by other investigators (2, 8). Their value of 81.5 dynes was established with the use of only one contact angle liquid, α-bromonaphthalene. We are inclined to believe that this one measurement is in error, inasmuch as the values they obtained with other liquids (assuming the reference value above mentioned to be in error) are similar to those obtained by other investigators. If it be true that this value is in error, it follows that the adhesion tension values of all the hydrophilic solids measured thus far give values of approximately the same magnitude.

is adsorbed. We are led to agree with other investigators (10, 13, 15, 16) that a primary water film is tenaciously adsorbed on the surface of hydrophilic solids and that the water molecules are definitely oriented.

Although considerable care has been exercised in all the displacement pressure researches in this laboratory to produce a reasonably clean surface on the solids used, it is doubtful if the procedure followed has prevented the formation of a water film (which may or may not be complete, i.e., it may be polymolecular or even monomolecular in thickness) on the capillary surfaces of the powdered membrane at some time before the final measurement was made. With the barite and aluminum oxide investigations conditions were certainly favorable for the formation of a complete water film, for the equilibrium pressure measurements were made by forcing the organic liquid into membranes which were already wetted by water. Under these conditions, however, it could be shown experimentally that this film was such that it possessed properties different from those of a liquid in mass. For example, when the organic liquid was forced into the water-wet barite membrane rapidly by building up an opposing pressure considerably above the equilibrium pressure and then the system allowed to come to an apparent equilibrium, in a short time a pressure was obtained which was the same as the pressure value demanded by a zero interfacial angle, that is a value of $A_{13} - A_{12}$ equal to the interfacial tension value of the organic liquid–water system was obtained. This indicated the presence of a complete water film, having the properties of a plane surface of water. In other words, this procedure gave a method, as had been previously pointed out (8), for measuring interfacial tension of organic liquid against water in water-wet capillaries. On the other hand, if the opposing pressure was built up slowly so that the organic liquid displaced the water slowly and the equilibrium pressure was only slightly exceeded, then a stable equilibrium condition was finally reached at a pressure lower than that demanded by the interfacial tension value. This indicated that a finite contact angle had formed and indicated further that no complete water film was present which possessed the property of a plane surface of water. The values given in tables 1 and 2 were obtained by the latter method.

It has previously been shown (2, 8) that the same values for adhesion tension of a given organic liquid against a solid are obtained by measurement of the solid–organic liquid–air contact angle as are obtained by measurement of the solid–organic liquid–water contact angle. The question may be raised as to the reliability of the adhesion tension data obtained with the pressure of displacement method, particularly with solids whose surfaces are not distinctly free from water films. Will data obtained enable one to detect differences in surface conditions of a strongly hydrophilic solid? The answer is that the data obtained are indicative of the nature of the surfaces as they actually exist, and that such data do enable one to predict the behavior to be expected with solids possessing such surfaces.

SUMMARY

A modification of the original pressure of displacement method for determining adhesion tension, termed a receding contact angle method, is described in some detail. This method is far more rapid, is easier to operate, and can be used with less danger of experimental error than the original method. An improved method is described for the preparation of membranes from finely divided powders. This method involves packing of powder by tamping. A tamping apparatus is described which gives a uniformly packed powder. The adhesion tension value of each of a series of liquids against barite is given. Comparison of the adhesion tension values of each of a series of liquids against each of several different hydrophilic solids shows that corresponding values are of very nearly the same magnitude. From this fact the conclusion is drawn that the surfaces of strongly hydrophilic solids are covered with an adsorbed film of water which gives to these solid surfaces such properties that their measured free surface energy values are of the same order of magnitude.

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ALTERATION OF THE SURFACE PROPERTIES OF STIBNITE AS REVEALED BY ADHESION TENSION STUDIES

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For adhesion tension studies, solids may be divided into two classes, hydrophilic solids which are wet more readily by water than by organic liquids, and hydrophobic solids which are wet more readily by organic liquids than by water.

Silica and oxides in general are hydrophilic. Carbon and various sulfides are hydrophobic. Quantitative experiments on Prussian blue indicate that it has non-selective wetting properties and is wet as readily by organic liquids as by water. Different hydrophilic solids show different degrees of preferential wetting by water, and different hydrophobic solids show different degrees of preferential wetting by organic liquids. In the present investigation a series of solids was sought whose wetting characteristics would cover the range from the extremely hydrophobic type to the extremely hydrophilic type. A major aim of this investigation was the correlation of the changes in free surface energy which occur when such a series of solids is wet by liquids.

Sulfides such as stibnite are slightly unstable at ordinary temperatures, and at slightly elevated temperatures they are readily oxidized. Preliminary tests showed that ordinary stibnite, Sb_2S_3, was hydrophobic, though not so strongly hydrophobic as carbon. Samples of stibnite were therefore subjected to successive limited oxidations to determine whether the material so treated could be caused to change its properties, step by step, from a hydrophobic solid to a hydrophilic solid.

PREPARATION OF MATERIALS

A quantity of relatively pure stibnite was ground and carefully graded. Samples of this stibnite will be referred to as stibnite A. Other samples of stibnite were prepared by heating stibnite A to 170°C. for different lengths of time. The series of stibnites was as follows:

Stibnite A = Unheated, finely ground stibnite graded to 250 to 300 mesh and air floated. Mixed thoroughly in a rotating cylinder for 2 hours.
Stibnite B = Stibnite A heated 1 hour
Stibnite C = Stibnite A heated 2 hours

Stibnite D = Stibnite A heated 3 hours
Stibnite E = Stibnite A heated 4 hours
Stibnite F = Stibnite A heated 5 hours
Stibnite G = Stibnite A heated 6 hours
Stibnite H = Stibnite A heated 8 hours
Stibnite I = Stibnite A heated 8 hours (400–420°C.) in a nitrogen atmosphere containing 0.7 per cent oxygen. This sample was graded to 250 to 300 mesh, but was not air floated.

Preliminary tests showed that stibnite I was hydrophilic and that each of the stibnites in the series with progressive degrees of oxidation was progressively less hydrophobic than stibnite A. It was observed also that if stibnite I were treated with hydrogen sulfide gas for a few minutes at a slightly elevated temperature, it could be converted back into the hydrophobic type.

TABLE 1

Adhesion tension data for water against different stibnites

Water–air–stibnite system

S_3 = 72.08 dynes per centimeter

STIBNITE	$r \times 10^{-4}$ CM.	P	COS Θ_{13}	Θ_{13}	A_{13}
		grams per cm².			*dynes per cm.*
A	8.52	135	0.785	38°	56.5
B	8.52	137	0.794	37°	57.2
C	8.52	139	0.806	36°	58.1
D	8.52	144	0.836	33°	60.3
E	8.52	154	0.890	27°	64.2
F	8.52	159	0.922	23°	66.5
G	8.52	169	0.979	12°	70.5
H	8.52			0°	76.0*
I	11.1			0°	77.1*

* Values obtained from interfacial contact angle determinations.

In addition to the stibnite powders, aluminum oxide was also used. It was graded to 300 to 350 mesh by sieving. The powder was treated twice with boiling hydrochloric acid (1:1) and allowed to stand in contact with the acid for several hours. It was washed six times with hot distilled water and was then washed twenty times with boiling distilled water while being filtered. It was dried at 110°C., then heated at 400° to 480°C. for 2 hours. The powder was thoroughly mixed, then heated at 510^5 to 530°C. for 8 hours and again mixed.

LIQUIDS

The water used was twice distilled and the accepted surface tension of 72.08 at 25°C. was used in all calculations for water.

The organic liquids used were very carefully purified and their surface tensions and interfacial tensions against water were determined and used in all calculations.

METHOD AND APPARATUS

The displacement pressure cells and method used in this investigation for the determination of adhesion tension were the same as developed by Bartell and Jennings (3). The temperature was maintained constant in an air thermostat at 25°C. ± 0.05°C.

TABLE 2

Adhesion tension data for contact angle liquids against stibnites H and I

STIBNITE	LIQUID	$r \times 10^{-4}$ CM.	P	θ_{12}	cos θ_{12}	S_1	A_{12}
			grams per cm².			*dynes per cm.*	*dynes per cm.*
H	α-Bromonaphthalene	8.52	104	8°	0.988	44.00	43.5
I	α-Bromonaphthalene	11.1	73.5	25°	0.910	44.00	40.0
I	Acetylene tetrabromide	11.1	79.8	28°	0.885	49.07	43.4

TABLE 3

Comparison of adhesion tension data of several liquids as determined against stibnite A and stibnite I

LIQUID	STIBNITE A ($r = 8.52 \times 10^{-4}$ CM.)					STIBNITE I ($r = 1.11 \times 10^{-3}$ CM.)		
	Surface tension	Interfacial tension	P	Cos θ_{23}	Adhesion tension	P	Cos θ_{23}	Adhesion tension
	dynes per cm.	*dynes per cm.*	*grams per cm².*		*dynes per cm.*	*grams per cm².*		*dynes per cm.*
1. Water	72.08	—	135	—	56.5	—	—	77.1*
2. Isoamyl alcohol	22.90	5.00	8.12	−0.679	59.9	5.70	0.621	74.0
3. *n*-Butyl acetate	24.06	13.17	23.0	−0.729	66.1	22.3	0.923	64.9
4. Benzene	28.22	34.31	52.3	−0.638	78.4	58.2	0.924	45.4
5. Acetylene tetrabromide	49.07	38.32	58.9	−0.642	81.1	79.8	—	43.4
6. α-Bromonaphthalene	44.00	41.57	68.2	−0.686	85.0	73.5	—	40.0
7. *n*-Heptane	19.80	49.40	69.9	−0.592	85.7	81.4	0.897	32.8

* Value obtained from interfacial contact angle determination.

ADHESION TENSION AND CONTACT ANGLE MEASUREMENTS

From pressure of displacement measurements it was found that with progressive oxidation of the stibnite surface, the contact angle between water and solid decreased progressively. This is shown from the data presented in table 1. The adhesion tension values for water against all the solids except stibnite H and stibnite I were determined directly from the solid-liquid-air displacement pressure data (4) and the values obtained ranged between 56.5 and 70.5 dynes per centimeter. Adhesion tension values for α-bromonaphthalene and acetylene tetrabromide against stibnite H and stibnite I were also determined directly. Having this latter data, the adhesion tension value of water against each of the two solids was obtained indirectly from liquid-liquid-solid displacement pressure data by using in turn each of these organic liquids and water against each of the stibnites. Stibnite H gave an adhesion tension value with water of 76.0 dynes per centimeter, and stibnite I gave a value of 77.1 dynes per centimeter (table 1).

TABLE 4

Adhesion tension data of zero contact angle liquids against different stibnites

Water-organic liquid-stibnite systems

STIBNITE	$r \times 10^{-4}$ cm.	A_{12}	BENZENE				n-BUTYL ACETATE				α-BROMONAPHTHALENE			
			P	Θ_{23}	$\cos \Theta_{23}$	A_{13}	P	Θ_{23}	$\cos \Theta_{23}$	A_{13}	P	Θ_{23}	$\cos \Theta_{23}$	A_{13}
		dynes per cm.	*gm. per cm².*			*dynes per cm.*	*gm. per cm².*			*dynes per cm.*	*gm. per cm².*			*dynes per cm.*
A	8.52	56.5	52.3	130°	−0.638	78.4	23.0	137°	−0.729	66.1	68.2	134°	−0.686	85.0
B	8.52	57.2	46.5	124°	−0.566	76.6	22.0	134°	−0.697	66.4	60.2	127°	−0.605	82.4
C	8.52	58.1	42.9	121°	−0.529	76.0	18.5	126°	−0.587	65.8	55.2	124°	−0.555	81.2
D	8.52	60.3	29.4	111°	−0.358	72.6	13.0	114°	−0.414	65.8	38.8	113°	−0.389	76.4
E	8.52	64.2		>90°				>90°				>90°		
F	8.52	66.5		<90°				<90°				<90°		
G	8.52	70.5	37.0	63°	−0.452	55.0	13.1	65°	−0.417	65.0	38.4	68°	−0.386	54.5
H	8.52	76.0	69.4	32°	−0.845	47.0	26.7	31°	−0.854	64.8	77.6	39°	−0.780	43.5
I	11.1	77.1	58.2	22°	−0.924	45.4	22.3	23°	−0.923	64.9	68.0	27°	−0.891	40.0

Interfacial angle <90°—water displaces organic liquid.
Interfacial angle >90°—organic liquid displaces water.

TABLE 5

Adhesion tension data for several liquids against aluminum oxide

$r = 8.42 \times 10^{-4}$ cm.

LIQUID	P	$\cos \Theta_{23}$	ADHESION TENSION
	grams per cm².		*dynes per cm.*
1. Water	—	—	76.7*
2. Isoamyl alcohol	6.77	0.556	73.9
3. n-Butyl acetate	29.4	0.924	64.5
4. Benzene	76.7	0.924	45.0
5. Acetylene tetrabromide	104	0.878	43.0
6. α-Bromonaphthalene	97	0.884	40.1
7. n-Heptane	105	0.877	33.4

* Value obtained from interfacial contact angle determination.

A comparison of adhesion tension data of several liquids against stibnite A and stibnite I may be made from the data given in table 3. Adhesion tension data for a series of liquids against the different stibnites are given in table 4. Data for a series of liquids against aluminum oxide are given in table 5.

CORRELATION OF ENERGY CHANGES OCCURRING ON THE WETTING OF SOLIDS

Bartell and Osterhof (1) had observed that when the adhesion tension values of carbon and silica were compared, the order of increasing adhesion tension values for the one solid against a series of liquids was just opposite to the order of increasing adhesion tension values of the other solid against this same series of liquids. They suggested (5) that the results might be correlated diagrammatically so as to show linear relationships for the adhesion tension values of a series of liquids against a series of solids when these values are plotted against the wetting characteristics of the solids. This proposed relationship had but little significance at the time, inasmuch as no adhesion tension data were available for systems whose wetting characteristics were intermediate between those of carbon and silica, with the exception of qualitative data on Prussian blue which showed that it was

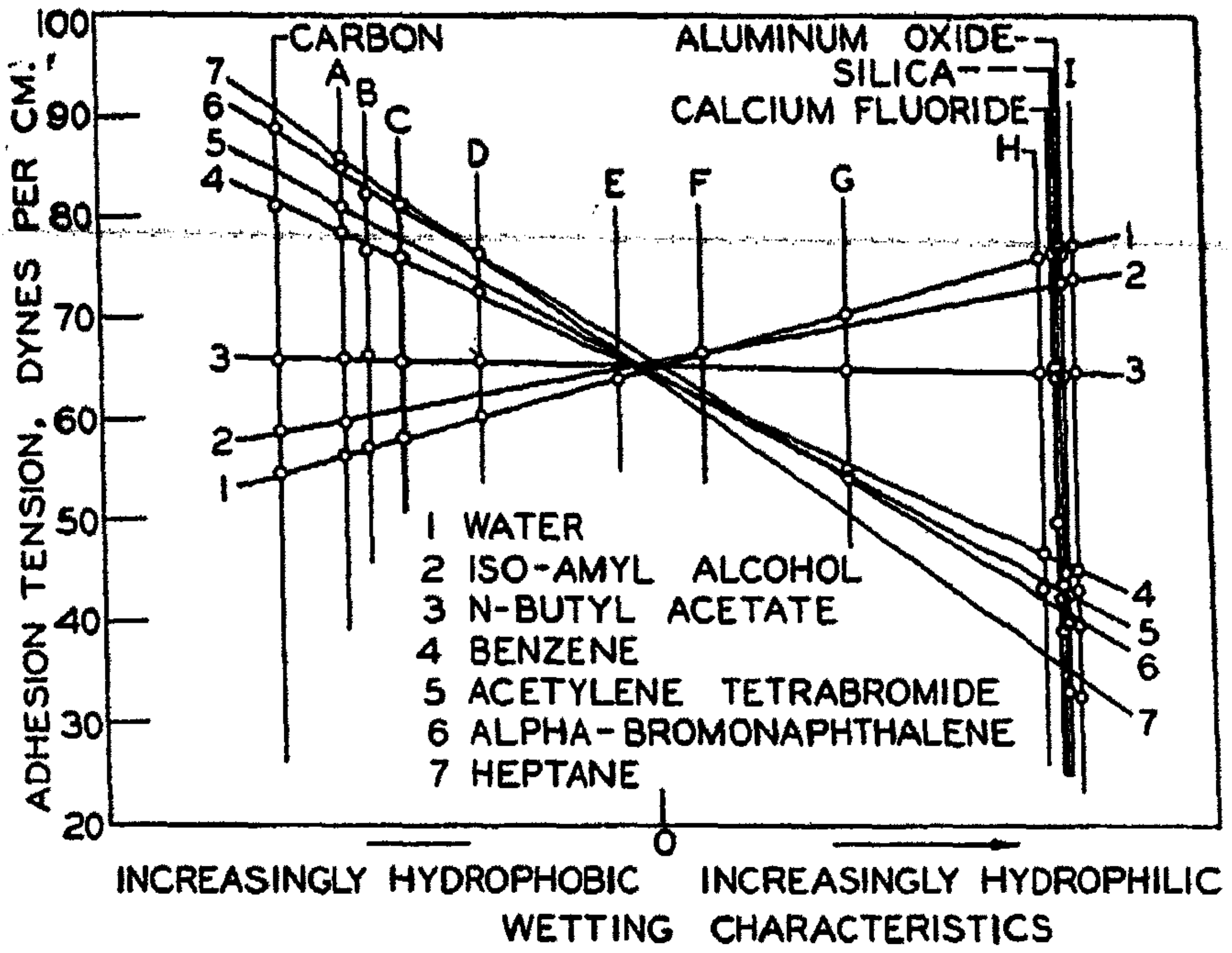

FIG. 1

wetted to practically the same degree by all the liquids used. Its wetting characteristics would then place it near the middle of such a diagram.

In this proposed diagram the adhesion tension values of the different liquids (i.e., liquids No. 1, 2, 3, 4, and 5) were to be plotted as ordinates and wetting characteristics, in arbitrary units, as abscissae. Such a diagram was constructed and an attempt was made to place the values for the different stibnites on it.

The adhesion tension values for carbon and silica were placed in vertical positions at the ends of the wetting characteristics axis. A straight "tie line" was drawn to connect the adhesion tension values for water against these solids. The positions for the adhesion tension values of water against the different stibnites were located upon this tie line and a vertical line drawn through each point. It was a fact of great interest that the adhesion tension values for the different liquids against each of the different stibnites were found to correspond to the ordinates of points on the "tie lines" set up between carbon and silica where these "tie lines" were intersected by the vertical lines. These relationships are shown in figure 1.

It may be noted that heat treatment of the original stibnite A for 1-hour and 2-hour periods had but little effect on the adhesion tension values. As the time of heating was increased, the surface energy changes were found to be greater and the state of the solid surface to have progressed toward that of the hydrophilic solids.

The adhesion tension values for water and for isoamyl alcohol against the solid were observed to have increased in a linear manner with increase of surface oxidation. The adhesion tension values for heptane, benzene, α-bromonaphthalene, and acetylene tetrabromide were observed to have decreased in a linear manner with increased oxidation. The adhesion tension of n-butyl acetate was observed to have remained at practically the same value for all samples of stibnite regardless of degree of oxidation. This liquid appeared to wet all the solids to practically the same degree.

The adhesion tension data for other solids against the same series of liquids were collected and also plotted (figure 1). The similar wetting tendencies of the hydrophilic solids should be noted.

It will be seen that as the middle of the diagram is approached from either side, the difference in energy levels becomes less and less, hence the degree of selective wetting of the different solids by given liquids becomes correspondingly less and less. At the center of the diagram the "tie lines" have almost a common point of crossing. If this were actually a common point, it would represent a "point of non-selective wetting." The interfacial contact angle at this point would be exactly 90°. If a solid possessed surface properties represented by this position on the diagram, it would be wetted equally well by all liquids (at least by liquids of the type of those studied). At this "point of non-selective wetting" all interfacial energy levels would be the same, and hence the adhesion tension values of all liquids against the solid would be the same. In a displacement pressure cell there would be no displacement of liquid by liquid (organic liquid–water) in either direction. That liquid which wetted the powder first would not tend to be displaced by the second liquid. Stibnites E and F fall near the middle of the diagram. The difference in energy levels of the different liquids against these solids was so low that accurate measurement of them was not possible. Accordingly adhesion tension values of the organic liquids against these solids were not determined. Our only criterion of their surface condition (i.e., the hydrophilic or hydrophobic nature) was obtained through the adhesion tension value of water, which was determined by measurement of the solid–water–air contact angle.

In passing outward in either direction from this region of non-selective wetting, the difference in energy levels becomes greater and greater. The ease with which one liquid will displace another from the solid becomes correspondingly greater.

QUALITATIVE TESTS FOR THE DETERMINATION OF RELATIVE DEGREE OF WETTING

When the quantitative work of the relative degree of wetting had been practically completed, it was decided to make some qualitative tests which might give further and optically convincing evidence that the surface properties of the original stibnite had been altered in a definite and regular manner. It was hoped that those tests might be indicative of the practical importance of the data obtained. Two series of qualitative tests were run. One series will be designated as the "drop on powder test" and the other as the "degree of packing upon settling test."

Drop on powder test

In the first series of tests a drop of water was placed on smoothed out samples of the different powdered stibnites. When placed on stibnite A the drop appeared to give a large contact angle against the powder and showed no tendency to disappear into the powder, but persisted until the water evaporated. When the stibnites with the progressively altered surface characteristics were tested, the drops of water which remained upon them were progressively smaller and the contact angles formed likewise were progressively smaller. When water was placed on stibnites H and I no drops formed, the angle of contact of water against the solid was zero, the water wetted the stibnite completely and disappeared entirely into the powder. The results obtained in this series of tests were what one might expect to obtain with a series of powders with surface properties ranging from strongly hydrophobic to strongly hydrophilic.

Degree of packing on settling test

In the second series of tests the powdered solid was suspended in liquid media and observations were made of the degree of packing of the powder on settling. This test was suggested by work previously done on "liquid absorption" (1, 2). Altogether six separate experiments were run.

The six experiments were as follows: (1) water, (2) *n*-butyl acetate, and (3) α-bromonaphthalene, with each of the nine different stibnites, and (4) stibnite A, (5) stibnite E, and (6) stibnite I with each of the seven different liquids.

In each of the experiments 10 g. of powder, together with 7 cc. of liquid, was put into each of a series of test tubes of uniform diameter, thoroughly mixed, and allowed to settle. The stibnite samples were similar to, but not the same as, those that were used in the adhesion tension work. The tests were made upon finely ground, ungraded stibnite which had been subjected to the same treatment as the previously described samples of graded powders. The symbols used to indicate the different heat treatments are the same as those used for the graded powders. The liquids used were numbered as for the adhesion tension experiments, viz., 1 = water, 2 = isoamyl alcohol, 3 = *n*-butyl acetate, 4 = benzene, 5 = acetylene tetrabromide, 6 = α-bromonaphthalene, and 7 = *n*-heptane. The test tubes labeled X contain 10 g. of stibnite, but no liquid medium.

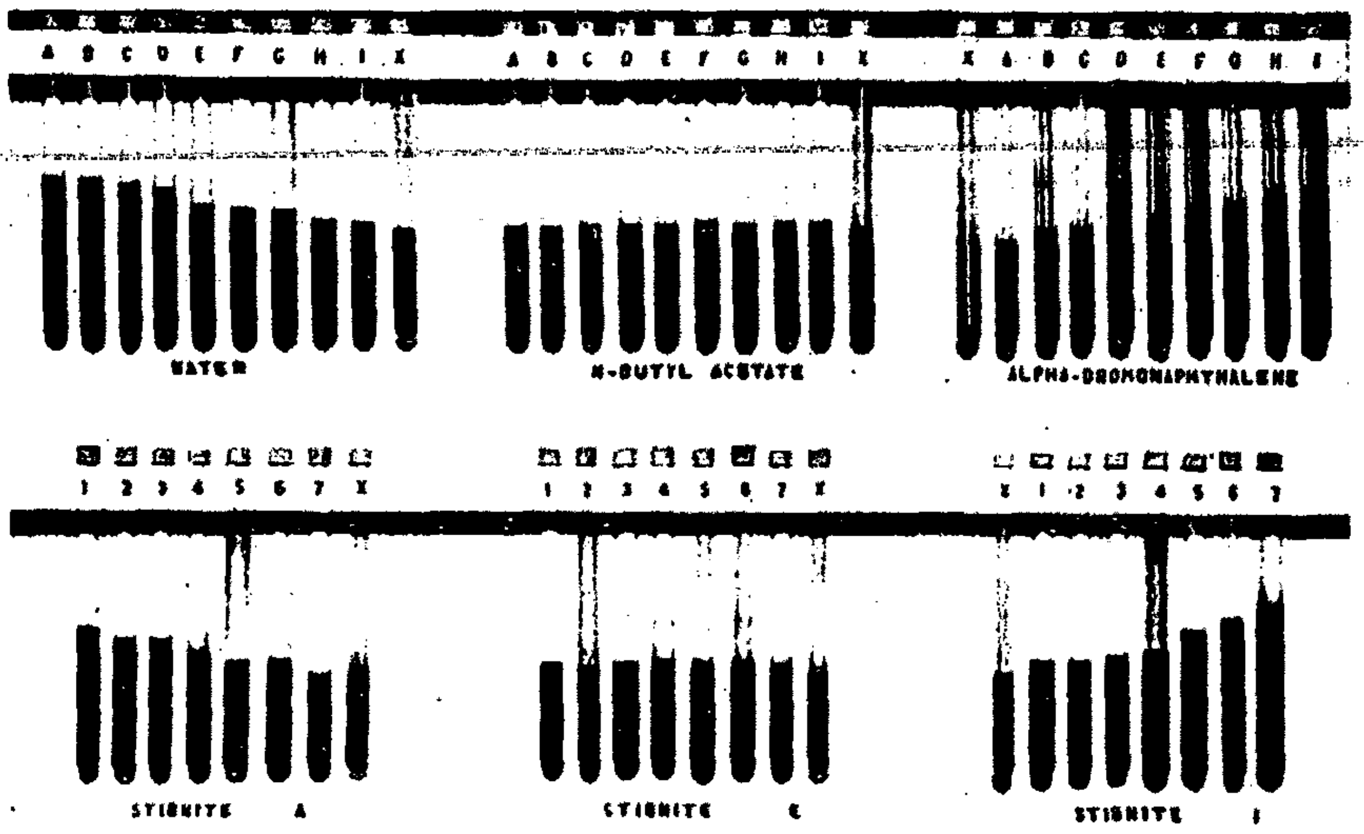

FIG. 2

A photograph of the tubes, figure 2, clearly presents the results obtained. The photograph was taken about a week after the settling test was started.

After four months the heights of the settled powders were practically unchanged. A similar set of settling tests made with finely divided silica (Silex) gave similar effects upon settling and the heights of the different powders have remained unchanged for a period of over two years.

The results obtained in each of the six experiments mentioned may be briefly summarized in the statement that the degree of packing of the powder upon settling is greatest in that liquid against which it possesses the greatest adhesion tension and is progressively less in those liquids against which it has a progressively lesser adhesion tension.

The experiments showed conclusively that the surface properties of the stibnites were altered by the simple heat treatment. They showed that it is possible to alter greatly the preferential wetting properties of certain solids; that one can cause surfaces to function either as hydrophobic or hydrophilic surfaces. Moreover, it is possible to reduce surfaces to a condition in which they show no selective wetting tendency, that is, they are preferentially wetted neither by water nor by organic liquids.

In the present paper we shall make no attempt to discuss the character of the different surfaces studied, nor of the theories pertaining to the change in surface properties. It may be of interest to mention that the appearance of the surfaces was unaltered, the particle size of the powder was unaltered, and the pore radii formed with each sample of the different graded powders were the same. This work is being considerably extended in our laboratories and we expect to present more comprehensive generalizations in the near future.

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X-RAY STUDIES ON THE HYDROUS OXIDES. IV

TITANIUM DIOXIDE

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Tetravalent titanium, like tin, is said to form two distinct acids: ortho- or alpha titanic acid and meta- or beta titanic acid. Since the work of several investigators has shown that the stannic acids (13) are in reality hydrous stannic oxides differing essentially in the size of the primary particles, it seems not unlikely that the so-called titanic acids are also hydrous oxides whose properties are determined by the size and physical character of the particles.

The product commonly called orthotitanic acid, or alpha titanic acid, is a white gelatinous precipitate formed by the addition of ammonia or alkali hydroxide to a solution of a tetravalent titanium salt. The highly hydrous gel is readily soluble in dilute acids and is easily peptized by dilute alkalies and suitable salts to give stable sols. On the other hand, the product referred to as meta titanic acid, or beta titanic acid, is a granular, difficultly soluble, and but slightly peptizable substance obtained (a) by the interaction of nitric acid and titanium, (b) by the aging under water of the precipitated gel of the so-called orthotitanic acid slowly in the cold and more rapidly in the hot, (c) by precipitation in the hot, and (d) by hydrolysis of solutions of tetravalent titanium salts.

The composition of the preparations referred to above varies with the method of precipitation and with the subsequent treatment. The only evidence for the existence of definite hydrates corresponding to the formulas of the acids that earlier investigators (2, 5, 9, 10, 11, 12) have assumed, is the analysis of the products formed and dried under arbitrary conditions. Carnelly and Walker (1) obtained a smooth temperature–composition isobar for a precipitated gel and hence concluded that no definite hydrates were formed, unless it is assumed that a large number exist, each stable over a very narrow temperature range. Morley and Wood (8) prefer to assume that the change from the so-called alpha to beta form consists of a condensation to complex salt-like compounds, but there is no experimental justification for this point of view. More recently Gutbier and coworkers (3) obtained smooth composition–temperature isobars for several preparations, indicating the absence of definite hydrates of titania.

No systematic study of the constitution of the alleged titanic acids has been made by the x-ray diffraction method. Hedvall (4) states that "titanium hydroxide" precipitated at some unspecified temperature is crystalline, since it gives a good interference pattern both when moist or when dried at room temperature. On the other hand Gutbier and coworkers (3) report that the freshly precipitated products give no interference pattern, but the gels thrown down with ammonia at 20°C. to 100°C. and subsequently ignited give the pattern of the mineral rutile or a mixture of rutile and anatase, and the product obtained by oxidizing $Ti_2O_3 \cdot xH_2O$, followed by heating to 490°C., gives the x-ray pattern of anatase.

In the following section will be given the dehydration isobars of two typical gels of titanium dioxide and the results of the x-ray examination of precipitated oxides obtained under widely varying conditions.

EXPERIMENTAL

1. Preparation of samples

Precipitation with ammonia. A solution of 17 g. of titanium tetrachloride in 75 cc. of 6 *N* hydrochloric acid was treated with ammonia at room temperature and the resulting precipitate washed thoroughly by decantation by the aid of the centrifuge until only a trace of chloride remained. This sample, which will be designated as No. 1, was treated in different ways, as given in table 2. A second sample, designated as No. 6, was prepared by treating a boiling solution of the tetrachloride with a small excess of ammonia, boiling the mixture for 15 minutes, and finally washing and drying like sample No. 1.

Oxidation of $Ti_2O_3 \cdot xH_2O$. A solution of 8 g. of titanium trichloride in 100 cc. of water was treated with 15 cc. of 15 *N* ammonia, the mixture diluted to 400 cc. and allowed to oxidize in the air. The original black precipitate changed rapidly to a gray color which changed slowly to white on conducting a current of air into the suspension. This precipitate (No. 2) was thoroughly washed and air-dried at room temperature.

Hydrolysis. A dilute solution of titanium tetrachloride in hydrochloric acid was hydrolyzed by boiling for four hours, using a reflux condenser. The resulting granular precipitate was washed with hot water and air-dried at room temperature. Similar preparations were made by hydrolysis of the nitrate and sulfate.

2. Isobaric dehydration

Temperature-composition isobars for sample No. 1 precipitated at room temperature and sample No. 2 made by oxidation of $Ti_2O_3 \cdot xH_2O$ were obtained in the following way. The samples in glass-stoppered weighing bottles were placed in a thermostated electric oven through which dry air was circulated at the rate of 72 liters per hour. The air was dried by passing it through a large calcium chloride tower, a sulfuric acid bottle, and finally through a tower filled with glass wool and phosphorus pentoxide.

TABLE 1

Thermal dehydration isobars of hydrous titanium dioxides

TEMPERATURE	COMPOSITION MOLES H_2O/TiO_2		TEMPERATURE	COMPOSITION MOLES H_2O/TiO_2	
	No. 1 Pptd. at room temperature	No. 2 Oxidation of $Ti_2O_3 \cdot xH_2O$		No. 1 Pptd. at room temperature	No. 2 Oxidation of $Ti_2O_3 \cdot xH_2O$
degrees C.			*degrees C.*		
35.1	0.970	1.030	122.5	0.288	0.291
71.3	0.562	0.590	150	0.218	0.217
87.2	0.425	0.454	184	0.184	0.154
92.6	0.415	0.402	205	0.114	0.101
100.0	0.362	0.361	224	0.081	0.084
105.4	0.308	0.306	255	0.054	0.061
110.0	0.295	0.296	270	0.046	0.053

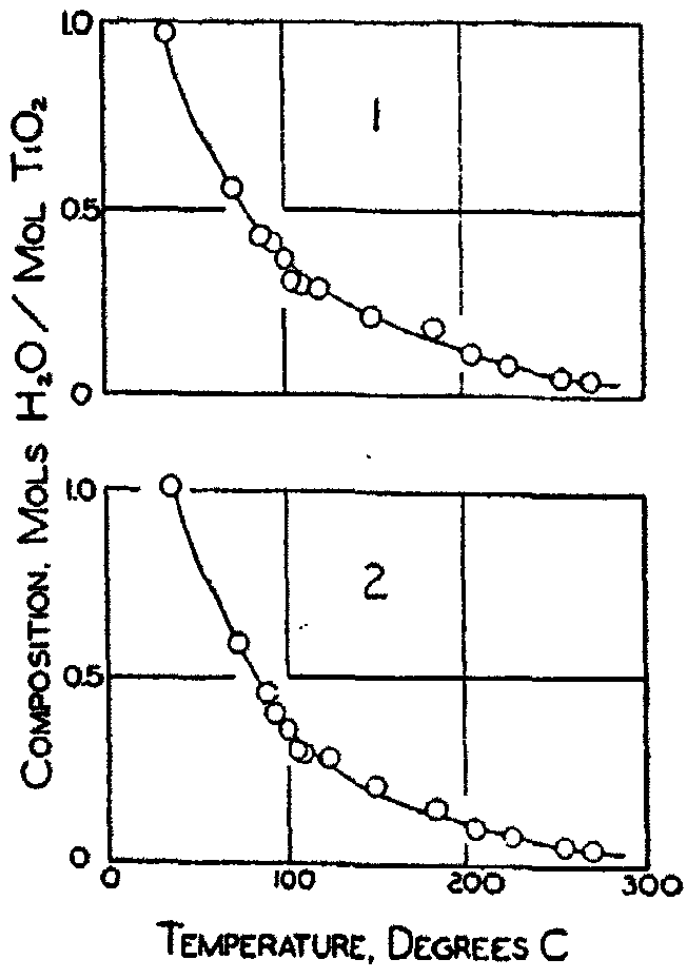

FIG. 1. DEHYDRATION ISOBARS OF HYDROUS TiO_2

1. Precipitated at room temperature. 2. Made by oxidation of $Ti_2O_3 \cdot xH_2O$ in air.

The rate was measured with a calibrated oil-filled flow meter left permanently in the line. The air was filtered through cotton just before passing into the oven. The air was preheated by passing through a 15-foot coil of glass tubing inside the oven and was then conducted into a small enameled pan with a loose fitting cover, which held the samples. This arrangement is similar to that of L. H. Milligan (6). The temperatures were measured with standardized thermometers and a standardized thermocouple. The temperature was kept constant to within 1 to 2°C. To attain equilibrium conditions at a given temperature, each sample was heated at least four days and in some cases for as long as thirty days. In general, less time was required to attain equilibrium at higher than at lower temperatures. The results are given in table 1 and figure 1. In agreement with the results of Gutbier, the smooth isobars for both samples indicate the absence of hydrates of the oxide corresponding to the alleged acids.

TABLE 2

X-ray examination of hydrous titanium dioxides

SAMPLE NO.	METHOD OF PREPARATION	RESULTS
1	Precipitated at room temperature	No visible lines or bands
3a	No. 1 aged at room temperature 14 weeks	No visible lines or bands
3	No. 1 aged at room temperature 30 weeks	Anatase pattern, very broad bands
5	No. 1 aged 6 hours at 100°C.	Anatase pattern, broad bands
4	No. 1 heated to 184°C.	Anatase pattern, broad bands
11	No. 1 heated to 1000°C.	Rutile pattern (and trace of anatase?)
6	Precipitated at 100°C.	Anatase pattern, broad bands
2	Oxidation of $Ti_2O_3 \cdot xH_2O$	No lines or bands visible
14	No. 2 heated to 184°C.	No lines or bands visible
12	No. 2 heated to 1000°C.	Rutile pattern (and trace of anatase?)
9	Hydrolysis of $TiCl_4$	Rutile pattern, broad bands
9a	Hydrolysis of $Ti(NO_3)_4$	Rutile pattern, broad bands
7	Hydrolysis of $Ti(SO_4)_2$	Anatase pattern, broad bands
10	Mineral rutile, TiO_2	Rutile pattern, sharp lines
8	Mineral anatase, TiO_2	Anatase pattern, sharp lines
13	Mineral brookite, TiO_2	Brookite pattern, sharp lines

3. X-ray analysis

The specimens listed in table 2 were examined as described in preceding papers of this series. The diffraction data are given in table 3 and are shown in chart form in figure 2 for purposes of comparison.

Densitometer curves of the films from samples 1, 4, 6, and 8 are given in figure 3. These curves were obtained with a simplified and inexpensive recording photodensitometer that has already been described (7). From these data it is apparent that the samples precipitated in the cold give little or no x-ray diffraction pattern, whereas both the aged oxide and the one thrown down at 100°C. give the anatase pattern. The precipitate freshly formed in the cold consists either of amorphous TiO_2 with adsorbed water or, what is more likely, of anatase crystals so minute that little or no x-ray diffraction effect is observed.

As already noted, Hedvall obtained an x-ray diffraction pattern with a precipitated titania. Since both Gutbier and ourselves failed to get a pattern with the cold precipitated oxide, it is probable that Hedvall's precipitate was obtained in the hot and that the pattern showed the lines of anhydrous TiO_2 (anatase modification) as we observed.

TABLE 3

X-ray diffraction data

SAMPLE NO. 4 (Heated at 184°C.)		SAMPLE NO. 5 (Aged at 100°C.)		SAMPLE NO. 6 (Pptd. at 100°C.)		SAMPLE NO. 8 (Anatase)		SAMPLE NO. 9 (Hydrolysis of $TiCl_4$)		SAMPLE NO. 10 (Rutile)		SAMPLE NO. 11 (Heated at 1000°C.)		SAMPLE NO. 12 (Heated at 1000°C.)	
D	I	D	I	D	I	D	I	D	I	D	I	D	I	D	I
3.50	10	3.50	10	3.50	10	3.49	10	3.24	10	3.24	10	3.51	1	3.23	10
2.37	5	2.37	6	2.37	5	2.37	5	2.48	8	2.48	9	3.24	10	3.00	1
1.890	8	1.890	8	1.890	8	1.883	8	2.18	3	2.29	1	2.48	8	2.84	1
1.669	5	1.695	5	1.694	6	1.695	6	2.045	2	2.18	4	2.29	1	2.47	8
1.472	5	1.670	5	1.675	6	1.655	6	1.685	10	2.04	2	2.18	5	2.29	1
1.260	4	1.480	5	1.471	5	1.477	5	1.616	3	1.685	10	2.05	2	2.18	3
1.160	3	1.360	2	1.356	1	1.358	2	1.480	2	1.617	3	1.895	1	2.11	1
		1.340	2	1.260	4	1.334	2	1.360	8	1.479	2	1.685	10	2.04	1
		1.261	3	1.160	3	1.261	4	1.337		1.448	2	1.623	3	1.89	1
		1.162	1			1.161	3	1.090	1	1.351	8	1.481	1	1.788	1
		1.04	1			1.044	2	1.038	1	1.240	1	1.450	1	1.683	10
						1.015	2			1.167	1	1.359	8	1.617	4
						0.951	1			1.144	1	1.242	1	1.474	1
						0.913	1			1.092	1	1.169	1	1.444	1
						0.892	1			1.037	1	1.145	1	1.428	1
						0.876	1					1.092	1	1.359	4
						0.843	1					1.039	1	1.345	4
						0.824	1							1.240	1
						0.806	1							1.167	1
						0.795	1							1.145	1
						0.740	1							1.093	2
						0.702	1							1.038	2
						0.668	1								

The samples ignited at about 1000°C. consist for the most part of rutile. Inspection of table 3 shows that sample No. 11 gives in addition to the rutile pattern very weak lines at 3.51 A.U. and 1.895 A.U. It will be observed that the two most intense anatase lines are 3.49 A.U. and 1.883 A.U. It seems likely that a small amount of unchanged anatase is present in this ignited sample. Sample No. 12 also consists of rutile with the addition of lines of weak intensity at 3.00 A.U., 2.11 A.U., 1.89 A.U., and 1.79 A.U. Since the sample was precipitated originally from $TiCl_3$ solution and oxidized in the air, it may contain some impurities not present in the other samples.

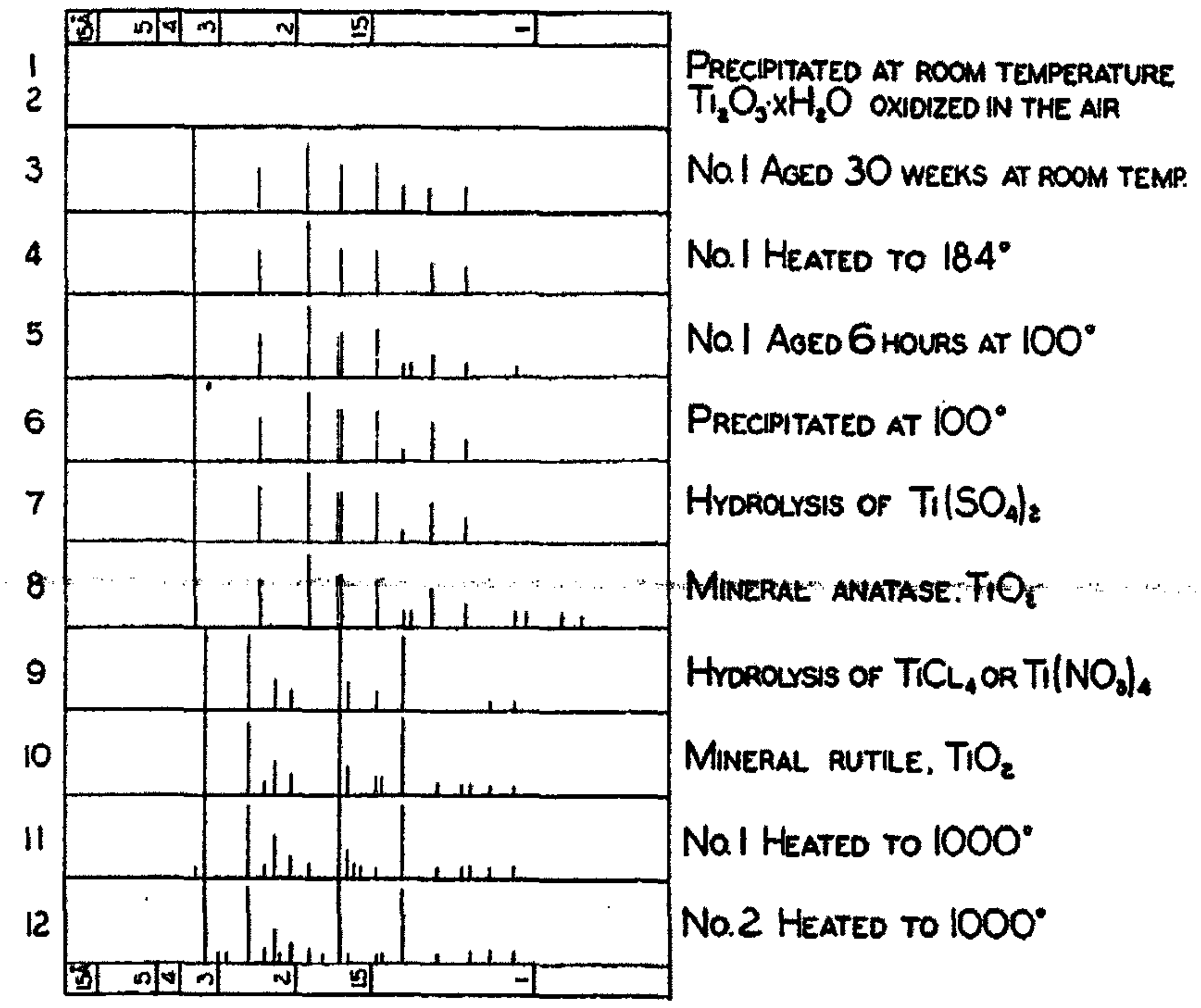

FIG. 2. CHART OF X-RAY DIFFRACTION PATTERNS

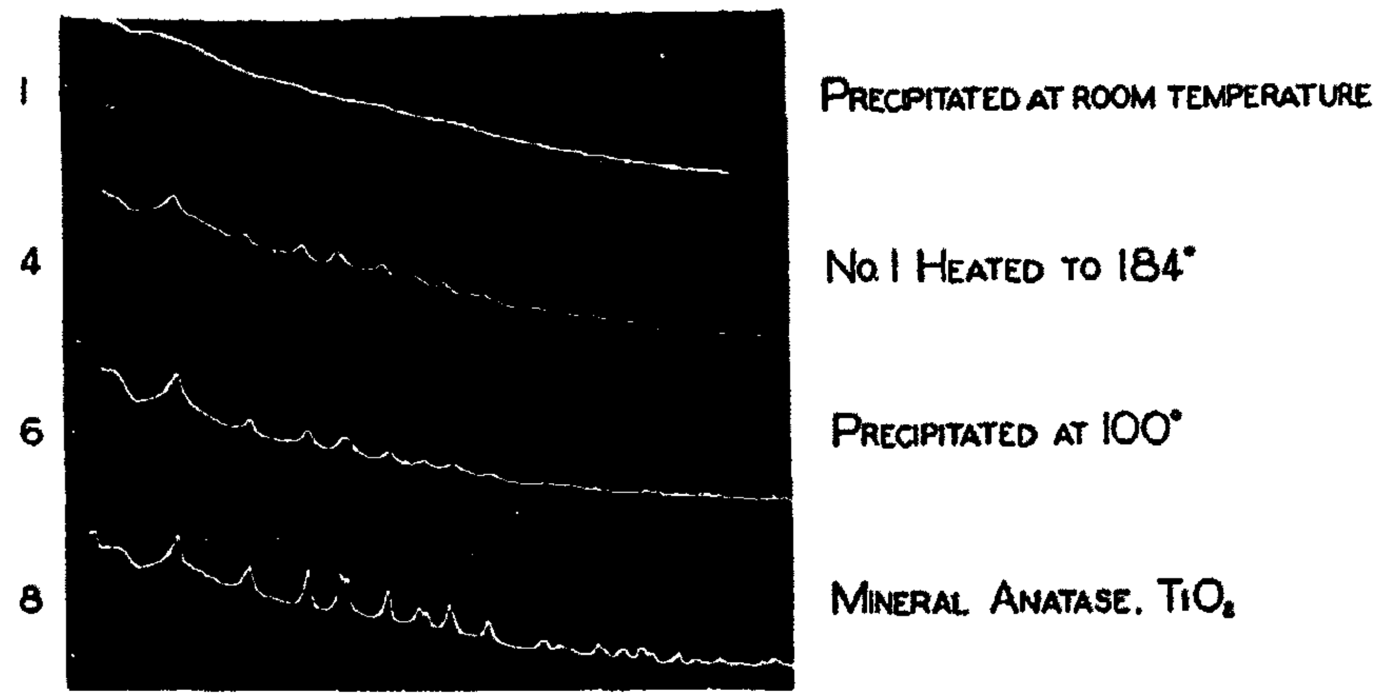

FIG. 3. DENSITOMETER CURVES OF X-RAY DIFFRACTION PATTERNS

SUMMARY

The following is a brief summary of the results of this investigation:

1. X-ray diffraction examination of hydrous titanium dioxide freshly precipitated at room temperature or freshly prepared by the oxidation in air of $Ti_2O_3 \cdot xH_2O$ gives no lines or bands. Thermal dehydration isobars for these two samples show the water to be given off in a continuous manner. The dehydration experiments of Gutbier and coworkers for their similar samples are confirmed. There is no indication of the existence of any definite hydrate.

2. Aging under water at room temperature for fourteen weeks of hydrous titanium dioxide precipitated at room temperature produces no change detectable by x-ray diffraction methods. Further aging of this sample for thirty weeks at room temperature or for 6 hours at 100°C. under water, gives minute anatase crystals; heating of the freshly formed material to 184°C. gives anatase.

3. Hydrous titanium dioxide precipitated at 100°C. shows the x-radiogram of anatase.

4. Hydrous titanium dioxide prepared by the hydrolysis at the boiling point of solutions of titanium tetrachloride and titanium nitrate, shows the x-radiogram of rutile, whereas hydrolysis of titanium sulfate under similar conditions gives anatase.

5. The product obtained by ignition at approximately 1000°C. of the hydrous oxide precipitated in the cold, shows the x-radiogram of rutile with indications of the presence of a little unchanged anatase.

6. X-ray analysis and thermal dehydration isobars indicate that no definite hydrates of titanium dioxide have been prepared.

7. Precipitated titanium dioxide is a hydrous oxide consisting, especially when precipitated or aged in the hot, essentially of anhydrous TiO_2 (anatase modification) and adsorbed water.

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HIGH CONCENTRATIONS OF RADIUM AND MESOTHORIUM I IN NATURE AND REGULARITY OF THEIR MIGRATION

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All beds of radioactive ores, as is well-known, are accumulations of uranium minerals. Accumulations of radium in large quantities have not been known without uranium and ionium. Usually it is considered that in nature there are neither concentrations of radium without parent elements nor separate radium minerals without uranium. Therefore, an individual geochemistry of radium without uranium and ionium seemed to be scarcely possible, owing to the short life of radium in the solid crust.

However, during the last few years several authors have published papers discussing discoveries of unexpected radium concentrations in natural waters (18), in which the radium was unaccompanied by corresponding equilibrium amounts of uranium.

The first papers, with results of analyses, were published in the Russian language and gave a great amount of material which is very interesting from many points of view. Namely, in the region of petroleum beds, some salt springs were discovered which contained radium in quantities up to 1.8×10^{-8} g. per liter of water.

Similarly, it was found by Cherepennikov that the spring which issues from the pit-hole "Kasennaya No. 1" in the petroleum district of Uchta in the northeastern part of European Russia contains 7.4×10^{-9} g. of radium per liter of water (4).

The precise radioactive and chemical analysis of the water of this pit-hole was carried out in the radiological laboratory of the University of Moscow, where the concentration of radium mentioned above was confirmed and a high concentration of mesothorium I was also found to be present.

Analyses of radium in the water from Grosny petroleum district were carried out in the Radium Institute of Leningrad and showed that the pit-holes No. 1/28, 3/28, and 1/31 contain 1.83×10^{-8} g. of radium per liter of water and that pit-hole No. 31/13 contains 3.5×10^{-9} g. of radium per liter of water (5).

The greatest amount of radium in the water of mineral wells and springs known previously was discovered by A. Becker (1) in the Radium-Sol-Terme of Heidelberg. It amounts to 1.79×10^{-9} g. of radium per liter of water, that is to say, the concentration is one-tenth of that in the new found radium-containing salt waters which are associated with the petroleum beds.

In table 1 are given the highest concentrations of radium in the newly found mineral springs under discussion and for comparison, the content of radium in the Radium-Sol-Terme of Heidelberg. In table 2 are given concentrations of radium discovered in the water of some other springs, together with old analyses of rich radium springs.

TABLE 1

Springs with the highest concentrations of radium

NAME AND GEOGRAPHICAL SITUATION OF THE SPRING	DEPTH OF THE PIT-HOLE AND OTHER CHARACTERISTICS OF THE WATER	CONTENT OF RADIUM IN GRAMS PER LITER OF WATER	AUTHOR
Pit-holes No. 1/28, 3/28, 1/31. Petroleum district Grosny. North Caucasus, Russia	600–700 meters. Layers of Chokraksky. Layer 13. Water without petroleum, contains SO_4^{--} ions	1.8×10^{-8}	B. A. Nikitin (1930)
Pit-hole No. 31/13. Petroleum district Grosny. North Caucasus, Russia	About 450 meters. Layers of Chokraksky. Layer 1. Water with petroleum emulsion contains SO_4^{--} ions	3.5×10^{-9}	B. A. Nikitin (1930)
Pit-hole "Kasennaya No. 1." Petroleum district of Uchta. Northeastern European Russia	Water without petroleum contains Ba^{++} and Cl^-; does not contain SO_4^{--} ions	7.4×10^{-9}	V. I. Baranov, I. D. Kurbatov, A. A. Cherepennikov (1928)
Radium pit-hole of Heidelberg in Germany	Depth of 998 meters. Salt-Terme	1.79×10^{-9}	A. Becker (1918)

The second fact of importance is the great flow of water, and accordingly the large quantity of radium brought up to the surface of the earth. The quantity of radium carried up by a group of springs in a single district often amounts to more than one gram per year.

Two scientific problems of special interest arise from these discoveries: (1) the geochemistry of radium, apart from that of uranium, in the earth's crust; (2) the development of a technique for separating the radium from salt waters without the necessity of using a large quantity of reagents.

MIGRATION OF THE RADIOACTIVE ELEMENTS RADIUM, MESOTHORIUM I, THORIUM X, AND RADIOTHORIUM IN NATURE

In studying the geochemistry of radium, it must first be made clear whether radium and its isotopes are formed directly from their parents in the mineral water of the spring, or whether they are extracted from the neighboring rocks.

TABLE 2

Springs of high radium concentrations

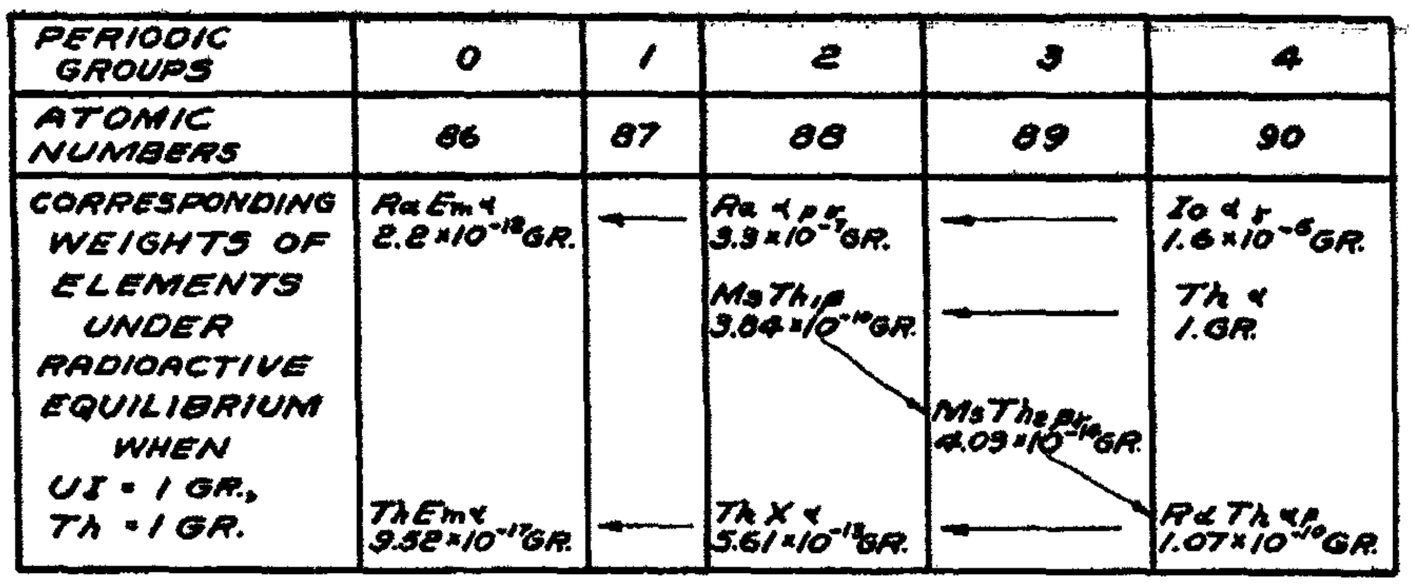
NAME AND GEOGRAPHICAL SITUATION OF THE SPRING	DEPTH OF THE PIT-HOLE AND OTHER CHARACTERISTICS OF THE WATER	CONTENTS OF RADIUM ELEMENTS IN GRAMS PER LITER OF WATER	AUTHOR
Pit-hole No. 1/35. Petroleum district of Grosny. North Caucasus. Russia	More than 1000 meters. Layer 22. Water with petroleum odor contains SO_4^{--} ions	3.0×10^{-10}	B. A. Nikitin (1930)
Pit-hole Stolb Berecley. Petroleum district Dagestan in Caucasus. Russia	—	3.0×10^{-10}	A. A. Cherepennikov (1928)
Spring Slavyanovsky. Watering place of Gelesnovodsk. North Caucasus. Russia	About 50 meters. The water is running from the trachyts of the Gelesnaya (mountain). Contains SO_4^{--} and Cl^- ions	2.21×10^{-10}	I. D. Kurbatov V. Baranov (1928)
Karlsbad, Czechoslovakia	Sprudel (9, 11)	1.0×10^{-10} 0.35 to 0.54×10^{-10}	W. Kolhorster (1912) H. Mache and F. Kraus (1928)
Saratoga, New York, America (12, 15, 16)	—	1.1×10^{-10} to 1.0×10^{-10}	H. Schlundt (1909), R. B. Moore and C. F. Whittemore (1914)
Bath, England (13)	—	1.4×10^{-10}	W. Ramsay (1912)

The parent substance of radium is ionium, that of mesothorium I is thorium, and that of thorium X is radiothorium. If radium and its isotopes are formed directly in the water, the parent substances of these elements would be present, either in quantities corresponding to radioactive equilibrium, or in amounts approximating it. It follows that we have to study the geochemistry of the radioactive elements—ionium, thorium and radiothorium—together with the geochemistry of radium and its isotopes.

The results of the radioactive analysis of the mineral springs cited above, as well as the method of analysis described, are naturally based on the chemical properties of these elements or on their place in the periodic system. Therefore, the genetic relation of these elements is given in figure 1 along with the weight proportions when in radioactive equilibrium.

We have studied the content of the radioactive elements, radium, mesothorium I, thorium X, and radiothorium, in mineral springs in the four watering places which are united under the title of mineral waters in North Caucasus.[1]

In this paper we will treat only the contents of radioactive elements in the spring waters of Gelesnovodsk, North Caucasus, and in the water of the pit-hole of the petroleum district of Uchta, North European Russia (see tables 3, 4, 5).



PERIODIC GROUPS	0	1	2	3	4
ATOMIC NUMBERS	86	87	88	89	90
CORRESPONDING WEIGHTS OF ELEMENTS UNDER RADIOACTIVE EQUILIBRIUM WHEN UI = 1 GR., Th = 1 GR.	RaEm α 2.2×10	←	Ra α β γ 3.3×10-7 GR. MsTh1 β 3.84×10-10 GR.	← ← MsTh2 βγ 4.09×10-14 GR.	Io α γ 1.6×10-5 GR. Th α 1.GR.

precipitation of barium and radium sulfates. In this way, one precipitation was sufficient to separate all of the radium and all of its isotopes from the water. Moreover, it was found that it was not necessary to add to the water a large excess of barium. It was quite sufficient to add from 0.5 g. to 0.4 g. of barium carbonate per liter of mineral water independent of the quantity of SO_4^{--} ions. By this method we received a small quantity of barium-radium sulfates and their slow conversion into chlorides was facilitated.

Nevertheless, barium chloride was added to the water for a control, and the process of precipitation of barium sulfate was performed a second time during the period of twenty-four hours.

B. The first and the second portions of barium-radium sulfate were separately transformed into chlorides. The solutions were then poured into standardized volumetric vessels.

C. Thorium X was measured by the emanation method by means of special equipment for that purpose. After that the vessel with the solution was sealed and put away for four to ten days for the accumulation of radium emanation (18). After the accumulation of the emanation, the measurement of radium was made by the same emanation method. For this measurement unifilar and bifilar electrometers were used, depending on the concentrations of active elements. The equipment was calibrated with standard solutions of radium and thorium X. After the measurement of radium, thorium X was measured again, then the measurement of radium was repeated. In this way a curve of decay of thorium X was obtained which gave the right quantity of thorium X and which checked the completeness of separation of thorium X from radiothorium.

D. After the decay of thorium X the vessel was put away for several months, for the accumulation of radiothorium from mesothorium I. Then the curve of the accumulation of radiothorium was measured by the emanation method once a month, and from this curve the content of mesothorium I was calculated.

E. After the elimination of radium and its isotopes from the water, the same sample of water was taken for the determination of thorium isotopes (ionium and radiothorium). Ferric chloride was added to the water and ferric hydroxide precipitated with ammonia. The ferric hydroxide was filtered, dissolved in hydrochloric acid, and then put into a standardized volumetric vessel. The solution was immediately measured by the emanation method in order to be certain of the absence of thorium X and radium. After that, the solution was put away for one month for the accumulation of thorium X from radiothorium. The curve of decay of radiothorium was measured and the quantity of radiothorium was calculated.

The results of analysis of the spring waters of Gelešnovodsk and of the pit-hole in the petroleum district of Uchta show that the radiothorium in

TABLE 3

*Watering place—Gelesnovodsk**

	SPRING SLAVYANOVSKY	SPRING NO. 1	SPRING SEMASHKO
Temperature of water on the surface (°C.)	55.5	44.0	55.0
1. Active elements in grams per liter of mineral water:			
Radium	2.2×10^{-10}	0.52×10^{-10}	0.60×10^{-10}
Thorium X	4.37×10^{-6} (Th-unit†)	26.8×10^{-6} (Th-unit)	32.3×10^{-6} (Th-unit)
Mesothorium I	3.65×10^{-6} (Th-unit)	19.5×10^{-6}	29.8×10^{-6} (Th-unit)
Radiothorium less than	5×10^{-6}	5×10^{-6}	5×10^{-6}
2. Other ions in grams per liter of mineral water:			
SO_4^{--}	0.8611	0.7602	0.7485
Cl^-	0.2898	0.2378	0.2506
HCO_3^-	1.3270	1.1956	1.1956
K^+	0.0364	0.0362	0.0338
Na^+	0.6369	0.5392	0.5517
Mg^{++}	0.0502	0.0477	0.0422
Ca^{++}	0.3035	0.2728	0.2755
Fe^{++}	0.0021	—	—
Dry residue	2.8850	2.5426	2.5470

* The watering place Gelesnovodsk is situated on the slopes of the mountain Gelesnaya. The water of these springs passes through eruptive rocks (Trachytes).

† In all calculations thorium X and mesothorium I are given in grams of thorium in radioactive equilibrium with the measured quantity of thorium X. This is designated (Th-unit). Owing to this designation, the calculation of decay and of rising is simplified. The standard solution was used for all measurements containing thorium, mesothorium I, radiothorium, and thorium X in equilibrium.

TABLE 4

Watering place—Gelesnovodsk (small springs)

NAME OF THE SPRINGS	TEMPERATURE OF THE SPRINGS	CONTENT OF RADIUM IN GRAMS PER LITER OF THE WATER
Nelubinsky	40.0	49×10^{-12}
Fransua	33.0	32×10^{-12}
Baryatinsky	19.0	Less than 3×10^{-12}
Neslobinsky	19.0	Less than 3×10^{-12}
Muravyewsky	17.0	Less than 1×10^{-12}

the water is undoubtedly not present in radioactive equilibrium with mesothorium I and thorium X. Moreover, the quantity of radiothorium in the water could not be determined in spite of applying the more sensitive unifilar electrometers for the measurement. The above-mentioned calculation of the contents of radiothorium in these spring waters must be considered as the limit of exact measurement.[2]

In spite of the absence of radioactive equilibrium in the thorium disintegration products, the data which were given show that in case any water increases its radium concentration, we may expect the concentration of mesothorium I and thorium X in the same water to increase also.

The amount of SO_4^{--} ions in the water is not an indication of the presence or absence of radium and its isotopes, but a higher temperature of the water at the surface of any spring which belongs to the group of active springs makes possible a greater content of radioactive elements.

THE PROCESS OF PRECIPITATION OF RADIUM FROM THE WATER OF MINERAL SPRINGS INTO THE SEDIMENTS

It is known that mineral springs deposit sediments and that these sediments contain radioactive elements if the water contains them. It would be very interesting to know under what conditions the separation of radium from the water takes place and in what compounds radium appears. Are there only radiobarites in nature or are there also other radium minerals without uranium? It has been possible to solve this problem by investigating the sediments of springs.

First, we were successful in showing one very important fact, namely, that the separation of radium from the water into the sediment does not depend on the presence of carbonate or sulfate ions in the water. Furthermore, it was found that the increase of radium in the sediments was greater when more ferric oxide was present, even in the case of the total absence of SO_4^{--} ions and HCO_3^- ions in the mineral water. To demonstrate this fact the following examples are given.

I. The sediments that are deposited by the water of the springs in Pyatigorsk consist mainly of calcium carbonate. These sediments are colored light yellow to brown by ferric hydroxide, according to the amount of ferric hydroxide present. The quantity of radium in the deposit is also

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[2] The quantity of radiothorium in a liter of the water, 5×10^{-6}g. (Th-unit), is equal to 5.35×10^{-16} g. of radiothorium; 4.76×10^{-22}g. of thorium emanation corresponds to the quantity of radiothorium at radioactive equilibrium. In the precipitation of radiothorium from 20 liters of the water, the quantity of the whole measured emanation is equal to 9.52×10^{-21} g. of thorium emanation or 26 atoms. It is possible to determine radiothorium by the emanation method even if the amount per liter of water is less than 5×10^{-6} g. (Th-unit). In this case it would be necessary to have larger and more complicated equipment to operate with larger volumes of water.

dependent upon the amount of ferric oxide. This is shown by the following data given in terms of grams per 100 g. of sediment.

	DEPOSIT 1	DEPOSIT 2	DEPOSIT 3	DEPOSIT 4
	grams	*grams*	*grams*	*grams*
Ra	3×10^{-10}	10×10^{-10}	59×10^{-10}	111×10^{-10}
Fe_2O_3	0.05	0.18	1.07	1.83

II. The spring of the pit-hole "Kasennaya No. 1," in the petroleum district of Uchta in the North of Russia, contains 7.4×10^{-9} g. of radium per liter of water. This spring does not contain sulfate ions, as was mentioned above. The sediment which is deposited at the surface contains 80.27 g. of ferric oxide and 40.8×10^{-8} gm. of radium per 100 g. of the deposit. From this it follows that the amount of adsorption of radium on ferric hydroxide under natural conditions can be calculated. 0.51×10^{-8} g. of radium corresponds to 1 g. of ferric oxide in the deposit. 20.82×10^{-8} g. of radium corresponds to 1 g. of ferric oxide in the water of the spring, in the form of ferrous iron.

TABLE 5

The pit-hole "Kasennaya No. 1" of the petroleum district Uchta[*]

THE CHEMICAL ELEMENTS	THE CONTENT IN GRAMS PER LITER OF MINERAL WATER
1. Active elements:	
Radium	7.4×10^{-9}
Thorium X	3.2×10^{-3}
Mesothorium I	5.3×10^{-2}
Radiothorium	2.0×10^{-3}
2. Other constituents:	
NaCl	49.5
SO_4^{--}	—
Fe^{++}	0.0252
Ca^{++}, Mg^{++}, SiO_2	Traces

[*] The pit-hole "Kasennaya No. 1," of the petroleum district Uchta, passes through sedimentary rocks. Their chemical composition and their content of radioactive elements were not investigated.

So we see that 1 gram of ferric oxide which is precipitated adsorbs 2.44 per cent of the radium from the water.

III. The springs of the watering place of Gelesnovodsk contain 2.21×10^{-10} g. of radium per liter of water. The deposit is principally calcium carbonate. Other constituents per 100 g. are Fe_2O_3, 7.78 g.; Al_2O_3, 0.88 g.; BaO and SrO, traces; Ra, 7.67 × 10^{-8} g.

The sediments of both this spring and the previous one contain mesothorium I and radiothorium, the latter in less than radioactive equilibrium with the mesothorium I.

We can calculate the adsorption of radium on the hydroxides of the trivalent metals. Thus, we find that 1 g. of trivalent metals which precipitates adsorbs 13.38 per cent of the radium from the water.

IV. The sediments from the mineral springs of Pyatigorsk contain, in addition to the oxides mentioned above, a small quantity of manganese dioxide. The amount of radium in the sediment increases as the amount of manganese dioxide increases. For example: (1) The brown sediment contains per 100 g. 47.85 g. of ferric oxide, 1.79 g. of manganese dioxide, and 6.22 × 10^{-8} g. of radium; (2) the black sediment contains per 100 g. 21.37 g. of ferric oxide, 33.24 g. of manganese dioxide, and 49.50 × 10^{-8} g. of radium. Also, 1 g. of manganese dioxide bears 1.43 × 10^{-8} g. of radium and 1 g. of ferric oxide bears 7.6 × 10^{-10} g. of radium.

TABLE 6

Action of adsorbents on Slavyanovsky spring water*

CONDITIONS OF THE EXPERIMENT	NUMBER OF EXPERIMENTS MADE WITH THE WATER	QUANTITY OF RADIUM PER LITER OF WATER AFTER THE EXPERIMENT	PERCENT OF RADIUM ADSORBED FROM THE WATER
A. Filtration through barium without penetration of air	1	218 × 10^{-12}	1.4
	2	180 × 10^{-12}	16.6
	3	173 × 10^{-12}	21.7
B. Air was blown through the water and the resulting precipitate of ferric hydroxide was filtered	1	107 × 10^{-12}	51.6
	2	73 × 10^{-12}	67.0
	3	35 × 10^{-12}	84.1
C. The water after having had air blown through it was filtered through a layer of ferric hydroxide	1	20 × 10^{-12}	91.0
	2	7 × 10^{-12}	96.8
	3	6 × 10^{-12}	97.3

* The water of the Slavyanovsky mineral spring (Gelesnovodsk) contains 2.21 × 10^{-10} g. of radium per liter.

Therefore, analyzing the sediments of the same spring, it was found that it was possible to calculate the amount of radium in the sediments if the quantities of ferric oxide and manganese dioxide were known. On the other hand, it was possible to calculate the amount of manganese dioxide in the sediment if the amount of radium and ferric oxide was determined. From this we can see that the natural separation of radium and its isotopes from the water of mineral springs is a very common process.

The quantity of radium in a deposit does not depend on the sulfates contained in the sediment, but depends on the quantity of ferric and manganese oxides in it. The per cent of radium adsorbed by the hydroxides deposited in the sediment varies among springs but has a characteristic value for each spring.

It is a very interesting question whether radium contained in active barites (so-called radiobarites) is a product of isomorphous crystallization of barium–radium sulfate, or whether radium in active barites arose from ionium. Radiobarites, according to all descriptions, contain ferric oxide, and they are yellow in color. As the age of some active barites must be more than the average life of radium, we are obliged to suppose ionium precipitated from solution with iron when the barites crystallized (8).

The water of the Slavyanovsky spring (Gelesnovodsk) was passed through several adsorbents. When the water had passed through barium sulfate, the radium was not adsorbed by the sulfate in noticeable quantities. If air was blown into the water and ferrous iron was oxidized, radium with ferric hydroxide was precipitated from the water. But the best results were obtained when the water, after having air blown through it, was passed through a layer of hydroxides. The quantities of the radium precipitated from the water are shown in table 6.

DISCUSSION OF RESULTS

From the studies of concentration of radium, thorium, and their isotopes in the water of natural springs, we can see that there is no radioactive equilibrium between the active elements. This result was to be expected, because near a pH of 7 the elements thorium, ionium, radiothorium, etc., must be in colloidal form or conglomerate accumulations and cannot exist in the form of ions (2, 3, 6, 19). The elements radiothorium, ionium, etc., if they are in a colloidal or conglomerate condition, precipitate from the water onto the surface of the rocks more easily than radium. The high concentration of radium and of its isotopes in comparison to that of their parent substances in the analyzed water of springs, shows us without question that radium, thorium X, and mesothorium I do not immediately rise in the water, but are extracted from the rocks. The nature of the rocks which yield radium in the water is quite well-known in some cases, for example, the water of the springs of Gelesnovodsk flows through trachyte before reaching the surface.

The trachytes were analyzed for radium, which was found to range from 5×10^{-12} g. of radium to 13×10^{-12} g. of radium per gram of rock.

Experiments made on the trachytes of Gelesnovodsk and Pyatigorsk have shown that radium passes easily into acidified water. Five liters of water without radium were warmed with 200 g. of trachyte for twenty hours at a temperature of 55°C. The following amounts of radium were found in the water: (a) 40×10^{-12} g., (b) 95×10^{-12} g., and (c) 127×10^{-12} g.

From the whole investigation we see that radium and its isotopes are quite movable elements in the upper parts of the solid crust.

In the geochemical process—*rocks → mineral springs → sediments on the surface*—we have a thousandfold increase of the concentration of radium.

Since radium is concentrated by ferric and manganous hydroxides, these might be regarded as new kinds of active minerals.

SUMMARY

1. High concentrations of radium and mesothorium I in natural waters are described. The highest concentrations of these elements, which amount to 1.8×10^{-8} g. of radium and 2×10^{-3} g. of mesothorium I (Th-units) per liter of water, have been found in salt water associated with petroleum beds.

2. A method of simultaneous determination of radium, mesothorium I, thorium X, and radiothorium is described.

3. It has been found that the presence of sulfate ions does not effect this high concentration of radium or mesothorium I in natural water.

4. The amount of radiothorium in natural active water was found to be less than that required for radioactive equilibrium with the mesothorium I which was present in this water.

5. A study of the process of migration of radium in nature has shown that radium and mesothorium I are easily transferred from eruptive rocks to mineral waters and from mineral waters to sediments in such a manner that the concentration of radium in sediments is increased a thousand times.

6. Precipitation of radium and mesothorium from water is associated with manganese and ferric hydroxides in sediments.

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STUDIES OF CELLS WITH LIQUID-LIQUID JUNCTIONS. V

Standards for Hydrogen Ion Measurements and the Second Dissociation Constant of Phosphoric Acid

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I. INTRODUCTION

A common type of cell used in the electrometric determination of hydrogen ions is the following:

$$\mathrm{Hg}\,|\,\mathrm{HgCl},\ 0.1\ N\ \mathrm{KCl}\,|\,3.5\ N\ \mathrm{KCl}\,|\,\mathrm{solution\ S}\,|\,\mathrm{H_2} \qquad (1)$$

The exact thermodynamic treatment of such cells has been discussed in a previous paper (6). The electromotive force is a definite but rather complicated function of the concentrations and transport numbers of all the ionic species and of the mean activity coefficients of all the electrolytes present, not only in the electrode solutions and the bridge solution but also in the transition layers between. The formulas, though thermodynamically exact, are of little practical use. To use them it would be necessary first to make measurements with a large (theoretically infinite) number of cells without liquid-liquid junctions in order to obtain the required values of mean activity coefficients, not to mention the required knowledge of transport numbers.

It is therefore expedient to use the formula

$$E = E_0 + E_D + \frac{RT}{F} \log C_{\mathrm{H^+}} f_{\mathrm{H^+}} \qquad (2)$$

where E is the electromotive force of the cell, E_0 is a constant, E_D is the ideal value for the diffusion potentials for the whole cell, and $C_{\mathrm{H^+}}$ is the concentration of hydrogen ion in the solution S, and $f_{\mathrm{H^+}}$ may be called the activity coefficient of the hydrogen ion in the solution S. This formula is actually a conventional definition of E_0 and of $f_{\mathrm{H^+}}$, the value of either depending on the value conventionally assigned to the other. However as long as the solution S is so dilute that the activity coefficient has approximately the same value for various electrolytes of the same electric type, and as long as the solution S contains only small concentrations of either hydrogen ion or hydroxyl ion, it is possible to assign to E_0 a value such that the value of f_{H^+} defined and measured according to equation 2 will to within a few units per cent be equal to that of $f_\pm$, the mean activity coefficient of a uni-univalent electrolyte in solution S. It is only to this approximation that there is any sense in regarding the activity coefficient f_{H^+} measured by such a cell as a thermodynamic quantity. Even at dilutions so great that the activity coefficients, $f_\pm$, of all uni-univalent electrolytes have the same value to within one per cent or less, it is possible for f_{H^+} to differ by as much as three or four per cent from $f_\pm$ of uni-univalent electrolytes. For this reason there does not seem to be much sense in determining values of $-\log C_{H^+} f_{H^+}$, or paH[1] as it is usually denoted, to a greater accuracy than 0.01, or at the most 0.005.

If the liquid-liquid junctions are made in a suitable manner (7, 9, 16, 19) the electromotive forces of these cells are about as reproducible and stable as most cells without such junctions and the value of E_D may be calculated by using Henderson's formula (12).

Bjerrum and Unmack (3) have made extensive measurements of cells of type 1 and have used formula 2 in their computations. The treatment of our own data is in principle the same as that of Bjerrum and Unmack. We wish however to draw attention to a few differences of detail.

First in computing E_D by the use of Henderson's formula, Bjerrum and Unmack use the value 0.497 for the transport number t_{K^+} of the potassium ion in potassium chloride. They discuss in some detail how their computations would be affected by the choice of a different value. Meanwhile accurate determinations of this quantity at 25°C. have been made by Longsworth (13) and by MacInnes and Dole (15). According to their measurements this transport number has the constant value 0.490 at all concentrations up to half molar. As most of the contribution to E_D comes from the more dilute end of the transition layer, we have used this value for t_{K^+}. Our values of E_D therefore differ somewhat from those of Bjerrum and Unmack. For the ions in the more dilute solutions S, the ionic conductivities require to be known only roughly.

Second, we do not believe there is anything to be gained in attempting to compute either f_{H^+} or related quantities with an accuracy greater than corresponds to the difference between the mean activity coefficients of two uni-univalent electrolytes.

Third, whilst in entire agreement with Bjerrum and Unmack as regards the principle to be used in choosing the best value for E_0, we make a different choice of solutions to which we attach most weight.

II. MEASUREMENTS

All the cells measured were of the type 1, the composition of the solution S being one of those given in table 1 and the temperature being 25°C.

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[1] paH is a conventionalized form of pa_H.

The solutions were prepared and standardized as described in the following paper (8). The experimental set-up was in all essential respects that used by Unmack and Guggenheim (19). In particular the junction was made by dipping the side-tube of the hydrogen electrode vessel into a U-tube containing 3.5 molar potassium chloride. The levels of the solutions in the U-tube and the electrode vessel were so adjusted that on opening the stopcock between the electrode and the side tube the liquid from the U-tube always slowly flowed about halfway up the side tube. The electromotive force reached a constant value usually within half an hour. This was reproducible within at least a tenth of a millivolt and stable for at least a day. Four calomel electrodes were prepared and these checked within 0.1 millivolt.

TABLE 1

Hg | HgCl, 0.1 *M* KCl | 3.5 *M* KCl | solution S | H_2 *at 25°C.*

COMPOSITION OF SOLUTION S			TOTAL IONIC STRENGTH	E. M. F. MEASUREMENTS*		paH
Acid constituent	Basic constituent	Neutral salt		Our values	Values determined by Bjerrum and Unmack	
moles per liter	*moles per liter*	*moles per liter*		*mv.*	*mv.*	
(a) 0.01 HCl		0.09 KCl	0.10	−458.30	−458.40	2.10
(b) 0.10 HCl			0.10	−400.80	−400.90	1.07
(c) 0.01 HAc	0.01 NaAc		0.01	−613.90		4.80
(d) 0.01 HAc	0.01 NaAc	0.09 KCl	0.10	−609.75		4.67
(e) 0.10 HAc	0.10 NaAc		0.10	−610.10		4.66
(f) 0.0025 NaH_2PO_4	0.0025 Na_2HPO_4	0.00242 NaCl	0.0125	−753.40	−753.10	7.07
(g) 0.025 NaH_2PO_4	0.025 Na_2HPO_4	0.0242 NaCl	0.125	−738.60	−738.20	6.835
(h) 0.050 NaH_2PO_4	0.050 Na_2HPO_4	0.0485 NaCl	0.250	−732.45		6.735

* Positive value of *E* means that electrode on right is positive (American convention).

The results of our measurements are recorded in table 1. The first four columns give the composition of the hydrogen electrode solution S. The fifth column gives the measured electromotive force corrected to the mean value of the calomel electrodes and to a hydrogen pressure of one atmosphere. The sixth column gives some electromotive force values of Bjerrum and Unmack (3), which agree fairly satisfactorily with our values. The last column will be discussed in the next section.

III. CHOICE OF E_0

The value of E_0 originally proposed by Sörensen was based on a misinterpretation of conductivity data at a time when it was believed that solutions of electrolytes obey the ideal laws. It is now generally agreed and admitted by Sörensen (18) that this value of −337.6 millivolts at 25°C. is not the most desirable. Various authors have suggested other values and some of these are discussed at length by Clark (4). But there has been a natural reluctance to adopt any other value until one could be chosen likely to be strongly established and permanent. Güntelberg and Schiödt (10) discuss the unfortunate confusion due to the continued use of the obsolete Sörensen value and estimate that values of paH or $-\log_{10} C_{H^+} f_{H^+}$ calculated from the Sörensen value are too low by 0.05 ± 0.015, but they agree that an alternative standard value should not be adopted until it could be fixed to within 0.01 in paH. We wish to put forward what we believe to be a strong case for the adoption of the value

$$E_0 = -333.7 \text{ millivolts at } 25°\text{C.}$$

according to which the Sörensen values of pH, assuming the computation of E_D has been correctly carried out, will be too low by 0.065. We shall show that for the five solutions (a) 0.01 *M* hydrochloric acid + 0.09 *M* potassium chloride, (b) 0.10 *M* hydrochloric acid, (c) 0.01 *M* acetic acid + 0.01 *M* sodium acetate, (d) 0.01 *M* acetic acid + 0.01 *M* sodium acetate + 0.09 *M* potassium chloride, and (e) 0.10 *M* acetic acid + 0.10 *M* sodium acetate, this value of E_0 leads to most reasonable values of f_{H^+} and f_{Ac^-}.

Solutions a and b have often before been suggested as standards. One of the objections raised against the use of solution b is the difficulty of obtaining definite values for E owing to the large diffusion potential. Actually there is no difficulty in obtaining reproducible and stable values if the junction is made in the correct manner. Solutions c, d, and e have become suitable for standards only quite recently, thanks to the accurate determination of the dissociation constant of acetic acid by Harned and Ehlers (11), who used cells without any liquid-liquid junctions.

Let us first consider cells made in the solutions a and b. In both these the value of C_{H^+} is known, being equal to the stoichiometric concentration of hydrochloric acid. According to the best values of the universal contants compiled by Birge (1) the value of $\frac{RT}{F} \log_e 10$ at 25°C. is 59.151 international millivolts. We therefore have, according to equation 2,

$$59.15 \log_{10} f_{H^+} = E - E_0 - E_D - 59.15 \log_{10} C_{H^+} \tag{3}$$

Inserting the numerical values of E, E_0, and E_D we obtain for cell a

$$59.15 \log_{10} f_{H^+} = -458.3 + 333.7 + 0.4 + 118.3 = -5.9$$

and for cell b

$$59.15 \log_{10} f_{H^+} = -400.8 + 333.7 + 3.64 + 59.15 = -4.3$$

The corresponding values of f_{H^+} are 0.795 in solution a and 0.85 in solution b.

An entirely different convention sometimes used (14, 17) for assigning values to ionic activity coefficients is to set the activity coefficient f_{Cl^-} of the chloride ion in both solutions a and b equal to the value 0.76 of the mean activity f_{KCl} of potassium chloride in 0.10 M potassium chloride. This convention leads to values of f_{H^+} equal to 0.80 in solution a and 0.84 in solution b. The agreement between these values and those obtained by the use of our value of E_0 is extremely satisfactory.

Let us now consider the three acetate buffers c, d, and e. Since each buffer contains equal concentrations of acetic acid and sodium acetate, we have, according to equation 2,

$$E = E_0 + E_D + \frac{RT}{F} \log_e K_{HAc} - \frac{RT}{F} \log_e \frac{f_{Ac^-}}{f_{HAc}} \qquad (4)$$

where K_{HAc} is the thermodynamic dissociation constant of acetic acid. Its value determined by Harned and Ehlers is 1.75×10^{-5} at 25°C. From the experimental value of E and the known values of E_0, E_D, and K_{HAc}, we are able to calculate f_{Ac^-}/f_{HAc}. The computations are shown in table 2. If we ignore the deviation of f_{HAc} from unity, then we obtain the values of f_{Ac^-} given in the last row of the table. It is to be noted that the value 0.90 for f_{Ac^-} at the ionic strength 0.01 is exactly equal to $f_{\pm}$ for any typical uni-univalent electrolyte at the same ionic strength. Moreover the values 0.80 and 0.81 of f_{Ac^-} at the ionic strength 0.10 are within the range of values of the mean activity coefficients of typical uni-univalent electrolytes at the same ionic strength.

We see then that the value we suggest for E_0 leads to eminently reasonable values for f_{H^+} in the solutions a and b, and equally reasonable values for f_{Ac^-} in the solutions c, d, and e. The corresponding values for $-\log_{10} C_{H^+}f_{H^+}$ or paH for all five solutions are given in the last column of table 1.

The rather large discrepancy between the value -333.7 which we have chosen for E_0 and the value -336.0 selected by Bjerrum and Unmack is due partly to their use of the value $t_{K^+} = 0.497$ in potassium chloride and partly to their attaching greater weight to much more dilute solutions of hydrogen chloride, where the experimental uncertainty is likely to be great. Even if the experimental values at these high dilutions are reliable, it seems to us preferable to choose for E_0 a value which leads to reasonable values of f_{H^+} and f_{Ac^-} in solutions of concentrations in the more generally useful range of 0.01 M to 0.1 M.

It should not be necessary to mention that in order to obtain the best results it is essential not to ignore E_D. Whereas its value is usually not more than about one millivolt, there seems to be a surprisingly widespread belief that it is vanishingly small. In the case of measurements on protein solutions and the like, where it is not possible to calculate E_D, one can obtain a rough estimate of its magnitude by the procedure proposed by Bjerrum (2), of comparing the values of E obtained by using as bridge solution first 3.5 M potassium chloride and second 1.75 M potassium chloride. Bjerrum and Unmack (reference 3, p. 50) give an emphatic warning against exaggerated ideas of the reliability of this procedure. It is to be recommended only when it is not possible to calculate E_D.

TABLE 2

Hg | HgCl, 0.1 M KCl | 3.5 M KCl | solution S | H_2 *at 25°C.*

	c	d	e
Composition of solutions S	0.01 NaAc 0.01 HAc	0.01 NaAc 0.01 HAc 0.09 KCl	0.10 NaAc 0.10 HAc
E	−613.9	−609.75	−610.1
	+1.85	+1.85	+1.85
E_D *	−3.33	−1.85	−2.46
	−1.48	0.00	−0.60
$E - E_D$	−612.42	−609.75	−609.5
E_0	−333.7	−333.7	−333.7
$E - E_D - E_0 = \frac{RT}{F} \log_e C_{H^+} f_{H^+}$	−278.7	−276.05	−275.8
$\frac{RT}{F} \log_e K_{HAc}$	−281.4	−281.4	−281.4
$-\frac{RT}{F} \log_e f_{Ac^-}$	+2.7	+5.35	+5.6
$\log_{10} f_{Ac^-}$	−0.045	−0.090	−0.095
f_{Ac^-}	0.90	0.81	0.80
paH = $-\log_{10} C_{H^+} f_{H^+}$	4.80	4.67	4.66

* The value +1.85 given first represents the contribution of the junction 0.1 M KCl | 3.5 M KCl. The value given next is the contribution of the junction 3.5 M KCl | solution S. The third value, representing E_D for the whole cell, is the algebraic sum of the first two.

IV. SECOND DISSOCIATION CONSTANT OF PHOSPHORIC ACID

Having chosen a value for E_0 we use our electrometric measurements in the phosphate buffers f, g, and h to compute values of $C_{H^+} f_{H^+}$ by exactly the procedure used by Bjerrum and Unmack. As the ratio $C_{HPO_4^{--}}/C_{H_2PO_4^-}$ is unity in each case, the thermodynamic dissociation constant $K_{H_2PO_4^-}$ is given by

$$K_{H_2PO_4^-} = \frac{C_{H^+} \cdot C_{HPO_4^{--}}}{C_{H_2PO_4^-}} \cdot \frac{f_{H^+} \cdot f_{HPO_4^{--}}}{f_{H_2PO_4^-}} = C_{H^+} f_{H^+} \cdot \frac{f_{HPO_4^{--}}}{f_{H_2PO_4^-}} \tag{5}$$

As already mentioned it is possible to compute such a quantity as $K_{H_2PO_4^-}$ from measurements of cells with liquid-liquid junctions only with an accuracy that ignores specific differences between the activity coefficients of two electrolytes of the same type. In a paper to be published shortly it will be pointed out that the activity coefficients of numerous electrolytes of all valence types are correctly given within a few units per cent up to an ionic strength of 0.1, if the activity coefficient of each ion of valency Z is calculated according to

$$-\log_{10} f = 0.50\, Z^2 \frac{\sqrt{\Gamma}}{1+\sqrt{\Gamma}} \tag{6}$$

where Γ is the total ionic strength of the solution. This formula is of the Debye-Hückel (5) type in which the parameter a, the "mean ionic diameter" is set equal to 3.0 A.U. According to this formula we have

$$\log_{10} \frac{f_{HPO_4^{--}}}{f_{H_2PO_4^-}} = -1.50 \frac{\sqrt{\Gamma}}{1+\sqrt{\Gamma}} \tag{7}$$

Combining the values of $f_{HPO_4^{--}}/f_{H_2PO_4^-}$ thus calculated with the values of $C_{H^+}f_{H^+}$ obtained from the electrometric measurements we are able to obtain values of $K_{H_2PO_4^-}$. The complete computations are given in table 3. The three independent values obtained for $K_{H_2PO_4^-}$ agree remarkably well. As the formula (7) for activity coefficients is not expected to be accurate at an ionic strength as high as 0.25, the agreement of the value of $K_{H_2PO_4^-}$ given by the third solution with those given by the other two is probably fortuitous. Taking the mean of the values given by the two most dilute solutions we obtain as the value of $K_{H_2PO_4^-}$, 5.97×10^{-8} with an estimated accuracy of 2 or 3 per cent. The value estimated by Bjerrum and Unmack (reference 3, p. 132) was 6.20×10^{-8}.

V. VALUES FOR E_0 AT OTHER TEMPERATURES

As already pointed out by Bjerrum and Unmack the selection of the most likely value for E_0 depends on the value assumed for t_{K^+} in potassium chloride. This uncertainty is however pronounced only in very dilute solutions. If then we choose standard solutions of total concentration 0.10 M we may without serious error assume that t_{K^+} in potassium chloride has the same value, 0.490, at other temperatures as at 25°C. On this basis and using Bjerrum and Unmack's measurements we come to the conclusion that the most reasonable values of E_0 at the various temperatures of their measurements are those given in table 4. We believe that these values are definite to within about one quarter of a millivolt, that is to within 0.005 of a pH unit or within 1 per cent in f_{H^+}. In the same table are given the values of f_{H^+} in three standard solutions corresponding to this choice of E_0

and also the values of f_{H^+} calculated on the convention of setting f_{Cl^-} equal to f_{KCl} in 0.1 *M* potassium chloride. The agreement between the two independent conventions is most satisfactory.

TABLE 3

Hg | HgCl, 0.1 *M* KCl | 3.5 *M* KCl | solution S | H_2 *at 25°C.*

	f	g	h
Composition of solutions S	0.01 Na^+ 0.0025 $H_2PO_4^-$ 0.0025 HPO_4^{--} 0.0025 Cl^-	0.10 Na^+ 0.025 $H_2PO_4^-$ 0.025 HPO_4^{--} 0.025 Cl^-	0.20 Na^+ 0.05 $H_2PO_4^-$ 0.05 HPO_4^{--} 0.05 Cl^-
Ionic strength Γ	0.0125	0.125	0.25
$\sqrt{\Gamma}$	0.112	0.353	0.50
E	−753.4	−738.6	−732.45
E_D *	+1.85 −3.24 −1.40	+1.85 −2.35 −0.50	+1.85 −2.21 −0.35
$E - E_D$	−752.0	−738.1	−732.1
E_0	−333.7	−333.7	−333.7
$E - E_D - E_0$	−418.3	−404.4	−398.4
paH = $-\log_{10}C_{H^+}f_{H^+}$	7.072	6.837	6.735
$C_{H^+}f_{H^+}$	0.847×10^{-7}	1.45×10^{-7}	1.84×10^{-7}
$-\log_{10}\dfrac{f_{H_2PO_4^-}}{f_{HPO_4^{--}}}$	0.151	0.391	0.500
$-\log_{10}K_{H_2PO^{4-}}$	7.222	7.226	7.235
$K_{H_2PO_4^-}$	6.00×10^{-8}	5.94×10^{-8}	5.82×10^{-8}

* The value +1.85 given first represents the contribution of the junction 0.1 *M* KCl | 3.5 *M* KCl. The value given next is the contribution of the junction 3.5 *M* KCl | solution S. The third value, representing E_D for the whole cell, is the algebraic sum of the first two.

TABLE 4

	TEMPERATURE				f_{H^+} ACCORDING TO CONVENTION $f_{Cl^-} = f_{KCl}$
	0°C.	18°C.	25°C.	37°C.	
E_0	−334.2	−334.2	−333.7	−332.7	
f_{H^+} in 0.01 *M* HCl + 0.09 *M* KCl	0.80	0.80	0.80	0.80	0.80
f_{H^+} in 0.01 *M* HCl + 0.09 *M* NaCl	0.83	0.82	0.82	0.82	0.82
f_{H^+} in 0.10 *M* HCl		0.84	0.85	0.85	0.84

We are pleased to learn from Professor Bjerrum that he is in complete agreement with the contents of the present paper and that he accepts our E_0 value at 25°C. as the most reasonable one to use on the available experimental material.

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SALT EFFECTS ON SULFONPHTHALEIN INDICATORS[1]

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I. INDICATOR-BUFFER EQUILIBRIA

According to the terminology of Brönsted (3) the two forms of any indicator function respectively as an acid and as a base.. Denoting the acid form by HI and the basic form by I there is an equilibrium of the form

$$HI \rightleftharpoons I + H^+ \tag{1}$$

The electric charge of the acid form HI may be positive, zero, or negative according to the nature of the indicator. The electric charge of the basic form I is of course algebraically one less than that of HI. Similarly a buffer solution may be regarded as a mixture of an acid HA and a base A which control the hydrogen ion concentration according to the equilibrium

$$HA \rightleftharpoons A + H^+ \tag{2}$$

The electric charge of the acid form HA may be positive, zero, or negative, while that of the basic form A is of course algebraically one less than that of HA.

The exact thermodynamic treatment of such equilibria was given by Brönsted (2) in 1921. Writing C for concentrations and f for activity coefficients the thermodynamic equilibrium conditions are

$$\frac{C_I \cdot C_{H^+}}{C_{HI}} = K_{(C)HI} = K_{HI} \cdot \frac{f_{HI}}{f_{H^+} \cdot f_I} \tag{3}$$

$$\frac{C_A \cdot C_{H^+}}{C_{HA}} = K_{(C)HA} = K_{HA} \cdot \frac{f_{HA}}{f_{H^+} \cdot f_A} \tag{4}$$

where K_{HI} is the thermodynamic acid constant of the indicator and K_{HA} that of the acid constituent of the buffer. For a given temperature and solvent K_{HI} and K_{HA} are true constants. The equilibrium concentrations products $K_{C(HI)}$ and $K_{C(HA)}$ on the other hand are not constants but depend on the concentration of electrolytes present.

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[1] We wish to express our indebtedness to Mr. E. Güntelberg of Copenhagen for reading through the manuscript of this paper and pointing out to us certain inaccuracies in formulas 14 to 17 which we have since corrected.

In the same paper Brönsted pointed out that instead of the two equilibria 1 and 2 one may consider directly the double acid-base equilibrium between the indicator and the buffer

$$\mathrm{HI} + \mathrm{A} \rightleftharpoons \mathrm{I} + \mathrm{HA} \tag{5}$$

The thermodynamic equilibrium condition is

$$\frac{C_{\mathrm{I}} \cdot C_{\mathrm{HA}}}{C_{\mathrm{HI}} \cdot C_{\mathrm{A}}} = K_C = \frac{K_{(C)\mathrm{HI}}}{K_{(C)\mathrm{HA}}} = \frac{K_{\mathrm{HI}}}{K_{\mathrm{HA}}} \cdot \frac{f_{\mathrm{HI}} \cdot f_{\mathrm{A}}}{f_{\mathrm{I}} \cdot f_{\mathrm{HA}}} \tag{6}$$

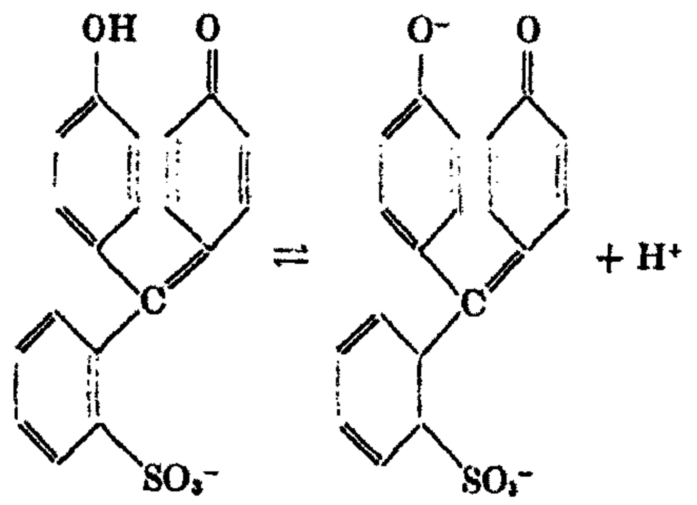
Whereas $K_{\mathrm{HI}}/K_{\mathrm{HA}}$ is a true constant, the equilibrium concentrations product $K_{(C)\mathrm{HI}}/K_{(C)\mathrm{HA}}$ or K_C depends on the concentration of electrolytes present. If then one observes the color of an indicator present in small amount in a buffer solution, the value of $C_{\mathrm{HA}}/C_{\mathrm{A}}$ is known from the composition of the buffer and that of $C_{\mathrm{I}}/C_{\mathrm{HI}}$ is given by the color. We are therefore able to calculate the value of K_C. By determining this product at various salt concentrations and extrapolating to infinite dilution, one obtains a value of $K_{\mathrm{HI}}/K_{\mathrm{HA}}$; thence by division one obtains directly values of the product $f_{\mathrm{HI}} \cdot f_{\mathrm{A}}/f_{\mathrm{I}} \cdot f_{\mathrm{HA}}$. This product is a measure of the salt effect on the indicator buffer equilibrium 5. If the value of either K_{HI} or K_{HA} is known from previous determinations, then we can calculate the other from the known ratio $K_{\mathrm{HI}}/K_{\mathrm{HA}}$. If moreover we can rely on some formula to give the activity coefficients product $f_{\mathrm{H}^+} \cdot f_{\mathrm{A}}/f_{\mathrm{HA}}$ which measures the salt effect of the buffer equilibrium 2, we can from the known value of $f_{\mathrm{HI}} \cdot f_{\mathrm{A}}/f_{\mathrm{I}} \cdot f_{\mathrm{HA}}$ calculate the value of the product $f_{\mathrm{H}^+} \cdot f_{\mathrm{I}}/f_{\mathrm{HI}}$ which measures the salt effect of the equilibrium 1.

In discussing or measuring the salt effect on indicators it is more usual to consider the indicator equilibrium 1 rather than the indicator–buffer equilibrium 5 as we do. Other authors determine $C_{\mathrm{I}}/C_{\mathrm{HI}}$ from the color and attempt to estimate the value of $C_{\mathrm{H}} \cdot f_{\mathrm{H}^+}$ by electrometric measurements on cells with liquid–liquid junctions. A thermodynamic analysis of such measurements (6), however, shows that the quantity measured is not $C_{\mathrm{H}} \cdot f_{\mathrm{H}^+}$, but rather $C_{\mathrm{H}^+} \cdot f_?$, where $f_?$ is a complicated function of the mean activity coefficients of all the electrolytes and the transport numbers of all the ions present, not merely in the electrode solution but also in the bridge solution and at each part of the transition layer between the electrode solution and the bridge solution. Estimates based partly on experiment and partly on approximate computations (16) indicate that the confusion between $C_{\mathrm{H}} \cdot f_?$ and $C_{\mathrm{H}} \cdot f_{\mathrm{H}^+}$ in even quite dilute solutions may in some cases lead to inaccuracies of the order of 4 per cent in a concentration, or 1 millivolt in an E.M.F., or 0.015 on the pH scale. It is by no means certain that the error may not sometimes be twice as great as this estimate. Any computation of the salt effect on an indicator equilibrium which is dependent on electrometric measurements of cells with liquid junctions is therefore likely to be uncertain by about 4 per cent. As it is possible to make colorimetric measurements with a higher accuracy than this, it seems to us preferable to make our determinations mainly independent of electrometric measurements.

Our criticism of the use of cells with liquid-liquid junctions does not apply to the measurements of Güntelberg and Schiödt (10), as they took care to make their liquid-liquid junction potentials negligibly small. Their procedure is however applicable only to comparatively concentrated salt solutions.

II. APPLICATION TO SULFONPHTHALEIN INDICATORS

Two indicators were used, both substitution derivatives of phenolsulfonphthalein. The various forms in which indicators of this type can exist have been discussed by Kolthoff (14). The only two forms which concern us are the derivatives of



I Yellow

II Blue

Form I is the yellow acid form with a single negative charge, which we may refer to as HI^-, and form II is the blue basic form with a double negative charge, which we may refer to as I^{--}.

The buffers chosen for our investigation were of the types

$$H_2PO_4^- \rightleftharpoons HPO_4^{--} + H^+ \tag{7}$$

and

$$HAc \rightleftharpoons Ac^- + H^+ \tag{8}$$

where Ac denotes acetate. It was desirable in each case to use a sulfonphthalein indicator whose acid constituent was of strength comparable to that of the acid constituent of the buffer. The most suitable ones for this purpose are dibromothymolsulfonphthalein (bromothymol blue) in the primary-secondary phosphate buffer, and tetrabromo-*m*-cresolsulfonphthalein (bromocresol green) in the acetic acid–acetate buffer. The indicator-buffer equations for these combinations are

$$\mathrm{HAc} + \mathrm{I}^{--} \rightleftharpoons \mathrm{Ac}^- + \mathrm{HI}^- \tag{9}$$

$$\mathrm{H_2PO_4^-} + \mathrm{I}^{--} \rightleftharpoons \mathrm{HPO_4^-} + \mathrm{HI}^- \tag{10}$$

$$K_C = \frac{C_{\mathrm{I}^{--}}}{C_{\mathrm{HI}^-}} \cdot \frac{C_{\mathrm{HAc}}}{C_{\mathrm{Ac}^-}} = \frac{K_{\mathrm{HI}^-}}{K_{\mathrm{HAc}}} \cdot \frac{f_{\mathrm{HI}^-} f_{\mathrm{Ac}^-}}{f_{\mathrm{I}^{--}} f_{\mathrm{HAc}}} \tag{11}$$

$$K_C = \frac{C_{\mathrm{I}^{--}}}{C_{\mathrm{HI}^-}} \cdot \frac{C_{\mathrm{H_2PO_4^-}}}{C_{\mathrm{HPO_4^{--}}}} = \frac{K_{\mathrm{HI}^-}}{K_{\mathrm{H_2PO_4^-}}} \cdot \frac{f_{\mathrm{HI}^-} f_{\mathrm{HPO_4^{--}}}}{f_{\mathrm{I}^{--}} f_{\mathrm{H_2PO_4^-}}} \tag{12}$$

According to the theory of Debye and Hückel (5) the activity coefficients may be calculated according to the formula

$$-\log_{10} f_i = 0.50 \frac{Z_i^2 \Gamma^{1/2}}{1 + 0.33a\Gamma^{1/2}} \tag{13}$$

where f_i denotes the activity coefficient of the ion i of valency Z_i, Γ is the ionic strength, and a is a certain mean ionic diameter in A.U. of the given ion and other ions in the solution. A somewhat similar formula to formula 13 with certain advantages over it and equally applicable at ionic strengths up to 0.1 is the following (7)

$$-\log_{10} f_i = 0.50\, Z_i^2 \frac{\Gamma^{1/2}}{1 + \Gamma^{1/2}} + \sum_k B_{ik} C_k \tag{14}$$

in which the coefficient of $\Gamma^{\frac{1}{2}}$ in the denomination is given the value unity, the specific differences between various ions being taken care of by the term $\sum\limits_k B_{ik} C_k$ where C_k denotes the concentration of the ionic species k; the quantities B_{ik} are constants, and the summation $\sum\limits_k$ extends over all ionic species k of *opposite sign to that of the species i.*

Applying formula[1] 14 to the indicator-buffer equilibria, we obtain

$$-\log_{10} \frac{f_{\mathrm{HI}} \cdot f_{\mathrm{A}}}{f_{\mathrm{I}} \cdot f_{\mathrm{HA}}} = \frac{0.50\, \Gamma^{1/2}}{1 + \Gamma^{1/2}} \left(Z_{\mathrm{HI}}^2 + Z_{\mathrm{A}}^2 - Z_{\mathrm{I}}^2 - Z_{\mathrm{HA}}^2\right) + \sum_k B_{ik} C_k \tag{15}$$

where Z_{HI} denotes the valency of HI, and so on. In the particular case of the sulfonphthalein indicators and the sodium phosphate buffers used formula 15 becomes

$$-\log_{10} \frac{f_{\mathrm{HI}^-} \cdot f_{\mathrm{HPO_4^{--}}}}{f_{\mathrm{I}^{--}} \cdot f_{\mathrm{H_2PO_4^-}}} = BC_{\mathrm{Na}^+} \tag{16}$$

where B is a constant, the coefficient of the term in $\Gamma^{\frac{1}{2}}$ being zero. For the equilibrium between sulfonphthalein indicator and the sodium acetate buffer on the other hand formula 15 becomes

$$-\log_{10}\frac{f_{\mathrm{HI}^-}\cdot f_{\mathrm{Ac}^-}}{f_{\mathrm{I}^{--}}\cdot f_{\mathrm{HAc}}} = -1.0\,\frac{C^{1/2}}{1+C^{1/2}} + BC \tag{17}$$

the ionic strength in this case being the same as the concentration C of either sodium ion or acetate ion.

Thus in the phosphate buffers the salt effect should be linear in the equivalent concentration, but in the acetates the salt effect should be "parabolic,"[3] that is to say, particularly pronounced at low concentrations. We shall see that these theoretical predictions are verified by our experiments.

III. EXPERIMENTAL PROCEDURE

Two different experimental procedures were made use of in the colorimetric measurement of the ratio $C_{\mathrm{I}^{--}}/C_{\mathrm{HI}^-}$. Our early measurements were made with test tubes, selected with bores uniform to within 4 per cent, in a comparator rack exactly as described by Clark (4). The difference between the values of the color ratios of two successive standards in the center range was approximately 12 per cent. The color of an unknown buffer–indicator solution could be interpolated between successive standards to quarters, and so the color ratio $C_{\mathrm{I}}/C_{\mathrm{HI}}$ measured with an accuracy of only about ±3 per cent.

Each color standard when prepared was freed from oxygen by bubbling nitrogen through the tube and the solution was corked in an atmosphere of nitrogen. In spite of this, it was found that the color of the basic solutions faded. The precaution was therefore taken of preparing new standards at least once a week. Kilpatrick and Chase (12) attribute this fading of the basic form of the indicator to a replacement of the bromine in the indicator compound by a hydroxyl group. They state that the greater the concentration of the hydroxyl ion, the faster the color of the indicator will fade.

Our later measurements were made with a colorimeter of the Gillespie

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[3] In the limit of small concentrations the law

$$-\log_e f = AC^n$$

is of the same form as

$$1-f = AC^n$$

It is therefore natural to speak of a "linear" effect when n is unity. In the case that n is one half, we may speak of a "parabolic" effect because if f be plotted against C the curve will be a parabola. Many authors refer to such a law as an "exponential" effect, but this terminology is ambiguous. For f is an exponential function of C when n is unity ("linear" effect). When n is one half ("parabolic" effect), f is an exponential function of $C^{1/2}$.

type made by the Bausch and Lomb Optical Company, used as described by Clark (reference 4, p. 168). The total thickness of solution looked through was in all cases 20 mm., so that the ratio C_{I^-}/C_{HI^-} was equal to $20 - x/x$, where x was the reading of the colorimeter which could be determined to within 0.05 mm. The reproducibility of results was on the average within 1 per cent. The colorimeter was not only more accurate but also more convenient to use. As new bicolor standards were prepared each day, there was no risk of fading.

The stock indicator solutions were prepared according to the directions given by Clark (reference 4, p. 91) and were kept in the dark. In the actual solutions with which measurements were made the concentration of indicator was approximately 6×10^{-5} molar.

The bromothymol blue was obtained from Coleman and Bell Company. Four samples of bromocresol green were used. The first was obtained from the Eastman Kodak Company; the second by recrystallization of the first from glacial acetic acid. The third sample was obtained from Hynson, Westcott and Dunning, Inc.,[3] and the fourth by recrystallization of the third from glacial acetic acid.

The potassium chloride was Baker's "analyzed," which we recrystallized. The hydrochloric acid solutions were made from some constant boiling mixture, which, as well as some carbon dioxide-free sodium hydroxide, was kindly supplied by Mrs. Laing McBain. The acetic acid was standardized by titration against the sodium hydroxide, which in turn was standardized against the hydrochloric acid. The sodium acetate was prepared from the acetic acid and the sodium hydroxide. All the phosphate was obtained from a preparation of Merck described as anhydrous Na_2HPO_4. Electrometric titrations and determinations of loss of weight on ignition, however, convinced us that this preparation, while dry, contained between 1.5 and 1.6 moles per cent of NaH_2PO_4. All solutions were made from ordinary distilled water freed from carbon dioxide by bubbling nitrogen through it.

All measurements were made in daylight using a north light. Before making measurements, the indicator-buffer solutions were put in test tubes and brought to 25°C. in a thermostat.

IV. EXPERIMENTAL RESULTS AND ACCURACY

All measurements were made at 25°C. The experimental results are conveniently given in tabular form. Table 1 gives an example of the results obtained with the colorimeter using buffers of approximately 0.05 equivalent concentration. The first three columns give the concentration of the various anions in each solution, the cations being in all cases Na^+. The fourth column gives the ratio of the concentrations of primary phos-

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[3] This sample was donated by Hynson, Westcott and Dunning, Inc., for which we wish to express our thanks.

phate to secondary phosphate; the fifth column gives the reading x of the colorimeter; the sixth column gives the observed ratio of basic to acid form of bromothymol blue indicator; and the seventh column gives K_C obtained as the product of the values in the fourth and sixth columns. It will be noticed that K_C is, within the experimental error, a constant at the given total equivalent concentration. In the test tube measurements it was found that at each total equivalent concentration K_C is constant to within ±4 per cent, whereas in the colorimeter measurements at each total equivalent concentration K_C was found constant to within ± 1.5 per cent. At each total equivalent concentration the colorimeter measurements confirmed the test tube measurements within the degree of accuracy of the latter.

TABLE 1

Colorimeter measurements with bromothymol blue

Total equivalent concentration = 0.0496

$c_{Cl^-} \times 10^2$	$c_{H_2PO_4^-} \times 10^2$	$c_{HPO_4^{--}} \times 10^2$	$\frac{c_{H_2PO_4^-}}{c_{HPO_4^{--}}}$	x	$\frac{c_{I^{--}}}{c_{HI^-}}$	$\frac{c_{I^{--}} \cdot c_{H_2PO_4^-}}{c_{HI^-} \cdot c_{HPO_4^{--}}}$
0.40	0.44	2.06	0.213	5.5	2.64	0.56
0.60	0.64	1.86	0.345	7.45	1.68	0.58
0.80	0.84	1.66	0.510	9.4	1.13	0.58
1.00	1.04	1.46	0.710	11.1	0.802	0.57
1.20	1.24	1.26	0.984	12.7	0.575	0.57
1.40	1.44	1.06	1.36	14.1	0.418	0.57
1.60	1.64	0.86	1.91	15.4	0.299	0.57
1.80	1.84	0.66	2.79	16.65	0.201	0.56
Average $Kc = \frac{C_{I^{--}} \cdot C_{H_2PO_4^-}}{C_{HI^-} \cdot C_{HPO_4^{--}}}$						0.57±0.007

There is no trend in the values of K_C from the basic to the acid forms of the buffer in table 1. But in more dilute solutions, there was a definite trend which became more pronounced with dilution. This trend in the value of K_C is illustrated by table 2 where the values of K_C range from 0.51 to 0.60. This is probably due to the solutions becoming accidentally contaminated with carbon dioxide, although every precaution was taken to remove carbon dioxide from the water used to make up the solutions. This effect was observed only at equivalent concentrations of 0.005 and below. It increased rapidly at lower concentrations. At these concentrations the values of K_C given by the more basic solutions were rejected. This seems justifiable because there was no corresponding trend observed in the values of K_C for the acetate buffer and bromocresol green, even in concentrations as low as 0.002.

TABLE 2

Colorimeter measurements with bromothymol blue

Total equivalent concentration = 0.00496

$c_{\mathrm{Cl}^-} \times 10^3$	$c_{\mathrm{H_2PO_4^-}} \times 10^3$	$c_{\mathrm{HPO_4^{--}}} \times 10^3$	$\frac{c_{\mathrm{H_2PO_4^-}}}{c_{\mathrm{HPO_4^{--}}}}$	x	$\frac{c_{\mathrm{I^{--}}}}{c_{\mathrm{HI^-}}}$	$\frac{c_{\mathrm{I^{--}}} \cdot c_{\mathrm{H_2PO_4^-}}}{c_{\mathrm{HI^-}} \cdot c_{\mathrm{HPO_4^{--}}}}$
0.40	0.44	2.06	0.214	5.9	2.39	0.51
0.60	0.64	1.86	0.344	7.8	1.56	0.54
0.80	0.84	1.66	0.506	9.5	1.11	0.56
1.00	1.04	1.46	0.712	11.05	0.810	0.57
1.20	1.24	1.26	0.984	12.55	0.594	0.585
1.40	1.44	1.06	1.38	14.0	0.429	0.59
1.60	1.64	0.86	1.91	15.25	0.311	0.59
1.80	1.84	0.66	2.79	16.45	0.216	0.60
1.90	1.94	0.56	3.43	17.05	0.173	0.60

TABLE 3

Colorimeter measurements with bromocresol green

Total equivalent concentration = 0.10

$c_{\mathrm{Cl}^-} \times 10$	$c_{\mathrm{HAc}} \times 10$	$c_{\mathrm{Ac}^-} \times 10$	$\frac{c_{\mathrm{HAc}}}{c_{\mathrm{Ac}^-}}$	x	$\frac{c_{\mathrm{I^{--}}}}{c_{\mathrm{HI^-}}}$	$\frac{c_{\mathrm{I^{--}}} \cdot c_{\mathrm{HAc}}}{c_{\mathrm{HI^-}} \cdot c_{\mathrm{Ac^-}}}$	INDICATOR SAMPLE*
0.24	0.24	0.76	0.316	5.7	2.51	0.79	a
0.32	0.32	0.68	0.471	7.3	1.74	0.82	a
0.40	0.40	0.60	0.666	8.95	1.23	0.82	a
0.40	0.40	0.60	0.666	8.95	1.23	0.82	b
0.40	0.40	0.60	0.666	9.0	1.22	0.81	c
0.40	0.40	0.60	0.666	8.95	1.23	0.82	d
0.48	0.48	0.52	0.923	10.6	0.877	0.81	a
0.56	0.56	0.44	1.27	12.1	0.653	0.83	a
0.56	0.56	0.44	1.27	12.15	0.646	0.82	b
0.56	0.56	0.44	1.27	12.1	0.653	0.83	c
0.56	0.56	0.44	1.27	12.15	0.646	0.82	d
0.64	0.64	0.36	1.78	13.7	0.460	0.82	a
0.72	0.72	0.28	2.57	15.15	0.320	0.82	a
0.80	0.80	0.20	4.00	16.6	0.205	0.82	a
0.80	0.80	0.20	4.00	16.6	0.205	0.82	b
0.80	0.80	0.20	4.00	16.6	0.205	0.82	c
0.80	0.80	0.20	4.00	16.6	0.205	0.82	d
0.88	0.88	0.12	7.33	18.0	0.111	0.81	a
Average $K_C = \frac{C_{\mathrm{I^{--}}} \cdot C_{\mathrm{HAc}}}{C_{\mathrm{HI^-}} \cdot C_{\mathrm{Ac^-}}}$ ……						0.82±0.008	

* Bromocresol green indicator samples: (a) obtained from Eastman Kodak Company; (b) same as a, but recrystallized from acetic acid; (c) donated by Hynson, Westcott, and Dunning, Inc., (d) same as c, but recrystallized from acetic acid.

Table 3 gives results obtained with the colorimeter using the acetate buffer with bromocresol green. All columns have the same interpretation as in table 1, except that there is an extra column giving the sample of indicator used in each measurement which is explained in the footnote. It is clear that the values of K_C obtained for the four samples are identically equal. All the measurements made with the acetic acid–acetate buffer and bromocresol green were measured with the colorimeter. No trend in the values of K_C was observed even at concentrations as low as 0.002.

All the results for measurements at various concentrations are collected in tables 4 and 5. Table 4 gives the results for both test tube and colorimeter measurements for bromothymol blue and phosphate buffer. It is seen that these two sets of measurements agree within the experimental error of the test tube set. Table 5 gives the results for all four samples of bromocresol green and acetate buffer.

TABLE 4

K_C values for bromothymol blue phosphate buffer equilibrium

TOTAL EQUIVALENT CONCENTRATION	$K_c = \frac{C_{I^{--}} \cdot C_{H_2PO_4^-}}{C_{HI^-} \cdot C_{HPO_4^{--}}}$	ROOT MEAN SQUARE DEVIATION	METHODS* USED TO MEASURE $\frac{C_{I^{--}}}{C_{HI^-}}$
0.00245	(0.60)	–	a
0.00496	(0.595)	–	a
0.00496	(0.58)	–	b
0.00995	0.59	±0.007	a
0.00993	0.59	±0.01	b
0.01983	0.58	±0.02	b
0.04963	0.57	±0.007	a
0.04963	0.57	±0.02	b
0.09925	0.54	±0.005	a
0.09925	0.56	±0.02	b
0.19850	0.48	±0.008	a

* Methods used to measure ratio $\frac{C_{I^{--}}}{C_{HI^-}}$: (a) colorimeter; (b) bicolor standards in test tubes.

The values of K_C for the most dilute solutions given in parentheses were obtained from the more acid solutions, the more basic ones being rejected.

V. THEORETICAL DISCUSSION

The values of K_C given in tables 4 and 5 are plotted against total salt concentration in figures 1 and 2. First, considering bromothymol blue in the primary–secondary phosphate buffer, we see in figure 1 that the "salt effect" is linear in the concentration. This is in accordance with the theory, because both indicator and buffer are of the same electric type.

TABLE 5

K_C values for bromocresol green acetate buffer equilibrium

TOTAL CONCENTRATION	$C^{1/2}$	$K_C = \frac{C_{I^-} \cdot C_{HAc}}{C_{HI^-} \cdot C_{Ac}}$	ROOT MEAN SQUARE DEVIATION	DETERMINATIONS*
0.002	0.045	0.65	±0.015	a
0.002	0.045	0.65	±0.01	b
0.005	0.071	0.67	±0.01	a
0.005	0.071	0.67	±0.01	b
0.010	0.100	0.69	±0.009	a
0.010	0.100	0.70	±0.007	b
0.020	0.142	0.72	±0.01	a
0.020	0.142	0.73	±0.007	b
0.050	0.224	0.77	±0.008	a
0.050	0.224	0.78	±0.007	b
0.100	0.316	0.82	±0.01	b
0.200	0.446	0.86	±0.005	b

* The measurements marked a were made at an earlier stage of our investigation than those marked b.

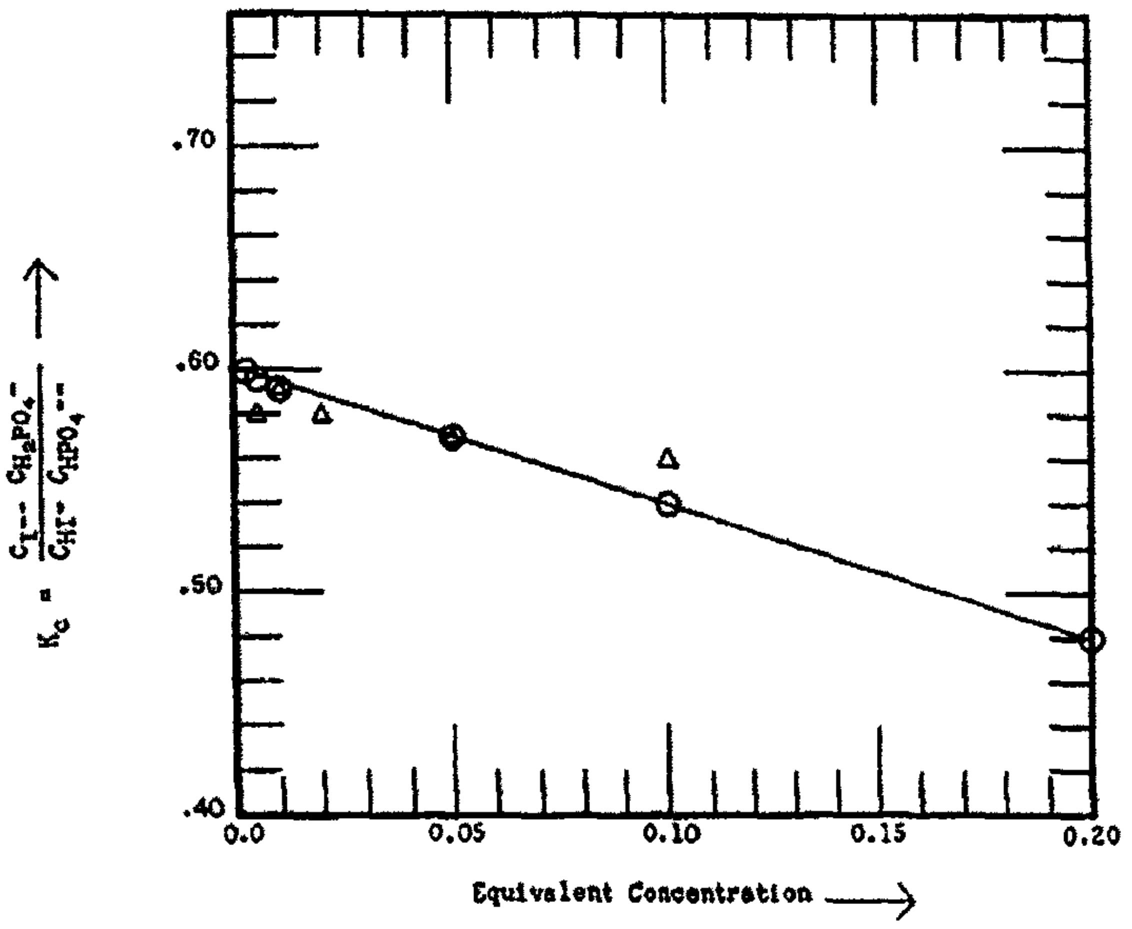

FIG. 1

△ Test tube measurements
○ Colorimeter measurements

Assuming that the trend in dilute solutions is due to contamination by carbon dioxide and that the more acid solutions give the correct values of K_C, the extrapolation is small and fairly safe. The extrapolation gives 0.60 as the value for the ratio $K_{HI}/K_{H_2PO_4^-}$ where K_{HI^-} and $K_{H_2PO_4^-}$ are the true thermodynamic acid constants of bromothymol blue and of $H_2PO_4^-$ respectively.

On the other hand, if we observe the shape of the curve for bromocresol green in the acetic acid-acetate buffer in figure 2, we find a pronounced curvature even at low concentrations, which makes extrapolation more uncertain. This pronounced "salt effect" at low concentrations is in accordance with the theory due to the fact that the indicator and buffer are of different electric types. Formula 17 leads to a limiting law at infinite dilution

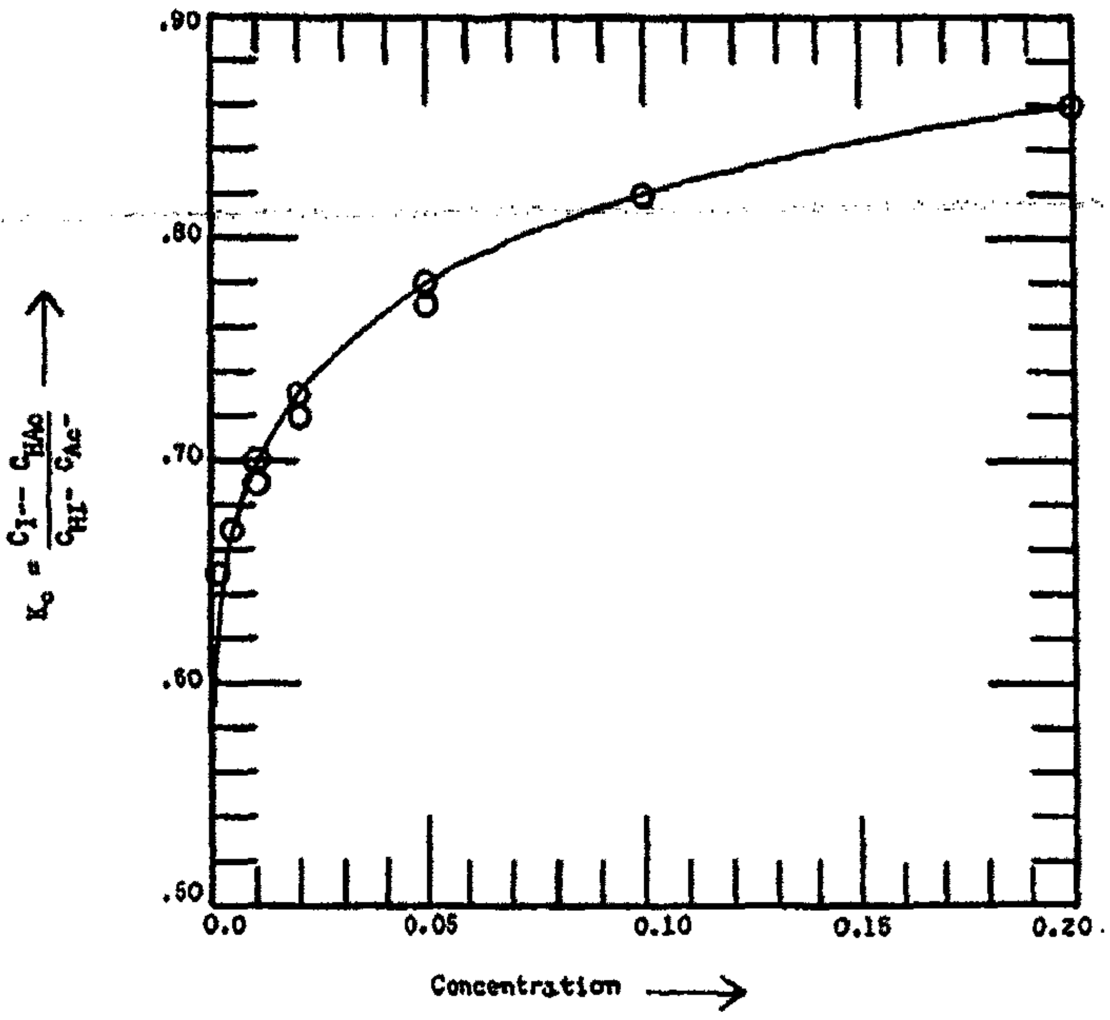

FIG. 2

$$-\log_{10}\frac{f_{HI^-}\cdot f_{Ac^-}}{f_{I^{--}}\cdot f_{HAc}} = -1.0\,C^{1/2} \tag{18}$$

or

$$\frac{f_{HI^-}\cdot f_{Ac^-}}{f_{I^{--}}\cdot f_{HAc}} = 1 + 2.30\,C^{1/2} \tag{19}$$

If then we plot K_C against $C^{\frac{1}{2}}$ and extrapolate, the curve should have at zero concentration a finite slope equal to the product of 2.30 and the limiting value of K_C. This is shown in figure 3. If this extrapolation is correct, the value of K_{HI}/K_{HAc} is 0.59, where K_{HI} and K_{HAc} are the true thermodynamic acid constants of bromocresol green and acetic acid respectively.

In figure 3 are included values of $C_{I^{--}} \cdot C_{HAc}/C_{HI^-} \cdot C_{Ac^-}$ for bromocresol green calculated from the test-tube experiments of Sendroy and Hastings (15), all of which were made with only one buffer ratio C_{HAc}/C_{Ac^-} equal to 0.233. We have no explanation of the large discrepancy between their results and ours, especially as they also used bromocresol green obtained from Hynson, Westcott and Dunning.

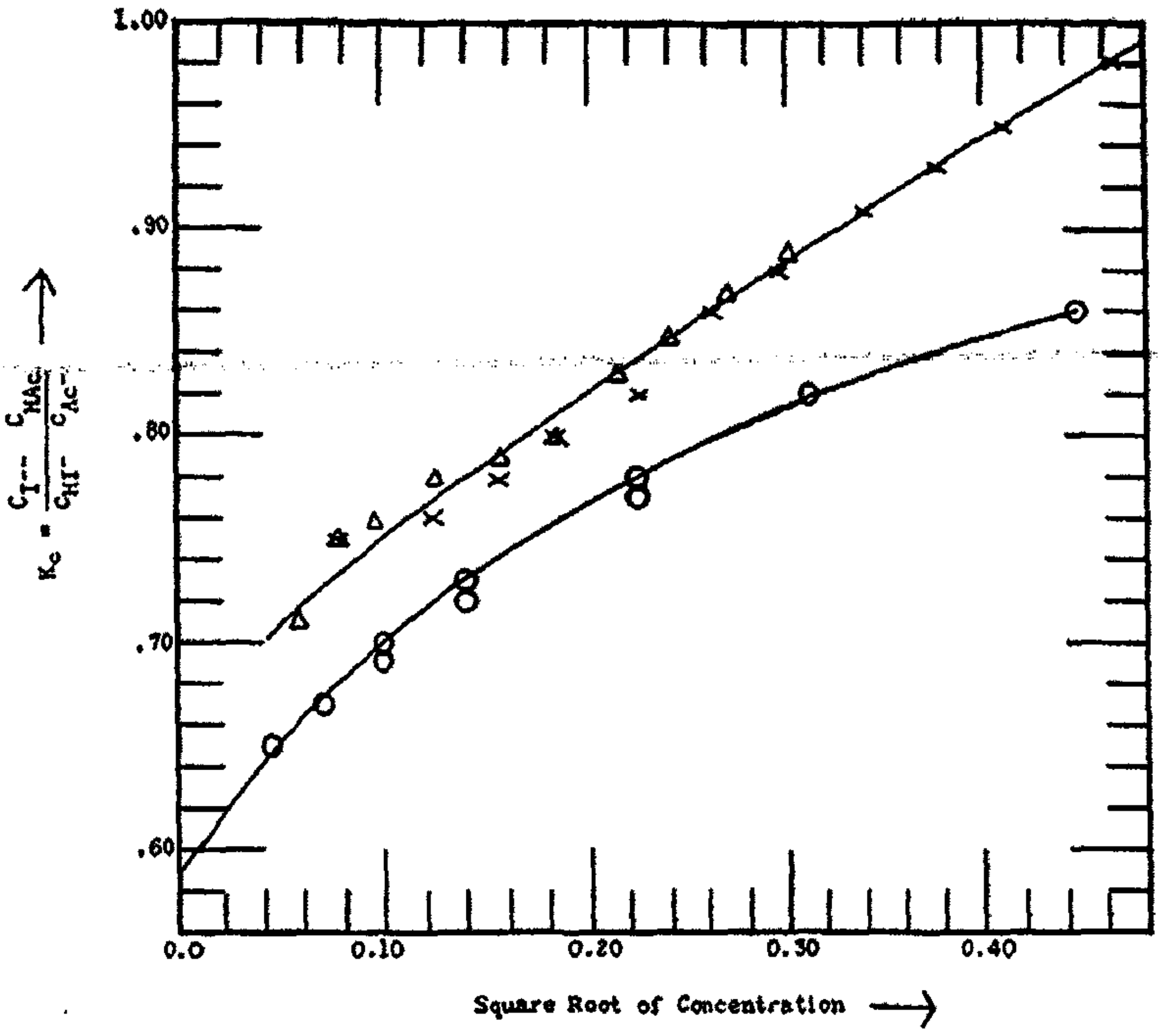

FIG. 3

○ Our measurements
Hastings and Sendroy's measurements:
△ In HAc + NaAc
× In HAc + NaAc + NaCl

VI. ACID CONSTANT OF BROMOCRESOLGREEN

Having obtained values of K_C or $K_{(C)HI}/K_{(C)HA}$ experimentally and values of K_{HI}/K_{HA} by extrapolation, if we have independent values of $K_{(C)HA}$ or K_{HA}, we can by multiplication calculate values of $K_{(C)HI}$ or K_{HI} for the indicator.

In the case of acetic acid reliable data are available for K_{HA}. Harned and Ehlers (11) have evaluated K_{HAc} by electrometric measurements without liquid junction potentials. Combining their value 1.75×10^{-5} for K_{HAc} with our value 0.59 for K_{HI}/K_{HAc}, we obtain 1.03×10^{-5} as the value for the true thermodynamic acid constant K_{HI} of bromocresol green. This is probably accurate to within 1 or 2 per cent.

The $K_{(C)HI}$ value of bromocresol green in an acetate buffer solution at a salt concentration of 0.10 molar may be estimated as follows. According to the very accurate measurements of Güntelberg (9) the value of f_{HCl} in 0.1 M sodium chloride is 0.79. If we assume this same value for $f_{H,Ac}$, the mean activity coefficient of the hydrogen and acetate ions in an acetate buffer of total salt concentration 0.1, the error can hardly be more than 2 or 3 per cent. On this assumption we obtain for $K_{(C)HI}$ at an ionic strength 0.1 the value 2.30×10^{-5} with a probable accuracy of about 5 per cent.

The perfect agreement between this value and that of 2.33×10^{-5} computed by Kilpatrick and Chase (12) from the data given by Kolthoff is fortuitous, as the accuracy claimed for Kolthoff's value is only 12 per cent. Kilpatrick and Chase have themselves made a study of the "salt effect" of bromocresol green in buffers of benzoic acid–benzoate, acetic acid–acetate, and hexahydrobenzoic acid–hexahydrobenzoate. Their measurements were mostly at concentrations greater than those used by us, their lowest salt concentration being 0.1 molar. At this concentration they assign the value 3.07×10^{-5} to $K_{(C)HI}$ of bromocresol green. We are unable to explain the discrepancy between this value and ours. It is only partially accounted for by the dependence of Kilpatrick and Chase's values on electrometric measurements of cells with liquid–liquid junctions. For, according to a private communication from Dr. Kilpatrick, their mean values for the ratio $C_{I^{--}}\, C_{HAc}/C_{HI^-}\, C_{Ac^-}$ in 0.1 M acetate buffers were 0.94 with a commercial sample of indicator and 1.03 with a special sample of indicator, as compared with our value 0.82. The discrepancy can hardly be due to difference in the indicator sample, as we obtained identical values with all four samples and that obtained from Hynson, Westcott and Dunning was the same preparation as supplied by them to Kilpatrick and Chase.

VII. ACID CONSTANT OF BROMOTHYMOL BLUE

To determine the acid constant of bromothymol blue from our value of $K_{HI}/K_{H_2PO_4^-}$ we require to have a value for $K_{H_2PO_4^-}$. No values are available for this quantity other then those obtained by means of cells with liquid–liquid junctions. Bjerrum and Unmack (1) on the basis of such measurements assign the value 6.20×10^{-8} to $K_{H_2PO_4^-}$ at 25°C. According to electrometric measurements described in another paper (8) we are able to confirm Bjerrum and Unmack's experimental electromotive force values to within 0.4 millivolt, but for reasons there given we consider that a more probable value for $K_{H_2PO_4^-}$ is 5.97×10^{-8}. Combining this value of $K_{H_2PO_4^-}$ with an extrapolated value 0.60 for $K_{HI}/K_{H_2PO_4^-}$, we obtain for the thermodynamic acid constant K_{HI} of bromothymol blue the value 3.58×10^{-8} with an estimated accuracy of 2 or 3 per cent.

For the reasons given above we prefer to give our results mostly in a form independent of computations based on electrometric measurements of cells with liquid-liquid junctions. We have, however, for the sake of comparison with values given by Kolthoff (13), combined our colorimetric data with our electrometric data to compute values of $-\log_{10} C_{H^+} f_{H^+} \cdot C_I/C_{HI}$ called pK_I by Kolthoff. As seen from table 6 our values are in good agreement with those given by Kolthoff.

TABLE 6

Ionic strength	0.0125	0.10	0.125	0.15	0.25
Our pK_I values	7.30		7.10		7.05
Kolthoff's pK_I values		7.10		7.06	

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NEW BOOKS

The Sanitation of Public Water Supplies. By MURRAY P. HORWOOD. 15 x 23 cm.; 181 pp. Baltimore: Charles C. Thomas, 1932.

In the first chapter, dealing with public health activity, the author divides the history of development of the field into successive periods in which the sanitary engineer, the bacteriologist, and the physiologist exercised a dominant influence. He regards the control of environment as principally responsible for advances made —an opinion which will not be shared by many public health workers. A more extended discussion of vital statistics would be a welcome addition to this chapter. In chapters II and III the development of public water supplies is treated historically and statistically; information concerning several large cities is cited. Chapter IV discusses the requirements of drinking water, dealing with physical, mineral, and bacteriological standards. The relation of water and disease is comprehensively treated in chapter V, particular attention being given to typhoid fever.

Methods of water treatment are detailed in chapters VI to X, inclusive, titled successively: "The Purification and Improvement of Water Supplies," "Water Softening," "Slow Sand Filtration," "Rapid Sand Filtration," and "Disinfection." The chapters on "Softening" and "Rapid Sand Filtration" are exceptionally good, typical chemical reactions and descriptions of operating conditions characterizing the discussion. Disinfection by use of hypochlorite, chlorine, and chloramine, with discussion of the chemical "mechanism" is treated in the final chapter, with methods of use for various conditions. The use of ultra-violet light is also described.

The material in this book covers the title comprehensively in an elementary manner, and it should be of value to the general reader, although each technical reader perhaps would prefer to arrange and emphasize the material differently while agreeing that its selection is substantially satisfactory.

FREDERIC BASS.

Phase Rule Studies. By J. E. WYNFIELD RHODES. 19 x 13 cm.; x + 131 pp. London: Oxford University Press, 1933. Price: $2.25.

In the introduction E. L. Rhead says: "Owing to its many practical applications a knowledge of the Phase Rule has become indispensable in the equipment of the modern chemist. . . . The Phase Rule is capable of application in many directions, not only to subjects that are palpably chemical in their nature, but to others that are not essentially so, or, at any rate, are not usually approached from a chemical standpoint. The principles of the Phase Rule are eminently applicable in geology, mineralogy, and metallurgy, although the introduction is generally by avenues other than a course in pure Chemistry."

The chapters are entitled: introductory; one-component systems; two-component systems in which mixed crystals are not formed; two-component systems in which mixed crystals are formed; three-component systems, isothermal diagrams; three-component systems, the polythermal model and its projections; miscellaneous applications of the phase rule; systems of four or more components and their graphical representation; experimental methods employed in phase rule work.

Short as this book is, the author suggests that "students who do not need the whole of the subject matter of this book but desire only to make a general survey, should read chapters I, II, III, IV, and IX."

WILDER D. BANCROFT.

The Lyophilic Colloids (Their Theory and Practice). By MARTIN H. FISHER and MARIAN O. HOOKER. 240 pp.; 84 illustrations; 3 parts. Springfield, Illinois, and Baltimore, Maryland: Charles C. Thomas, 1932. Price $4.25.

This book contains the work of the authors during the last fifteen years. The first two-thirds is devoted to a general discussion of lyophilic colloids. In this first part the authors develop the idea from such systems as phenol-water, quinoline-water, and gelatin-water, of the solution of water in these various substances, as well as the solution of these substances in water. This is the central theme of the book. Extensive usage is made of resistance measurements. The authors plunge themselves into a wilderness of heterogeneous systems without adequate physicochemical tools. The result is confusion. It seems meaningless to the reviewer to distinguish in kind between a solution of phenol in water and that of water in phenol. H. R. Kruyt and H. G. B. de Jong receive no recognition.

The second part is devoted to chemical applications. Here again they emphasize the idea of mutual solubility. They state that when dealing with lyophilic systems ". . the electrical properties, ions, isoelectric points, Donnan equilibria and pHs and CHs all pass out of the picture." There are short sections on greases and the livering of points.

The third section deals with the biological applications. They criticize the osmotic concept of the cell and point out the prevailing confusion in these matters. They discuss a colloid chemical theory of water absorption based on their concepts. They adduce for proof that protoplasm is a solution of water in X, the fact that a man may go in swimming or be rained upon and not dissolve. They declare that there is no free water in protoplasm but they fail to note that there has been an increasing effort on the part of chemists and physiologists to devise accurate methods to determine the exact state of this water and thus dispense with vague speculations.

This book makes interesting reading. It gives us a description of the bogs and morasses from which colloid chemistry emerged some fifteen years ago.

HENRY B. BULL.

Struktur der Materie: vier Vorträge. By P. DEBYE. 22 x 15 cm.; iv + 50 pp. Leipzig: S. Hirzel, 1933. Price (stiff paper covers): 3 R. M.

The subjects of the four lectures are: (1) Interferometric measurement of molecular structures; (2) Electrical structure of molecules; (3) Molecular structure of liquids; (4) Structure of electrolytic solutions. The book deals exclusively with modern developments—such as the application of x-ray and electron diffraction to stereochemical problems, the determination of dipole moments, and other typical branches of the beautiful work with which Debye and his school have been so closely associated during the past decade.

The treatment is entirely elementary and descriptive. The booklet provides an excellent and stimulating survey for non-specialists and young students; its value would be appreciably enhanced by the addition of even a few references to original papers.

H. R. ROBINSON.

THE DECOMPOSITION OF α-NITROCARBOXYLIC ACIDS

WITH SOME REMARKS ON THE DECOMPOSITION OF β-KETOCARBOXYLIC ACIDS

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The object of this paper is to contribute to our understanding of the tendency of α-nitrocarboxylic acids to split off carbon dioxide.

$$>\mathrm{CNO_2\cdot COOH} \longrightarrow\ >\mathrm{CHNO_2} + \mathrm{CO_2}$$

The simplest acid of this type, nitroacetic acid, was studied kinetically by Heuberger (2, 3) and, independently, by the author of this paper (7). In the latter work, the rate of decomposition was determined on solutions of hydrochloric acid of various concentrations and in buffer solutions, mainly acetate buffers (pH = 4 to 5). The rate increases with decreasing hydrogen-ion concentration and reaches a maximum value in the acetate buffers. Here it is independent of the hydrogen-ion concentration. In sufficiently alkaline solution nitroacetic acid is stable.

While the free nitroacetic acid consists of two tautomers

$$\mathrm{O_2N\cdot CH_2\cdot COOH} \quad \text{and} \quad \mathrm{HOON\colon CH\cdot COOH}$$

there are three possible forms of the univalent nitroacetate ion

$$\mathrm{O_2N\cdot CH_2\cdot CO_2^-},\quad \mathrm{^-O_2N\colon CH\cdot COOH}, \quad \text{and} \quad \mathrm{HOON\colon CH\cdot CO_2^-}$$

and only one divalent ion

$$\mathrm{^-O_2N\colon CH\cdot CO_2^-}$$

The experiments agree with the assumption that both the free acid and the divalent ion are stable, while one of the univalent ions is unstable. From the experiments the first dissociation constant of nitroacetic acid (about 0.02) was calculated. It could not be settled from the experiments on nitroacetic acid which of the three forms of the nitroacetate ion is unstable, or, in other words, whether the instability of the α-nitrocarboxylic acids is connected with the formation of an aci-form of the nitro compound. In order to solve this problem α-nitroisobutyric acid (dimethylnitroacetic acid) is studied in the present paper. This substance is not a pseudo acid. It forms only the ion $O_2NC(CH_3)_2CO_2^-$. It is found that it splits off carbon dioxide in the same way as nitroacetic acid and with a similar velocity. Consequently, the unstable form of the α-nitrocarboxylic acids is the ion $>CNO_2 \cdot CO_2^-$.

However, while nitroacetic acid gives carbon dioxide and nitromethane as final reaction products, the carbon dioxide cleavage of α-nitroisobutyric acid in hydrochloric acid is followed by a secondary reaction by which more gas is developed. From the experimental results given below the following mechanism is suggested

$$O_2NC(CH_3)_2CO_2^- \rightarrow {}^-O_2N{:}C(CH_3)_2 + CO_2 \qquad (1)$$
$$H^+ + {}^-O_2N{:}C(CH_3)_2 \rightarrow HOON{:}C(CH_3)_2 \qquad (2)$$
$$HOON{:}C(CH_3)_2 \rightarrow OC(CH_3)_2 + \tfrac{1}{2}N_2O + \tfrac{1}{2}H_2O \qquad (3)$$

Reaction 1 is followed by the instantaneous reaction 2, and this by the decomposition 3. In not too weak hydrochloric acid, reaction 3 is so much quicker than reaction 1 that the carbon dioxide cleavage determines the velocity of the total reaction.

In acetate buffer solutions the production of gas in excess of one mole per mole of α-nitroisobutyric acid is extremely slow. Probably the aci-form produced by reaction 2 is transformed into the nitro compound

$$HOON{:}C(CH_3)_2 \rightarrow O_2NCH(CH_3)_2 \qquad (4)$$

sufficiently quickly to avoid the decomposition 3. This quick rearrangement in the acetate buffer is in conformity with earlier work (10) in which it was found that the prototropic isomerization of aliphatic nitro compounds is catalyzed by acetate ions and other bases.

α-Nitroisobutyric acid was prepared by the method of Steinkopf and Supan (14). The beautiful white crystals obtained were used for the kinetic experiments without purification. The acid could only be recrystallized with very great loss. When an experiment was repeated with different preparations (m.p., 93–95°C.) concordant results were obtained.

The decomposition was investigated at 17.84 and at 9.78°C. Experiments were carried out in hydrochloric acid and acetate buffer solution by observing the increase in pressure above the solution during reaction by means of an apparatus described in an earlier paper (9).

For comparison some experiments on nitroacetic acid were carried out under the same circumstances. The substance was prepared as described in the paper on nitroacetic acid (7).

When a little nitroisobutyric acid was dissolved in barium hydroxide the solution kept clear for some seconds. Then a precipitate of barium carbonate began to be formed. This shows that the nitroisobutyrate ion is unstable.

EXPERIMENTS IN ACETATE BUFFER SOLUTIONS

Here

c = the initial concentration of the reacting acid.

$c - x$ = its concentration t minutes after the start.

P = the difference between the final pressure readings and the reading at the time t.

P_0 = the value of P, when $t = 0$.

ϕ = the proportionality factor $P_0/c = P/(c-x)$ (cm. of mercury per mole per liter).

k^* = unimolecular velocity constant. By an asterisk we denote that the constant has been calculated by means of decadic logarithms. k^* is computed in the usual way by plotting log P against t.

The agreement with the unimolecular law is good. The carbon dioxide cleavage was finished a few hours after the start. After that time a very slow pressure increase was noticed. This secondary reaction was sufficiently slow to allow an accurate determination of the end point of the primary reaction. When the primary reaction was near its end the solution assumed a greenish color.

The results of experiments in different acetate buffer solutions are given in table 1. Each experiment was carried out with 60 cc. of solution and enough nitroisobutyric acid to make it 8 to 10 × $10^{-3}M$. The total pressure increase (about 6 cm. of mercury) corresponds to an average value of $\varphi = P_0/c = 643$ for the experiments at 17.84°C. This is only 3.4 per cent more than the value $\varphi = 622$ found by adding a known amount of sodium carbonate to 60 cc. of the acetate buffer. The discrepancy may be due to a small vapor pressure of the other reaction product. Hence, one mole of carbon dioxide is produced per mole of nitroisobutyric acid in the acetate buffers.

As seen from table 1 the velocity of decomposition is not affected by a considerable variation of the ratio between the concentrations of acetic acid and sodium acetate. In the last experiment at 17.84°C. the final pressure was not determined as accurately as usual. It was therefore omitted when taking the mean values. The fourth column gives the number of the preparation of nitroisobutyric acid. It is seen that different preparations decompose with the same velocity.

In table 2 are given the results of experiments on the decomposition of nitroacetic acid carried out under the same experimental conditions.

EXPERIMENTS IN HYDROCHLORIC ACID

Here the pressure increase was approximately one and a half times as great as would be expected from the experiments in acetate buffer solutions. According to the mechanism suggested in the schemes 1 to 3, one mole of carbon dioxide and half a mole of nitrous oxide should be produced per mole of nitroisobutyric acid. In order to test this assumption the following calculations were carried out.

First the total volume, v cc., of the reaction vessel was determined by adding a known amount of sodium carbonate to the flask which contained a known volume, u cc., of 0.1 M hydrochloric acid at 17.84°C. If we denote by p_0 (cm. of mercury) the pressure increase per mole of sodium carbonate and by f the Ostwald absorption coefficient (the ratio between the concentrations of a gas in liquid and gaseous phase at equilibrium), the following formula holds

$$p_0 (v - u + fu) = RT$$

where $RT = 1.815 \times 10^6$. From the investigation of Geffcken (1) we find for carbon dioxide at 17.84°C. $f = 0.988$. The results are given in table 3. The average value of the volume is $v = 173.6$ cc.

TABLE 1

Decomposition of α-nitroisobutyric acid in acetate buffer solutions

TEMPERATURE	(CH_3COOH)	(CH_3CO_2Na)	PREPARATION	φ	k^*
degrees C.					
17.84	0.100	0.100	1	646	0.0449
	0.100	0.100	1	641	0.0446
	0.050	0.050†	1	643	0.0449
	0.050	0.100	1	642	0.0448
	0.180	0.100	1	(652)	(0.0440)
Average values				643	0.0448
9.78	0.100	0.100	1	570	0.01396
	0.100	0.100	3	575	0.01394
Average values				572	0.01395

† Containing 0.050 M sodium chloride

TABLE 2

Decomposition of nitroacetic acid in acetate buffer solutions

TEMPERATURE	(CH_3COOH)	(CH_3CO_2Na)	k^*	AVERAGE VALUE OF k^*
degrees C.				
17.84	0.100	0.100	0.02464	0.02460
	0.100	0.100	0.02456	
	0.050	0.050	0.02460	
9.78	0.100	0.100	0.00772	0.00774
	0.100	0.100	0.00776	

The molar pressure increase p_2 for nitroisobutyric acid added to hydrochloric acid is given in the fifth line of table 3. By subtraction of p_0, the molar pressure increase for sodium carbonate added to hydrochloric acid, we find the partial pressure p_3 (per mole of nitroisobutyric acid) of the gas which is produced in addition to the carbon dioxide. If we assume that n moles of a gas with the absorption coefficient f is produced per mole of the acid, we have

$$p_3(v - u + fu) = nRT$$

or

$$173.6p_3 = 1.815 \times 10^6\, n + (1 - f)\, p_3 u$$

When the experimental values of u and p_3 are introduced we get as result $n = 0.538$ mole of a gas with the absorption coefficient $f = 0.728$ (compare the sixth and seventh line of table 3). From Geffcken's paper we get for nitrous oxide at 17.84°C. $f = 0.718$.

TABLE 3

u, volume of solution	20	60	100
p_0, pressure increase per mole of Na_2CO_3 in 0.1 *M* HCl	1.042×10^4	1.046×10^4	1.061×10^4
v, total volume of vessel	174.3	174.2	172.2
p_1, pressure increase per mole of nitroisobutyric acid in acetate buffers	(1.068×10^4)	1.072×10^4*	(1.088×10^4)
p_2, pressure increase per mole of nitroisobutyric acid in 0.03–0.3 *M* HCl	1.623×10^4	1.667×10^4†	1.729×10^4
$p_3 = p_2 - p_0$ (observed)	0.581×10^4	0.621×10^4	0.668×10^4
p_3 (calculated from $f = 0.728$ and $n = 0.538$)	0.581×10^4	0.621×10^4	0.667×10^4
$p_4 = p_2 - p_1$ (observed)	0.555×10^4	0.595×10^4	0.641×10^4
p_4 (calculated from $f = 0.716$ and $n = 0.513$)	0.554×10^4	0.594×10^4	0.641×10^4

* Average of four experiments (table 1).

† Average of six experiments (table 4).

If instead of subtracting the molar pressure increase for sodium carbonate in hydrochloric acid we subtract that for nitroisobutyric acid in acetate buffers (p_1), we get an even better agreement. Only the value of p_1 for 60 cc. of buffer solution has been determined by experiment. For the calculation of the values in parentheses we have used the assumption that the ratio p_1/p_0 is independent of the volume u. We find (compare the last two lines of the table) $n = 0.513$ and $f = 0.716$.

In order to show that one mole of acetone is formed per mole of nitroisobutyric acid (scheme 3), samples were taken from the reaction vessel after some of the experiments. Acetone was determined by the method of Messinger (6) in the form suggested by Ljunggren (5). By addition of sodium hydroxide and an excess of iodine solution iodoform was precipitated. The excess of iodine was titrated with thiosulfate after the solution had been acidified with sulfuric acid. The analysis gave as result that 0.96 to 1.00 moles of acetone had been formed per mole of nitroisobutyric acid. After the iodine set free by the addition of the acid had been titrated, more iodine was slowly liberated. The solution seemed to contain a substance which catalyzes the oxidation of hydriodic acid by the air. The deviation from 1.00 found in the analysis may have its origin in this source of error.

Shortly after the start of the reaction the solution assumed a light green color which vanished when the reaction was finished.

We shall now see that a comparison of the experiments in hydrochloric acid and acetate buffers leads to the following explanation. In the acetate buffers the acid is completely ionized and the velocity constant k found here is that for the decomposition of the nitroisobutyrate ion. In hydrochloric acid the fraction α which is ionized decomposes with the velocity constant k, while the unionized acid is stable. This is formally equivalent to saying that all the nitroisobutyric acid (free and ionized) decomposes with the velocity constant αk. We test the explanation by calculating the dissociation constant K of the nitroisobutyric acid from the degree of dissociation α found as the ratio between the velocity constants in hydrochloric acid and in acetate buffers.

We first assume that reaction 3 is so rapid compared with reaction 1 that the latter determines the velocity of the total reaction.

In computing the velocity constant we must take into account that the hydrogen-ion concentration of the solution of the acid in hydrochloric acid is diminished a little when the acid decomposes. We denote by a the concentration of hydrochloric acid, by α_0, α, and α_∞ the degrees of dissociation of the nitroisobutyric acid at the times 0, t, and ∞. According to the mass action law we have

$$\frac{\alpha}{1-\alpha}\,[a+\alpha\,(c-x)] = K$$

From this we obtain

$$\alpha = \frac{K}{a+\alpha(c-x)+K} \quad \text{and} \quad \alpha_\infty = \frac{K}{a+K} \tag{5}$$

The velocity is given by

$$\frac{dx}{dt} = k\alpha(c-x) \tag{6}$$

When equation 5 is introduced equation 6 may be written

$$k\alpha_\infty \mathrm{d}t = \left(\frac{1}{c - x} + \frac{\alpha_\infty}{a + K} - \frac{\alpha_\infty - \alpha}{a + K}\right) \mathrm{d}x$$

By integration we get

$$- k\alpha_\infty t = \text{const.} + l(c - x) + \frac{\alpha_\infty}{a + K}(c - x) - \int_c^{c-x} \frac{\alpha_\infty - \alpha}{a + K}\, \mathrm{d}(c - x)$$

If we introduce $P = \varphi\ (c - x)$, equation 5, and $k^* = 0.4343k$, we may write the expression as follows

$$- k^*\alpha_\infty t = \text{const.} + \log P + \beta P + \Delta \qquad (7)$$

where

$$\beta = \frac{0.4343K}{\varphi(a + K^2)}$$

and

$$\Delta = \beta \int_{P_0 - P = 0}^{P_0 - P} \frac{\alpha_\infty - \alpha}{\alpha_\infty}\, \mathrm{d}\,(P_0 - P) < \beta P_0 \frac{\alpha_\infty - \alpha_0}{\alpha_\infty}$$

For the calculation of the correction βP we must know K. This is found sufficiently accurately by calculating α_∞ from a preliminary value of the velocity constant $\alpha_\infty k$. The correction Δ is of no importance except in the most dilute solutions of hydrochloric acid. Here we may compute it by rough graphical integration.

The results of the experiments on nitroisobutyric acid are given in tables 4 and 5. The velocity constant $k^*\alpha_\infty$ is found by plotting the sum of log P and βP and, if necessary, the correction Δ against t. For the most concentrated solutions of hydrochloric acid we get points that fall well on a straight line. For 0.1 M and less concentrated acid the points fall on a curve which approaches more quickly to a straight line the more concentrated the acid. This result is what one would expect when a part of the gas is developed by a consecutive reaction whose velocity is less predominating the smaller the hydrogen-ion concentration. For the velocity constant $\alpha_\infty k^*$ of the primary reaction we take the numerical value of the slope of the straight line. While the approach to the straight line was sufficiently quick in 0.1 M hydrochloric acid to allow a good determination of $\alpha_\infty k^*$, this was uncertain even in 0.05 and 0.033 M, and in 0.02 and 0.01 M hydrochloric acid the straight line could not be drawn accurately enough. However, if we calculate $\alpha_\infty k^*$ for the experiment in 0.02 M HCl + 0.08 M NaCl according to the interpretation given above, using the dissociation constant K found for the same salt concentration in more acid solution, a line with the slope $-\alpha_\infty k^*$ fits well as an asymptote to the curve.

For the calculation of α_∞ from $\alpha_\infty k^*$ we use the value of k^* found in the experiments in acetate buffer solutions. It is seen from the tables that $K = a\frac{\alpha_\infty}{1 - \alpha_\infty}$ is constant when the concentration of hydrochloric acid is varied, while the total salt concentration is kept constant. In order to see if the values of K at different salt concentrations agree among themselves and to find the activity dissociation constant K_0 we proceed in the following way. According to the Debye-Hückel law we have

TABLE 4

Decomposition of α-nitroisobutyric acid in hydrochloric acid at 17.84°C.

(HCl)	PREPARATION	φ	$\alpha_\infty k^*$	α_∞	K	$-\log K$	μ	$-\log K + 0.998\sqrt{\mu}$	$1.928 + 0.873\mu$	$\delta \times 10^3$
0.3006	1	1006	0.003165	0.0706	0.0229	1.641	0.3008	2.190	2.190	0
0.1994	1		0.00445	0.0993	0.0220	1.657	0.1997	2.103	2.102	+1
0.1001	1	999	0.00746	0.1665	0.0200	1.699	0.1006	2.016	2.016	0
0.5005†	1	1000	0.01286	0.2870	0.0202	1.696	0.1009	2.013	2.016	−3
0.05005†	2	1000	0.01272	0.2839	0.0198	1.702	0.1009	2.019	2.016	+3
0.05005	1	997	0.01196	0.2670	0.0182	1.739	0.0509	1.964	1.972	−8
0.03337	1	997	0.01560	0.3482	0.0178	1.749	0.0345	1.935	1.958	−23
0.02016‡	1	(910)								
0.01008§	1	(991)								

† Containing 0.0500 *M* sodium chloride.

‡ Containing 0.0800 *M* sodium chloride.

§ Containing 0.0900 *M* sodium chloride.

TABLE 5

Decomposition of α-nitroisobutyric acid in hydrochloric acid at 9.78°C.

(HCl)	PREPARATION	$\alpha_\infty k^*$	α_∞	K	$-\log K$	μ	$-\log K + 0.986\sqrt{\mu}$	$1.871 + 0.873\mu$	$\delta \times 10^3$
0.3006	2	0.001052	0.0754	0.0245	1.611	0.3009	2.152	2.133	+19
0.2007	2	0.001548	0.1110	0.0251	1.601	0.2011	2.044	2.046	−2
0.2014	2	0.001538	0.1103	0.0250	1.603	0.2018	2.047	2.047	0
0.1004†	4	0.00276	0.1978	0.0248	1.606	0.2011	2.049	2.046	+3
0.1001	3	0.00257	0.1842	0.0226	1.646	0.1007	1.959	1.959	0
0.05005	3	0.00412	0.2953	0.0210	1.678	0.0512	1.902	1.916	−14

† Containing 0.100 *M* sodium chloride.

$$-\log K = -\log K_0 - A\sqrt{\mu} + B\mu \tag{8}$$

where μ is the ionic strength and A a constant (at 18°C. 0.998, and at 10°C. 0.986), while B approaches to a constant value when $\mu \rightarrow 0$. For μ we use a mean value found by adding $\frac{1}{2}\alpha_0 c$ to the sum of the concentrations of hydrochloric acid and sodium chloride. If we plot $-\log K + A\sqrt{\mu}$

against μ for each of the two series of experiments, the points fall fairly well on straight lines. Only the points for the most dilute hydrochloric acid deviate a little, probably owing to the greater error in computing the velocity constants. The neglect of these points in extrapolating to zero salt concentration is to some extent justified by the results on nitroacetic acid in hydrochloric acid (tables 6 and 7), where we have no consecutive reaction. Here there is a linear relation between $-\log K + A\sqrt{\mu}$ and μ down to the greatest dilution ($0.3 - 0.01\ M$). The last column in tables 4 to 7 shows the agreement of the experimental results for nitroisobutyric and nitroacetic acids with expression 8, using the values of K_0 and B computed in this way. δ is the difference $(-\log K + A\sqrt{\mu}) - (-\log K_0 + B\mu)$.

TABLE 6

Decomposition of nitroacetic acid in hydrochloric acid at 17.84°C.

(HCl)	$\alpha_\infty k^*$	α_∞	K	$-\log K$	μ	$-\log K + 0.998\sqrt{\mu}$	$1.682 + 0.927\mu$	$\delta \times 10^3$
0.3006	0.002816	0.1145	0.0389	1.410	0.3011	1.959	1.960	−1
0.2007	0.00388	0.1577	0.0376	1.425	0.2015	1.874	1.869	+5
0.1000	0.00632	0.2569	0.0346	1.461	0.1014	1.779	1.775	+4
0.05010	0.00952	0.3870	0.0316	1.501	0.0519	1.728	1.730	−2
0.05010	0.00950	0.3862	0.0315	1.502	0.0519	1.729	1.730	−1
0.02014	0.01432	0.5821	0.0280	1.552	0.0228	1.703	1.703	0
0.01009	0.01777	0.7224	0.0262	1.581	0.0131	1.695	1.694	+1

TABLE 7

Decomposition of nitroacetic acid in hydrochloric acid at 9.78°C.

(HCl)	$\alpha_\infty k^*$	α_∞	K	$-\log K$	μ	$-\log K + 0.986\sqrt{\mu}$	$1.661 + 0.927\mu$	$\delta \times 10^3$
0.2007	0.001280	0.1654	0.0398	1.400	0.2016	1.844	1.848	−4
0.1000	0.002067	0.2671	0.0364	1.438	0.1015	1.757	1.755	+2
0.0501	0.003065	0.3960	0.0328	1.484	0.0523	1.710	1.709	+1

TABLE 8

K_0 and k^* for nitroisobutyric acid nitroacetic acids

ACID	K_0		k^*		Q
	At 17.84°C.	At 9.78°C.	At 17.84°C.	At 9.78°C.	
					kg.-cal.
Nitroisobutyric acid	0.0118	0.0135	0.0448	0.01395	32.7
Nitroacetic acid	0.0208	0.0218	0.0246	0.00774	23.5

Table 8 gives the dissociation constants K_0 and the velocity constants

k^* for the two acids. In the last column is given the heat of activation (Q kg-cal.) calculated from k^* in the usual way.

THE VELOCITY OF BROMINATION OF NITROISOBUTYRIC ACID

In the explanation given in the schemes 1 and 2 it is assumed that the decomposition leads directly to the aci-form of the nitro-hydrocarbon. In order to test this some experiments on the bromination of nitroisobutyric acid were carried out.

The aci-forms of aliphatic nitro compounds are brominated practically instantaneously, while the nitro compounds themselves are not brominated directly. From the work of Junell (4) we know that secondary nitropropane is brominated extremely slowly at 18°C. in a strong acid, the velocity being probably determined by the slow isomerization to the aci-form (see also Pedersen (10)).

TABLE 9

Bromination of nitroisobutyric acid at 17.84°C.

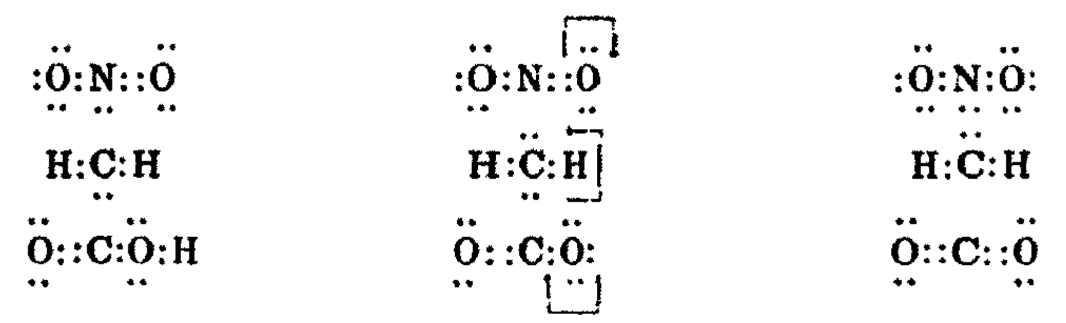
IN 0.0998 M HCl				IN 0.0101 M HCl + 0.0900 M NaCl			
t	$c \times 10^3$	$x \times 10^3$	ak^*	t	$c \times 10^3$	$x \times 10^3$	ak^*
10.7	7.340	1.18	0.00711	2.8	7.181	1.186	0.0280
19.8	8.002	2.212	0.00710	8.8	5.808	2.49	0.0276
35.6	7.271	3.260	0.00726	17.1	5.324	3.49	0.0270
46.5	8.110	4.375	0.00724				
56	7.293	4.451	0.00730	Mean value................			0.028
82	7.425	5.495	0.00714	(Indirectly from decomposition experiments........			
105.5	7.967	6.557	0.00713				0.028)
Mean value................			0.0072				
(From decomposition experiments................			0.0074)				

If the explanation expressed in the schemes 1 and 2 is true, the secondary nitropropane should be brominated as soon as it is formed. Thus it should be possible to determine the velocity of decomposition of the nitroisobutyric acid by measuring the velocity of disappearance of the bromine, when the acid is dissolved in bromine water.

To 0.0998 M hydrochloric acid containing bromine at 17.84°C. in a flask with glass stopper was added a known excess of nitroisobutyric acid. The time t which elapsed between the addition of the substance and the disappearance of the brown color was determined. In different experiments with the same concentration of hydrochloric acid and nearly the same initial concentration, c, of nitroisobutyric acid the time of reaction was varied by varying the concentration of bromine. The decrease in the molar concentration of bromine during the time t serves as a measure of the decrease x in concentration of nitroisobutyric acid. In table 9 the unimolecular velocity constant $\alpha k^* = \frac{1}{t}\log\frac{c}{c-x}$ has been calculated. The mean value $\alpha k^* = 0.0072$ is in agreement with the constant $\alpha k^* = 0.0074$ found by measuring the gas pressure for the same concentration of hydrochloric acid.

In the bromination experiments we avoid the troublesome secondary reaction. It is of interest to do experiments in a solution where the secondary reaction made it impossible to determine directly the velocity constant of the carbon dioxide cleavage. In 0.0101 M HCl + 0.0900 M NaCl the velocity constant of the bromination $\alpha k^* = 0.028$ was found (table 9). In order to compare this result with those for the gas evolution experiments we make the following calculation. From experiments in more acid solution we know that $K = 0.0200$, when $\mu = 0.1$. The hydrogen-ion concentration is $(H^+)_\infty = 0.0101$, when $t = \infty$, and $(H^+)_0 = 0.010 + 0.004 = 0.014$, when $t = 0$, or in average $(H^+) = 0.012$. Hence we find $\alpha = 0.0200/0.032 = 0.62$ and $\alpha k^* = 0.62 \times 0.0448 = 0.028$, in good agreement with the bromination experiments. This shows that the impossibility of determining the constant directly by the pressure method in the most dilute solutions of hydrochloric acid actually is due to a secondary reaction.

We have now seen that the carbon dioxide cleavages of nitroacetic and α-nitroisobutyric acids follow the same laws. In both cases the undissociated acid is stable, while the univalent ion is decomposed. The velocities are of the same order of magnitude and the heats of activation are the same. From this we may conclude that the unstable form of α-nitrocarboxylic acids in general is not the aci-form of the nitro compound, but the ordinary ion $>CNO_2CO_2^-$. The decomposition leads directly to the aci-form of the corresponding nitrohydrocarbon. From these facts we may try to form a picture of the details of the decomposition. The reaction may be expressed as follows by means of electron valency formulas. It is suggested that the decomposition is caused by a displacement of valency electrons in the direction shown by the arrows.

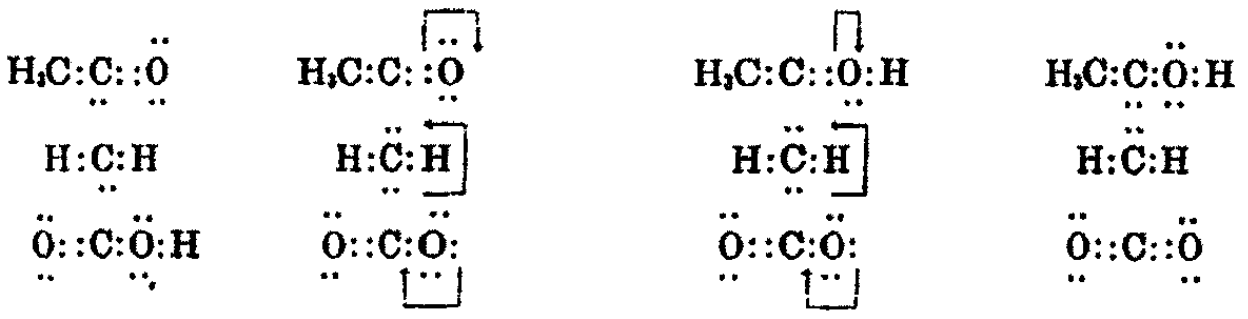


(O_2NCH_2COOH) ($O_2NCH_2CO_2^-$ → $^-O_2N:CH_2 + CO_2$)

THE DECOMPOSITION OF β-KETOCARBOXYLIC ACIDS

It is interesting to compare the α-nitrocarboxylic acids with another group of unstable acids, the β-ketocarboxylic acids. The simplest acid of this type, acetoacetic acid, has mainly been examined by Widmark (12, 13) and Ljunggren (5). Here the undissociated acid decomposes with considerable velocity ($CH_3COCH_2COOH \rightarrow CH_3COCH_3 + CO_2$), while the ion decomposes very slowly. The reaction is catalyzed by primary amines. Secondary amines have a small and tertiary amines hardly any effect. From the work on acetoacetic acid it was impossible to decide whether the keto or enol form is active. By studying α,α-dimethylacetoacetic acid, which can not be rearranged into an enol form, Pedersen (8) found that the keto form is unstable. To this can now be added the following result. By making kinetic experiments on the bromination of α,α-dimethylacetoacetic acid in the same way as described above for nitroisobutyric acid and comparing them with earlier experiments on the rate of evolution of carbon dioxide, it was found that bromine is taken up with the same velocity as the keto acid is decomposed (one mole of bromine per mole of keto acid). From these experiments we may conclude that the decomposition of β-ketocarboxylic acids leads directly to the enol form of the reaction product. Thus, there seems to be a close analogy between the mechanism of decomposition of α-nitrocarboxylic acids and β-ketocarboxylic acids.

For β-ketocarboxylic acids we may tentatively suggest the following mechanism. The ordinary form of the undissociated acid (I) is stable. The acetoacetate ion (II) decomposes very slowly. Owing to the weak basic properties of the keto group it will to a small extent take up hydrogen ions. The concentration of the ampho ion (III) thus formed is proportional to the concentration of the ordinary undissociated acid. Consequently it is impossible to decide from the kinetic experiments which of them is unstable. Owing to the attraction of the positive charge it is reasonable to assume that the ampho ion decomposes much more quickly than the ion (II). By the decomposition we get the enol form of the reaction product (IV).



(H_3CCOCH_2COOH) $(H_3CCOCH_2CO_2^-)$ $(H_3CC(OH^+)CH_2CO_2^- \rightarrow CH_3COH{:}CH_2 + CO_2)$

I II III IV

In order to explain the amine catalysis we assume that an equilibrium of the type

$$> CO + H_2NR \rightleftarrows > CNR + H_2O \qquad (9)$$

is quickly established. The group CNR has much stronger basic properties than the keto group. Although the substance >CNR may only be formed in very small concentration by equilibrium 9, we may get a greater concentration of ampho ion than before, and a quicker decomposition.

SUMMARY

This paper contains a kinetic study of the decomposition of α-nitroisobutyric and nitroacetic acids at 17.84°C. and 9.78°C. in acetate buffer solutions and in hydrochloric acid of different concentrations.

From the results it is concluded that the carbon dioxide cleavage of the α-nitrocarboxylic acids consists of a decomposition of the ion with a negative charge at the carboxyl group and leads directly to the aci-form of the corresponding nitro hydrocarbon

$$> C(NO_2)CO_2^- \rightarrow > CNO_2^- + CO_2$$

The dissociation constants of the two acids have been calculated from the kinetic experiments.

The analogy between the carbon dioxide cleavage of the α-nitrocarboxylic acids and the β-ketocarboxylic acids has been pointed out. An attempt has been made to suggest a mechanism which explains the decomposition of both groups of acids and the amine catalysis of the cleavage of the keto acids.

My thanks are due to Professor Niels Bjerrum for his kind interest in my work.

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AN ELECTROMETRIC STUDY OF THE PRECIPITATION OF MERCUROUS HYDROXIDE

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Britton and Robinson (5) find in some cases of the precipitation of the hydroxide or a basic salt from a salt solution by sodium hydroxide, that the reaction is governed by the solubility product of the hydroxide, calculated from the titration curve, whereas in other cases the solubility product so calculated is far from constant.

They include in their paper one curve for the precipitation of a basic nitrate from a solution of mercurous nitrate acidified with nitric acid, by the addition of sodium hydroxide, using the glass electrode as an indicator electrode, but they have not attempted to calculate the solubility product in this case. Accordingly, the work to be described was undertaken and the precipitation of a basic nitrate from acid mercurous nitrate solutions of three different concentrations was studied, the solubility product of mercurous hydroxide being calculated from the titration curves obtained. Three fairly concordant values of the solubility product of mercurous hydroxide have already been published (1, 6, 8), and the reaction seems a very suitable one to test the statement of Britton and Robinson (5) that the solubility product principle is untenable in the case of the precipitation of basic precipitates generally.

EXPERIMENTAL

Preparation and analysis of the solutions

Pure mercurous nitrate was used in this work, and was dissolved in cold water with the addition of sufficient pure dilute nitric acid to prevent the separation of a basic salt. The solution was analyzed before use. Mercury was determined by titration with thiocyanate (7) and total nitrate by reduction to ammonia in caustic soda solution with Devarda's alloy and titration of the ammonia distilled off (10).

pH values of solutions

An attempt was made to use the quinhydrone electrode for the determination of the pH values of the solutions, as this electrode has been stated to behave normally in dilute nitric acid solutions (2), but in all cases tried it was found to give low readings. Thus in one titration the quinhydrone electrode indicated a pH of 3.0, and the pH values of parallel solutions by the colorimetric and glass electrode methods were 4.1 and 4.05, respectively. It is possible that the quinhydrone electrode is affected by the mercurous–mercuric potential set up at the platinum electrode. After a number of trials the quinhydrone electrode was abandoned in favor of the glass electrode, which has been examined by Britton and Robinson and found suitable for studying precipitation reactions.

The electrode used was of the bulb type filled with normal hydrochloric acid saturated with quinhydrone. It was mounted in a waxed cork supported on an insulated stand, and it dipped into the solution contained in a beaker, the contents being agitated by a mechanical stirrer and connected by means of a saturated potassium nitrate bridge to a saturated calomel electrode. The E.M.F. of the cell was measured with a valve electrometer of standard type used with external potentiometer, both supplied by the Cambridge Instrument Co.

A number of electrodes provided for use with the instrument were examined, using the universal buffer of Britton and Robinson (4), plotting pH against the E.M.F. of the cell. The electrodes all gave a graph differing very little from a straight line, but the sensitivities varied considerably. The most sensitive electrode was used for the work to be described and was standardized using $N/20$ potassium hydrogen phthalate and $N/20$ borax before each titration, a calibration curve being constructed from which the pH could be read off direct. This particular electrode possessed a sensitivity of 0.057 volt per pH unit.

Titration

The curves for the three titrations are reproduced in figure 1. A 10-cc. portion of stock mercurous nitrate solution containing 0.0367 g. of mercury and 0.0320 g. of total nitrate was added to 200 cc. of water and titrated with 1.213 $N/50$ sodium hydroxide to give curve I, and 20-cc. and 30-cc. portions of the same solution with 200 cc. of water were used for curves II and III, respectively. The precipitation was carried out at room temperature, 18°C.

Equilibrium was quickly reached after each addition of alkali, in most cases within two minutes, but longer time was allowed at the bends. Some precipitation took place at the beginning of the titration; most of the precipitate dissolved on prolonged stirring, but the solution remained opalescent. The bulk of the precipitation took place however after the first bend at J', K', and L'. That precipitation was complete after the final bend was shown by filtering the solution, evaporating to small bulk, faintly acidifying, and testing for absence of mercury with hydrogen sulfide.

The initial pH of precipitation is higher than that given by Britton and

Robinson (5), which is approximately 3.0, but their solutions were much more concentrated than those used by the author and precipitation would be expected to occur at a lower pH in such solutions. The pH values at the completion of precipitation were 4.84, 4.88, and 4.92; the pH value of practically complete precipitation of mercurous hydroxide can thus be taken as 4.9.

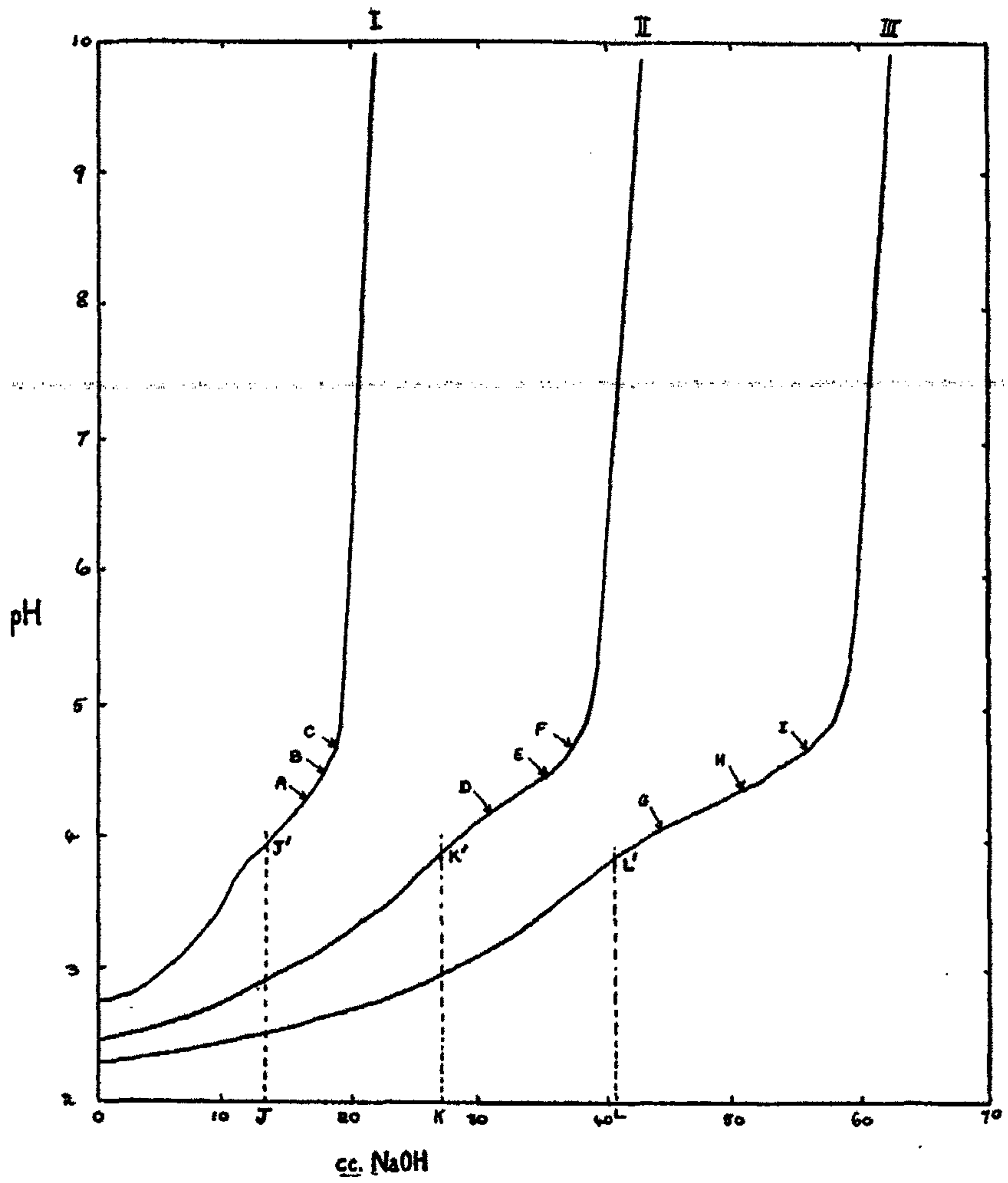

FIG. 1. CURVES FOR THE TITRATIONS

COMPOSITION OF THE PRECIPITATE

From the analytical figures for total NO_3 and Hg in the solution the amount of free HNO_3 was calculated and the theoretical volume of alkali required to neutralize the latter. The points J, K, and L indicate the theoretical points of neutralization of the free acid. There are slight inflections of the curves corresponding to these points, but they are much too gradual to fix the points by means of the curves. The difference between the calculated volume of alkali required to neutralize the free acid and the observed amount needed for precipitation, read off from the curve, gives the amount needed for the precipitation of mercurous hydroxide. In all three cases this was less than the theoretical, the ratios of observed to theoretical being 0.722, 0.755, and 0.766. The calculations are set out in table 1.

This would appear to indicate that a basic nitrate of the approximate composition $3Hg_2O \cdot 2HgNO_3 \cdot xH_2O$ was being precipitated, in which the molecular ratio of Hg to NO_3 was 4:1. That this was indeed the composition of the precipitate was proved by conducting a duplicate precipitation using the same amounts of solutions as in experiment III and determining the total NO_3 in the solution at the end of the titration. All the Hg in the solution had been precipitated and it was thus possible to calculate the amount of NO_3 combined with the Hg. This calculation gave a molecular ratio of Hg to NO_3 in the precipitate of 4.1:1, in good agreement with the value of 4:1 obtained from $3Hg_2O \cdot 2HgNO_3 \cdot xH_2O$. This is more basic than any definite basic nitrate which has been described (9), and it is probable that the precipitate produced is a mixture of a less basic nitrate and mercurous oxide or hydroxide.

TABLE 1

Sodium hydroxide required

	Curve I	Curve II	Curve III
Actual NaOH required to react with $HgNO_3$ and HNO_3	19.0 cc.	38.5 cc.	58.0 cc.
Theoretical NaOH required for HNO_3	13.6 cc.	27.2 cc.	40.8 cc.
Actual NaOH required for $HgNO_3$	5.4 cc.	11.3 cc.	17.2 cc.
Theoretical NaOH required for $HgNO_3$	7.48 cc.	14.96 cc.	22.44 cc.
Ratio of observed to theoretical	0.722	0.755	0.766

CALCULATION OF THE SOLUBILITY PRODUCT

Britton (3) has shown that the pH values necessary for the precipitation of a large number of basic salts from metallic salt solutions, differ very little from the pH values necessary to precipitate the corresponding hydroxides. It is thus obvious that the solubility product of the hydroxide is the predominant factor in the precipitation of such basic salts. This is confirmed by the fact that the solubility product $[Hg_2^{++}]^2 [OH^-]^3 [NO_3^-]$ corresponding to the basic salt $(Hg_2)_2NO_3(OH)_3$ is less constant than that of the hydroxide, and assuming the above, it is possible to calculate the solubility product of mercurous hydroxide from the curves above described. A method of calculation similar to that used by Britton and Robinson (5) is used. Three points on each curve were arbitrarily chosen (points A, B, C, D, E, F, G, H, I). Knowing the volume of alkali required for complete precipitation, the $[Hg_2^{++}]$ still in solution could be calculated at each point. From the pH, the $[OH^-]$ can be calculated, taking the ionic product of water as 0.73×10^{-14} at 18°C. Thus $[Hg_2^{++}]$ $[OH^-]^2$ can be obtained. The calculations are set out in table 2.

TABLE 2

Calculation of the solubility product

POINT ON CURVE	pH	$[H^+] \times 10^4$	$[OH^-] \times 10^{10}$	NaOH ADDED AT POINT CHOSEN	$[Hg_2^{++}]$ AT BEGINNING OF TITRATION $\times 10^3$	$[Hg_2^{++}]$ AT POINT CHOSEN $\times 10^3$	$[Hg_2^{++}] [OH^-]^2 \times 10^{24}$
				cc.			
A	4.3	0.50	1.46	16.7	0.4356	0.1718	3.6
B	4.5	0.32	2.28	18.0		0.0743	3.9
C	4.7	0.20	3.65	18.8		0.0148	2.0
D	4.2	0.63	1.16	31.0	0.8317	0.4837	6.5
E	4.5	0.32	2.28	35.4		0.1965	10.2
F	4.7	0.20	3.65	37.3		0.0755	10.1
G	4.1	0.80	0.913	44.7	1.1933	0.7720	6.4
H	4.4	0.40	1.83	51.2		0.3860	12.9
I	4.7	0.20	3.65	56.0		0.1116	14.9

Mean solubility product.. 7.8×10^{-24}

It will be observed that the solubility product obtained is not constant. but having regard to the fact that a basic nitrate is actually precipitated and to the presence of sodium nitrate in the solution, the product is sufficiently constant to show that the reaction is governed by it. Other determinations of the solubility product of mercurous hydroxide have been made by Bugarsky (6), Immerwahr (8), and Allmand (1), who obtain the values 1.82×10^{-24}, 8.05×10^{-24}, and 4.8×10^{-24}, respectively. The mean of the values obtained from table 2 is 7.8×10^{-24}, in reasonable agreement with those above. It is quite obvious in this particular case that the titration curve does provide a means of calculating the solubility product of the hydroxide, although a high degree of accuracy cannot be expected.

The constancy of the solubility product is not improved by correcting for the "activities" of the ions and the total ionic strength of the solutions.

HYDROLYSIS

It is well known that considerable hydrolysis occurs in mercurous nitrate solutions, but no direct determination of the extent of the hydrolysis has been made, owing to the difficulty of obtaining the [H^+] in such solutions. The glass electrode renders this determination possible; accordingly the hydrolysis of mercurous nitrate in the three solutions used for the titration, all of which contain free nitric acid, was calculated. In order to simplify the calculation it was assumed that the free nitric acid was completely ionized,—a justifiable assumption having regard to the dilute solutions used. The salt effect of the mercurous nitrate on the pH of the solution was also neglected. The figures are set out in table 3, and it will be seen that even in the presence of a considerable excess of free nitric acid, hydrolysis is very marked, decreasing with an increase in the total concentration of nitric acid and mercurous nitrate.

TABLE 3

Hydrolysis of mercurous nitrate

SOLUTION	INITIAL pH	[H^+] $\times 10^3$	CALCULATED [H^+] DUE TO $HNO_3 \times 10^3$	[H^+] DUE TO HYDROLYSIS $\times 10^3$	[NO_3^-] FROM $HgNO_3 \times 10^3$	PER CENT OF HYDROLYSIS
I	2.73	1.95	1.58	0.37	0.87	42.5
II	2.44	3.60	3.02	0.58	1.66	34.9
III	2.30	5.00	4.34	0.66	2.39	27.6

SUMMARY

1. The quinhydrone electrode gives high readings in dilute nitric acid solutions of mercurous nitrate. The glass electrode may be used in such solutions.

2. When dilute sodium hydroxide is added to dilute nitric acid solutions of mercurous nitrate, a basic nitrate is precipitated having the approximate composition, $3Hg_2O \cdot 2HgNO_3 \cdot xH_2O$.

3. The precipitation is governed by the solubility product of mercurous hydroxide, which is calculated to be 7.8×10^{-24}.

4. Mercurous nitrate is hydrolyzed to a considerable extent in the dilute nitric acid solutions studied.

The author wishes to express his thanks to Dr. H. J. S. Sand for his interest and advice during the course of this work.

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THE THEORY OF PROTOLYTIC REACTIONS AND PROTOTROPIC ISOMERIZATION

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According to Brönsted's (3) definition of acids and bases any neutral molecule or ion which can give off a proton is called an acid, and any neutral molecule or ion which can take up a proton is called a base. When

$$A \rightleftarrows B + H^+$$

A is an acid and B the corresponding base. Lowry (27) has independently suggested the same definition. The proton being incapable of independent existence, an acid can only give off a proton to a base. Thus the characteristic acid and base function is the transference of protons from the acid to the base as expressed in the scheme

$$A_1 + B_2 \rightleftarrows B_1 + A_2 \tag{1}$$

where the base B_1 corresponds to the acid A_1, and the acid A_2 to the base B_2. Brönsted (6) calls this a protolytic reaction.

The relative strength of two acids or bases is defined by means of the degree of displacement of equilibrium 1. If K_A is the strength of an acid A and K_B that of a base B, we use the definition

$$\frac{K_{A_1}}{K_{A_2}} = \frac{K_{B_2}}{K_{B_1}} = \frac{(B_1)(A_2)}{(A_1)(B_2)} \tag{2}$$

In this way we can compare the strengths of two acids or bases in any solvent. The relative strength is usually dependent on the solvent. If the solvent S is a base we get the equilibrium

$$A_1 + S \rightleftarrows B_1 + SH^+$$

In this case we define the strength of the acid A_1 and the base B_1 in the solvent by

$$K_{A_1} = \frac{1}{K_{B_1}} = \frac{(SH^+)(B_1)}{(A_1)} \tag{3}$$

Where there can be no misunderstanding we often call the ion SH^+ the hydrogen ion and denote it by H^+. In the solvent water SH^+ is the hydroxonium ion H_3O^+.

Protolytic reactions are generally very rapid. It has not yet been possible to show with certainty that the interaction of ordinary acids and bases takes a finite time. Only the so-called pseudo acids, which will be dealt with later, react in some cases with measurable velocity. By means of the flowing stream method of Hartridge and Roughton (20) it has been shown by Saal (38) that the reaction between hydroxyl ions and different weak acids and between hydrogen ions and different weak bases is complete in less than 0.004 second. La Mer and Read (24) found by the same method that the reaction between 0.05 *N* solutions of acetic acid and ammonia at 25°C. was only 95 per cent complete 0.002 second after mixing. These authors intend to repeat the experiment with an improved apparatus. It will be of interest to see whether the result will be confirmed.

It is reasonable to assume that the velocity of the protolytic reaction is to some extent determined by the strength of the reacting acid and base. The weaker the acid and base the slower the reaction. However, by purely static considerations we cannot find a relation between the velocity and the strengths of the acid and base. If we denote by v_{A_1, B_2} and π_{A_1, B_2}, respectively, the velocity and the bimolecular velocity constant for the transference of a proton from A_1 to B_2 (scheme 1), we have

$$v_{A_1,B_2} = \pi_{A_1,B_2}(A_1)(B_2) \qquad \text{and} \qquad v_{A_2,B_1} = \pi_{A_2,B_1}(A_2)(B_1)$$

At equilibrium $v_{A_1, B_2} = v_{A_2, B_1}$, and consequently

$$\frac{\pi_{A_1,B_2}}{\pi_{A_2,B_1}} = \frac{(B_1)(A_2)}{(A_1)(B_2)}$$

By means of equation 2 we get the relation

$$\frac{\pi_{A_1,B_2}}{\pi_{A_2,B_1}} = \frac{K_{A_1}}{K_{A_2}} = K_{A_1} \times K_{B_2} \tag{4}$$

Only the ratio between the velocity constants of the balanced reaction 1, not the separate constants, is given by expression 4, which is all we can get in this way. Only kinetic experiments can decide whether the velocity is determined by the strengths of the acid and base.

It has been found, first by Brönsted and his coworkers (7–10, 12–15), afterwards by many other investigators (16, 17, 23, 26, 31, 33, 34, 35, 36, 42), that a great number of reactions are catalyzed by acids or bases in general, that is, all sufficiently strong acids or bases catalyze, and the effect increases with increasing acid or basic strength of the catalyst. Brönsted has developed a theory of this general acid and basic catalysis (4, 5).

According to this theory the velocity is determined by a protolytic reaction between the substrate and the catalyst. We have general acid or basic catalysis if the substrate molecule by receiving or by giving off a proton gets into an unstable state which immediately (or very quickly compared with the velocity of the protolytic reaction) leads to the reaction which we examine. If in acid and basic catalysis we call the substrates R and RH respectively, the velocities are determined by the reactions

$$\mathrm{R} + \mathrm{A} \rightarrow \mathrm{RH}^{+} + \mathrm{B} \tag{5}$$

and

$$\mathrm{RH} + \mathrm{B} \rightarrow \mathrm{R}^{-} + \mathrm{A} \tag{6}$$

The substrate is an extremely weak base or acid, and since the corresponding acid (RH^+) or base (R^-) disappears practically immediately after its formation, it is possible to follow the protolytic reaction.

If the velocity of the protolytic reaction is determined mainly by the strengths of the reacting acid and base while other factors have a minor influence, by plotting the catalytic constants (k_A for the acid catalyst A, and k_B for the basic catalyst B) for a series of catalysts of the same reaction against the acid or basic strength, we should get points which fall not far from a continuous curve. Actually it has been found for a great number of reactions that the points fall very close to a straight line when log k_A is plotted against log K_A and log k_B against log K_B. Thus it follows from the experiments that we may express the dependence of the catalytic constant upon the strength of the catalyzing acid or base by the equations

$$k_{\mathrm{A}} = \pi_{\mathrm{A,R}} = gK_{\mathrm{A}}{}^{\alpha} \tag{7}$$

and

$$k_{\mathrm{B}} = \pi_{\mathrm{RH,B}} = gK_{\mathrm{B}}{}^{\beta} \tag{8}$$

The influence of the strength of the catalyzing acid or base is expressed by K_A^{α} or K_B^{β} respectively, where α and β are constants characteristic of the reaction examined. The factor g usually does not vary much within a series of acid or basic catalysts of the same reaction. For the transference of a proton from RH^+ to B we get by means of equation 4

$$\pi_{\mathrm{RH^+,B}} = \frac{\pi_{\mathrm{A,R}}}{K_{\mathrm{A}} \times K_{\mathrm{R}}} = gK_{\mathrm{RH^+}} \times K_{\mathrm{B}}{}^{1-\alpha}$$

If we assume that an increase of K_A tends to increase $\pi_{A,\,R}$ while an increase of K_B tends to increase $\pi_{RH^+,\,B}$, both α and $1 - \alpha$ must be positive, that is $0 < \alpha < 1$. In the same way we find that $0 < \beta < 1$. These results are in agreement with the experiments.

STATISTICAL FACTORS (CF. BRÖNSTED (4, 5, AND 12))

The number of protons which an acid molecule can give off and the number of vacant places on a base molecule where a proton can be taken up has an influence on the velocity of transference of a proton from the acid to the base, and therefore on g in the expressions 7 and 8. We assume that $g = G$ when A can give off only one proton and B can take up only one proton. We shall compare this simple case with a more general one where A has p protons, each bound with the same strength as in the simple case, and B has q vacant places, each with the same tendency to take up a proton as in the simple case. It is a necessary, though not sufficient, condition for a transference of a proton from A to R that the active part of the molecule R hits A within a certain area round a proton which can be given off. If we assume that the active areas of A do not overlap, $\pi_{\mathrm{A, R}}$ will be p times as great as in the simple case. We find in the same way, when we assume that the active areas of B do not overlap, that $\pi_{\mathrm{RH^*, B}}$ will be q times as great as in the simple case. By means of equation 4 we find that K_{A} will be p/q times as great. Consequently we get

$$\frac{k_{\mathrm{A}}}{p} = G\left(\frac{p}{q}K_{\mathrm{A}}\right)^{\alpha} \tag{9}$$

or $g = p^{1-\alpha}\, q^{\alpha}\, G$. By similar considerations we find for basic catalysis

$$\frac{k_{\mathrm{B}}}{q} = G\left(\frac{p}{q}K_{\mathrm{B}}\right)^{\beta} \tag{10}$$

or $g = q^{1-\beta}\, p^{\beta}\, G$.

It seems reasonable to assume that more protons bound to the same atom in an acid count as one when determining the statistical factor. Thus $p = 1$ for H_3O^+ and NH_4^+, while $p = 2$ for H_2SO_4. Similarly, when a base can take up more protons at the same atom, this place is only counted as one. Thus $q = 2$ for $CH_3CO_2^-$ and $q = 1$ for OH^-.

THE INFLUENCE OF THE ELECTRIC CHARGE OF THE CATALYST

The value of g in equations 7 and 8 depends on the electric charge of the catalyst. Let us consider basic catalysis and only reactions where the substrate RH is uncharged. We assume that equation 8 holds for a series of bases with no electric charge when g has the value g_0, and for a series of bases with one negative charge when $g = g_-$. We now consider two hypothetical bases B^- and B differing only in their electric charge. We compare the reactions

$$\mathrm{RH} + \mathrm{B}^- \rightleftarrows \mathrm{R}^- + \mathrm{BH} \tag{11}$$

and

$$\mathrm{RH} + \mathrm{B} \rightleftarrows \mathrm{R}^- + \mathrm{BH}^+ \tag{12}$$

We assume that β in equation 8 is independent of the charge. We have

$$k_{\mathrm{B}} = g_0 K_{\mathrm{B}}{}^{\beta} \quad \text{and} \quad k_{\mathrm{B}^-} = g_- K_{\mathrm{B}^-}{}^{\beta}$$

Hence

$$\frac{g_0}{g_-} = \frac{k_{\mathrm{B}}}{k_{\mathrm{B}^-}} \left(\frac{K_{\mathrm{B}^-}}{K_{\mathrm{B}}} \right)^{\beta} \tag{13}$$

We have

$$\frac{k_{\mathrm{B}}}{k_{\mathrm{B}^-}} = \frac{\pi_{\mathrm{RH,B}}}{\pi_{\mathrm{RH,B}^-}}, \quad K_{\mathrm{B}} = \frac{\pi_{\mathrm{RH,B}}}{\pi_{\mathrm{BH}^+,\mathrm{R}^-}}, \quad \text{and} \quad K_{\mathrm{B}^-} = \frac{\pi_{\mathrm{RH,B}^-}}{\pi_{\mathrm{BH,R}^-}}$$

which we introduce into equation 13. Hence

$$\frac{g_0}{q_-} = \left(\frac{\pi_{\mathrm{RH,B}}}{\pi_{\mathrm{RH,B}^-}} \right)^{1-\beta} \left(\frac{\pi_{\mathrm{BH}^+,\mathrm{R}^-}}{\pi_{\mathrm{BH,R}^-}} \right)^{\beta} \tag{14}$$

In going from reaction 11 to 12 the velocities change in the following way. It will be more difficult for B to take up a proton than for B^-, but it will be easier for BH^+ to give off one than for BH, and, in addition to this effect, the electric attraction between BH^+ and R^- will increase the velocity of the reaction from right to left. From this we conclude that the following relation will probably hold

$$\frac{\pi_{\mathrm{BH}^+,\mathrm{R}^-}}{\pi_{\mathrm{BH,R}}} > \frac{\pi_{\mathrm{RH,B}^-}}{\pi_{\mathrm{RH,B}}} > 1$$

By introducing this into equation 14 we find, that $g_0 < g_-$ when β is very small, and $g_0 > g_-$ if β is sufficiently great and always if $\beta > 1/2$.

The influence of more negative charges can be examined in the same way. For a base with two negative charges ($g = g_{--}$), we find that $g_{--} > g_-$ when β is very small, and $g_{--} < g_-$ when β is sufficiently great and always if $\beta > 1/2$.

If we compare bases of the same strength we may express the effect of the electric charges as follows. The base with the greatest number of positive charges (smallest number of negative charges) is the strongest catalyst, when β is sufficiently great, and always if $\beta > 1/2$. The greater β, the greater the effect. When β is very small the effect goes in the opposite direction. The attraction between R^- and a positive ion is greater and increases more rapidly with increasing electric charge of the ion than the repulsion between R^- and a negative ion, the former being on the average nearer together than the latter. Consequently, the effect will increase more rapidly in the series B^-, B, B^+, B^{++} . . . than it will decrease in the series B^-, B^{--} . . . .

For acid catalysis we find analogous rules. Among acids of the same strength the strongest catalyst is the one with the greatest number of negative charges (smallest number of positive charges), when α is sufficiently great, and always if $\alpha > 1/2$. When α is very small the effect is opposite. The effect will increase more rapidly in the series A^+, A, A^-, A^{--} . . . than it will decrease in the series A^+, A^{++}. . . .

THE SALT EFFECT

Addition of salt will generally alter both the velocity constant (k_A or k_B) and the strength (K_A or K_B) of the catalyzing acid or base. When the substrate is uncharged the primary (5, 12) kinetic salt effect is generally small, but there is a considerable salt effect on K_A (except when A has one positive charge) and on K_B (except when B is uncharged). Therefore we may expect to get a better agreement with experiment when in formulas 9 and 10 we use, instead of K_A and K_B, their values at infinite dilution, K_A^0 and K_B^0:

$$\frac{k_A}{p} = G\left(\frac{q}{p}K_A^0\right)^{\alpha} \tag{15}$$

and

$$\frac{k_B}{q} = G\left(\frac{p}{q}K_B^0\right)^{\beta} \tag{16}$$

If the substrate molecule is charged it is very important not to neglect the different effect of salts on the velocity and on the acid and basic strength.

As an example of the application of the theory we shall give a summary of experiments on the decomposition of nitramide in aqueous solution at 15°C.

$$H_2N_2O_2 \rightarrow N_2O + H_2O$$

It was through the study of this reaction that general basic catalysis was first found (Brönsted and Pedersen (12)). The work has been continued by Brönsted and Duus (8) and by Brönsted and Volqvarts (14). Recently Brönsted and Vance (13) have examined the reaction in amyl alcohol.

Acids have no catalytic effect on the decomposition of nitramide in aqueous solution. In dilute solutions of strong acids a slow reaction with the unimolecular constant $k_0^* = 0.00038$ min.$^{-1}$ was found. (By an asterisk we denote that the constant has been calculated by means of decadic logarithms. Thus $k^* = 0.4343k$.) This so-called spontaneous reaction is simply explained as basic catalysis by the water. In solution containing bases B the velocity constant can be written $k = k_0 + \Sigma k_B(B)$ or, if we consider the water as a base of the concentration 55.5 and write $k_{H_2O} = k_0/55.5$, in the simpler way $k = \Sigma k_B(B)$.

Since the publication of the first paper our views on the effect of statistical factors have altered somewhat. Here the results have therefore been recalculated in accordance with formula 16. We have also in some cases deviated from the original papers in the determination of the statistical

TABLE 1

The decomposition of nitramide at 15°C.

CATALYST		p	q	k_B^*	$\log\frac{k_B^*}{q}$	$\log\frac{p}{q}K_B^0$	$G^* \times 10^6$
Bases with one negative charge $\beta = 0.80$ $G^* = 7.2 \times 10^{-6}$	Propionate ion	1	2	0.649	0.51-1	4.57	7.1
	Acetate ion	1	2	0.504	0.40-1	4.44	7.1
	Acid succinate ion	2	2	0.320	0.20-1	4.19	7.1
	Phenylacetate ion	1	2	0.232	0.06-1	3.98	7.6
	Benzoate ion	1	2	0.189	0.97-2	3.89	7.2
	Formate ion	1	2	0.0822	0.61-2	3.38	8.1
	Acid malate ion	2	2	0.0765	0.58-2	3.40	7.2
	Acid tartrate ion	2	2	0.0363	0.26-2	3.01	7.1
	Acid phthalate ion	2	2	0.029	0.16-2	2.92	6.6
	Salicylate ion	1	2	0.0206	0.01-2	2.70	7.1
	Primary phosphate ion	3	2	0.0079	0.60-3	2.30	(5.8)
	Dichloroacetate ion	1	2	0.0007	0.54-4	1.00	(5.5)
Bases with two negative charges $\beta = 0.87$ $G^* = 2.07 \times 10^{-6}$	Secondary phosphate ion	2	3	86	1.46	7.06	2.09
	Normal succinate ion	1	4	1.8	0.66-1	5.02	1.95
	Normal malate ion	1	4	0.72	0.26-1	4.51	2.19
	Normal tartrate ion	1	4	0.165	0.62-2	3.79	2.09
	Normal oxalate ion	1	4	0.104	0.42-2	3.57	2.04
Bases with no charge $\beta = 0.75$ $G^* = 17.0 \times 10^{-6}$	*p*-Toluidine	1	1	1.16	0.06	5.15	15.8
	m-Toluidine	1	1	0.64	0.81-1	4.82	15.5
	Aniline	1	1	0.54	0.73-1	4.70	16.2
	o-Toluidine	1	1	0.38	0.60-1	4.54	15.8
	p-Chloroaniline	1	1	0.21	0.32-1	4.04	19.5
	m-Chloroaniline	1	1	0.081	0.91-2	3.52	18.6
	o-Chloroaniline	1	1	0.018	0.26-2	2.68	17.8
	Water	1	1	6.8×10^{-6}	0.85-6	−1.74	(14)
Bases with two positive charges $\beta = 0.82$ $G^* = 780 \times 10^{-6}$	$[Rh(NH_3)_5(OH)]^{++}$	1	1	396	2.598	5.86	620
	$[Co(NH_3)_5(OH)]^{++}$	1	1	449	2.652	5.69	980
	$[Co(NH_3)_4(H_2O)(OH)]^{++}$	2	1	328	2.516	5.52	1000
	$[Co(NH_3)_3(H_2O)_2(OH)]^{++}$	3	1	135	2.130	5.20	740
	$[Al(H_2O)_5(OH)]^{++}$	6	1	121	2.083	5.73	(240)
	$[Cr(H_2O)_5(OH)]^{++}$	6	1	32.7	1.515	4.68	480
	$[Fe(H_2O)_5(OH)]^{++}$	6	1	2.28	0.358	2.98	830

factors by using the rules given above. The strengths of the bases are usually those given in the three papers (8, 12, 14). For the primary and secondary phosphate ion they are taken from the investigation by Bjerrum and Unmack (2), and for the succinate, malate, tartrate, and oxalate ion from Larsson's measurements (25).

A study of table 1 and figure 1 will show that there is a good agreement between the theory and the experiments. Formula 16 holds well within a group of bases with the same electric charge. The change of catalytic effect on going from one type of bases to another goes in the direction we would expect. In agreement with the theory, the effect of bases with two positive charges is especially great, about one hundred times as great as of bases with the same strength and one negative charge. The catalysis by water has the order of magnitude we would expect when we use for the basic strength of water the value $K_B = (H_3O^+)/(H_2O)\ (H_3O^+) = 55.5^{-1}$.

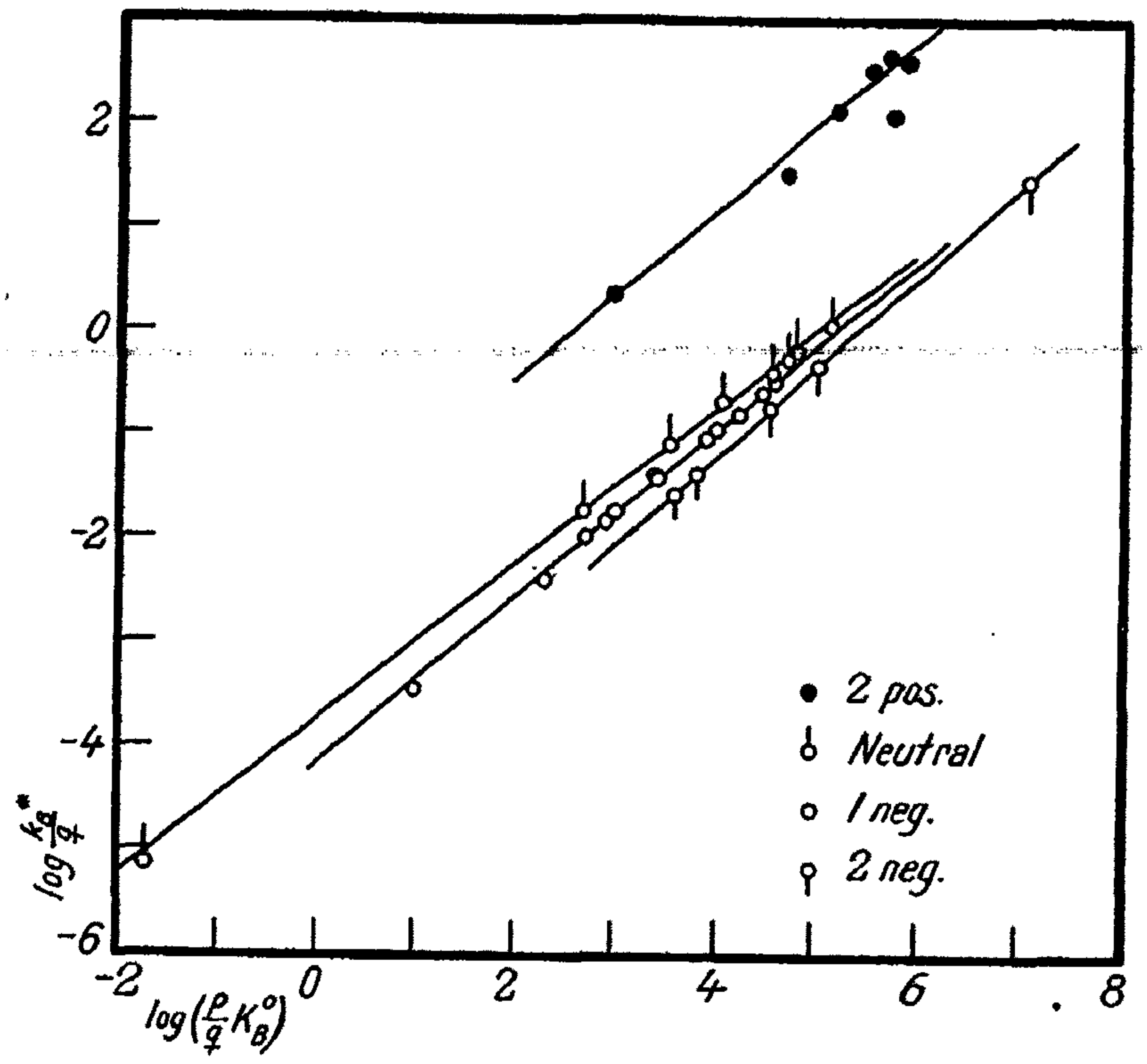


FIG. 1. THE DECOMPOSITION OF NITRAMIDE
Dependence of catalytic constant upon basic strength

Nitramide is a weak acid. Brönsted and King (11) have found by measurements of electrical conductivity that its apparent strength is $K^0 = 2.55 \times 10^{-7}$ at 15°C. It is seen from their measurements that the protolytic reaction by which the dissociation equilibrium is attained is very much quicker than the decomposition. Therefore the protolytic reaction which leads to decomposition must be another. We assume that the following equilibria are attained practically instantaneously

$$H_2NNO_2 \rightleftarrows HN{:}NO_2^- + H^+ \rightleftarrows HN{:}NOOH$$

Thus a constant, but very small, fraction of the undissociated nitramide is in the form HN:NOOH. We may explain the decomposition as taking place when the last proton bound to the nitrogen atom is given off to the base. This explanation is supported by the fact that nitramines of the type $RHNNO_2$, e.g. methylnitramine, are stable. Thus Thiele and Lachmann (40) have found that methylnitramine undergoes boiling with potassium hydroxide without decomposition. From this fact we may conclude that body hydrogen atoms in nitramide play a part in the decomposition.

It has been found by Brönsted (11, 14) that the nitramide ion is unstable and decomposes about twenty times more quickly than undissociated nitramide in pure water. This is also in conformity with the explanation. Owing to the negative charge of the ion $HN{:}NO_2^-$ the proton is bound much more strongly than the corresponding proton in HN:NOOH, and the protolytic reaction which leads to decomposition will therefore be much slower, but, on the other hand, all the nitramide ion is in the unstable form, while this is only the case with a small fraction of the undissociated nitramide.

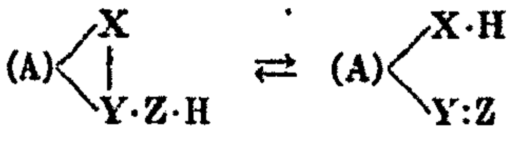
For other examples of general basic or acid catalysis we refer to the literature (4, 5, 7–10, 12, 13, 14–17, 23, 26, 31, 33–36, 42).

One of the best known forms of reversible isomerization is that characterized by the change of position in the molecule of a proton, which may be accompanied by a rearrangement of bonds (valency electrons). Lowry (28) has called this form of isomerism prototropy. Although Lowry only considers isomerizations with both proton- and bond-shifting it seems reasonable to include under the name prototropy also those where only proton-shifting takes place, e.g., $H_2NCH_2COOH \rightleftarrows {}^+H_3NCH_2CO_2^-$. However, we shall deal here mainly with the former class of prototropy.

The greatest number of reactions in which general acid or basic catalysis has been found are prototropic isomerizations. Thus the mutarotation of glucose (9, 31) and the enolization of acetone (17) are catalyzed by both acids and bases, while the enolization of acetoacetic ester and acid (35, 36) and the isomerization of nitromethane (34), $CH_3NO_2 \rightarrow CH_2{:}NOOH$, are catalyzed only by bases.

The best examined prototropic systems belong to the triad- or the ring-chain systems, respectively,

$$H{\cdot}X{\cdot}Y{:}Z \rightleftarrows X{:}Y{\cdot}Z{\cdot}H \quad \text{and}$$



$$(A)\begin{cases} X \\ | \\ Y{\cdot}Z{\cdot}H \end{cases} \rightleftarrows (A)\begin{cases} X{\cdot}H \\ Y{:}Z \end{cases}$$

where X, Y, and Z may be chosen among the three atoms O, N, and C (41). Of the prototropic reactions mentioned above, mutarotation belongs to the latter class, while the others belong to the former.

A great deal of work on prototropic systems has been carried out by Thorpe, Ingold, and their coworkers, although not from the point of view of general acid and basic catalysis. We shall here mention some of their most important results. The hydrogen atom is much more mobile when it goes from one nitrogen atom to another than when it goes from one carbon atom to another, and there is no doubt that it is even more mobile when it goes from oxygen to oxygen. Compared with this the nature of the third atom in the triad Y is of minor importance (21). Thus the mobility increases in the same order as the tendency to give off a proton (methane is a weaker acid than ammonia and this weaker than water). The mobility is dependent on substituents in the prototropic molecule. Electronegative groups, which increase the tendency to give off a proton, increase the mobility (22, 39). The mobility is catalyzed by bases, and in some cases also by acids, although usually to a less extent. The strong bases are the strongest catalysts, in water OH^-, in ethyl alcohol $C_2H_5O^-$, etc.

From work in this field it seems justifiable to conclude that the hydrogen cannot move spontaneously from one place to another in the molecule. If the prototropic equilibrium is apparently attained without catalyst, it has often been possible to show that the reaction is catalyzed by small amounts of acid and basic impurities. Thus, while the keto-enol equilibrium is attained quickly in acetoacetic ester of ordinary purity, Meyer (32) and Rice and Sullivan (37) have shown that the stability of the enol form can be increased apparently without limit by careful purification. Rice and Sullivan found that addition of traces of bases to the purified enol form increased the velocity of isomerization immensely. Thus the addition of 4×10^{-5} M ammonia increased it 4000 times, while 10^{-5} M oxalic acid increased it only 3.2 times.

The necessity for a catalyst has been shown most clearly by Lowry and Richards (30) for the mutarotation of tetramethylglucose. They even find that both an acid and a base must be present. If the solvent is both an acid and a base, like water, this alone can catalyze the reaction. If it is only an acid or only a base, no reaction can take place, unless we add respectively a base or an acid. Thus the mutarotation takes place with measurable velocity in water and is catalyzed by acids and bases, e.g., cresol and pyridine. In pure and dry pyridine or cresol the reaction is completely arrested, but in a mixture of pyridine and cresol it takes place with great velocity.

Supported by these experiments Lowry has given an explanation of the mechanism of prototropic isomerization in his electrolytic theory of catalysis (29), according to which it is a trimolecular reaction between the substrate, an acid, and a base. The following three things take place simultaneously: (a) the substrate molecule gives up a proton to the base, (b) it receives one in another place from the acid, and (c) a rearrangement of valency electrons takes place. Another mechanism has been suggested by Ingold, Shoppee, and Thorpe (22). They assume that (a) and (b) are consecutive bimolecular reactions. This idea is supported by experimental work of Baker (1).

In order to examine Lowry's explanation we consider the prototropic reaction RH → SH in a medium containing the acids A_1, A_2 . . . and their corresponding bases B_1, B_2 . . . . According to Lowry the isomerization is the result of the reaction

$$A_m + RH + B_n \rightarrow B_m + SH + A_n \qquad (17)$$

and the analogous reactions with the other acids and bases. If the trimolecular velocity constant of reaction 17 is called $k_{A_m,\,B_n}$, we get the following expression for the total velocity

$$v = (RH)\,\Sigma k_{A_m,B_n}(A_m)(B_n) \qquad (18)$$

where the sum should be taken for all combinations of m and n. Actually both Lowry's and other investigators' experiments in aqueous solution agree with the formula

$$v = (RH)\Sigma[k_A(A) + k_B(B)] \qquad (19)$$

where the sum is taken for all acids and bases present. Expressions 18 and 19 agree only if one of the partners in reaction 17 is always (or nearly always) a solvent molecule, because the solvent is the only catalyzing substance whose concentration has not been varied in the experiments. Thus it follows for aqueous solutions that water is always a partner in the reaction, acting as a base in acid catalysis and as an acid in basic catalysis.

It seems unlikely that this consequence of Lowry's theory is in agreement with experimental facts. Let us consider Dawson's (17) experiments on the enolization of acetone. From his results we calculate the relative velocities of the water, acetate ion, and acetic acid catalysis in an aqueous solution of 0.1 *M* acetic acid and 0.1 *M* sodium acetate. They are given below together with the trimolecular reaction by which that part of the total reaction takes place according to Lowry's theory.

		Relative velocity
Water catalysis	$H_2O + RH + H_2O$	1
Acetate ion catalysis	$H_2O + RH + Ac^-$	61
Acetic acid catalysis	$HAc + RH + H_2O$	18

From a comparison of the first two reactions it is clear that, when RH receives a proton from a water molecule, the amount of acetate ion present takes up a proton from RH much more quickly than the water does. This will probably also be the case when RH receives a proton from an acetic acid molecule. We would therefore expect the reaction HAc + RH + $\mathrm{Ac}^- \rightarrow$ to be quicker than the third reaction in the list. But actually it has not been possible to detect this reaction (cf. formula 19).

We may add that if one of the partners is always water, the acid catalysis of water would always have the same strength as its basic catalysis because both correspond to the same reaction $\mathrm{H_2O + RH + H_2O} \rightarrow$. However, some reactions are only catalyzed by bases. Thus the enolization of acetoacetic ester (35, 36) is catalyzed by water and bases, while even the strong acid, the hydroxonium ion, does not catalyze. It, therefore, seems unlikely that the very weak acid water has a considerable power as an acid catalyst.

From this examination we conclude that it is very unlikely that the prototropic isomerization is a trimolecular reaction between the substrate, an acid, and a base. We must therefore assume that the reaction is initiated by a bimolecular reaction in which a proton is either given off to the base or taken up from the acid. Lowry (29) rejects this mechanism for the following reason, using the mutarotation of glucose as an example. "The initial stage in this action is, however, an endothermic process, in which the molecules of the sugar are converted into ions of such an unstable character that the dissociation constant is said to be of the order of 10^{-13} and 10^{-19}. The exact amount of energy required to produce these ions is unknown, but it is obvious that, if we can regard the entrance and the exit of the proton as simultaneous, no energy at all is needed beyond the small amount that is required to cover the difference in energy content of the two isomerides, and perhaps to overcome the frictional resistance to the migration of an electron through the sugar." Lowry seems to forget the part played by the activation energy. This energy is not negligible. Thus Kilpatrick and Kilpatrick (23) found 19.3 kg-cal. for the mutarotation of glucose catalyzed by hydrogen ions.

In the following we shall discuss a mechanism of prototropic reaction based upon the results to which we have now come. It is, especially for basic catalysis, very similar to the mechanism suggested by Ingold, Shoppee, and Thorpe (22).

We assume that an intramolecular rearrangement in which only valency electrons are moved takes place spontaneously and very rapidly. If we as an example consider the triad system $\mathrm{HX\cdot Y{:}Z \rightleftarrows X{:}Y\cdot ZH}$, the bond-shifting may take place by the following balanced reaction

$$\mathrm{HX\cdot Y{:}Z} \rightleftarrows \mathrm{H\overset{+}{X}{:}Y\cdot\overset{-}{Z}} \quad (\mathrm{RH}) \tag{20}$$

$$\mathrm{\overset{-}{X}\cdot Y{:}\overset{+}{Z}H} \rightleftarrows \mathrm{X{:}Y\cdot ZH} \quad (\mathrm{SH}) \tag{21}$$

$$\mathrm{\overset{-}{X}\cdot Y{:}Z} \rightleftarrows \mathrm{X{:}Y\cdot\overset{-}{Z}} \quad (\mathrm{I}^-) \tag{22}$$

$$\mathrm{HX\cdot Y{:}\overset{+}{Z}H} \rightleftarrows \mathrm{H\overset{+}{X}{:}Y\cdot ZH} \quad (\mathrm{IH_2}^+) \tag{23}$$

The equilibria being attained immediately we may consider each pair of tautomers as a single substance, which we may denote as given in brackets above. At first we leave open the question by which of the reactions (20 to 23) the bond-shifting takes place.

We shall see that the prototropic rearrangement $RH \rightleftarrows SH$ appears as a general basic catalysis when the mechanism is as expressed by the scheme

$$RH + B \rightleftarrows I^- + A \rightleftarrows SH + B \tag{24}$$

while it appears as a general acid catalysis when the mechanism is the following

$$RH + A \rightleftarrows IH_2^+ + B \rightleftarrows SH + A \tag{25}$$

We first consider scheme 24. For simplicity we examine an irreversible prototropic isomerization $RH \rightarrow SH$. We may obtain the one-way reaction by removing the form SH as soon as it is formed. We assume that the medium contains the acids $A_1, A_2 \ldots$ and their corresponding bases $B_1, B_2 \ldots$. The concentrations of the acids and bases are constant during the reaction. We may therefore formally consider all the bimolecular reactions of scheme 24 as unimolecular, which simplifies the scheme to

$$RH \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} I^- \xrightarrow{k_2} SH \tag{26}$$

where k_1, k_{-1}, and k_2 are unimolecular velocity constants given by the expressions

$$k_1 = \Sigma\pi_{RH,B}(B), \qquad k_{-1} = \Sigma\pi_{A,I^-}(A) \qquad \text{and} \qquad k_2 = \Sigma\pi''_{A,I^-}(A)$$

Here π'_{A,I^-} denotes the bimolecular velocity constant for that particular transference of protons from A to I^- which leads to RH, while π'_{A,I^-} is the constant for the protolytic reaction between A and I^- leading to SH.

If the subscript E denotes equilibrium concentrations, and if K is the constant $(H^+)_E\,(I^-)_E/(RH)_E$ we have, according to scheme 26,

$$\frac{(H^+)_E}{K} = \frac{(RH)_E}{(I^-)_E} = \frac{k_{-1}}{k_1} \tag{27}$$

We now make the assumption that the hydrogen-ion concentration is so great that $(I^-) << (RH)$ even if the equilibrium $RH \rightleftarrows SH$ were attained. This is nearly always the case under ordinary experimental conditions. Consequently we have $k_{-1} >> k_1$.

If c is the initial concentration of RH and $c - x$ its concentration at the time t we find, remembering that (I^-) is negligible compared with (RH), the following differential equations for reaction 26,

$$\frac{dx}{dt} = k_1(c - x) - k_{-1}(I^-) \qquad \text{and} \qquad \frac{dx}{dt} = k_2(I^-)$$

from which we get by eliminating (I^-)

$$\frac{dx}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}(c - x)$$

Thus the reaction follows the ordinary unimolecular law with the constant

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \tag{28}$$

We now distinguish between three cases:

Case 1: $k_{-1} << k_2$. By introducing this into equation 28 we find $k = k_1 = \Sigma\, \pi_{\mathrm{RH,\,B}}\,(\mathrm{B})$. In this case we have general basic catalysis. We measure the velocity of transference of protons from RH to B.

Case 2: $k_{-1} >> k_2$. By equations 28 and 27 we get

$$k = \frac{k_1}{k_{-1}} k_2 = \frac{K}{(\mathrm{H}^+)} k_2 = \sum \frac{K}{(\mathrm{H}^+)} \pi''_{\mathrm{A,I^-}}(\mathrm{A}) = \sum \frac{K}{K_{\mathrm{A}}} \pi''_{\mathrm{A,I^-}}(\mathrm{B})$$

As seen from the last expression the reaction appears to be a basic catalysis of RH, but in reality we measure a general acid catalysis of the ion I^-, whose concentration is inversely proportional to the hydrogen-ion concentration.

Case 3: $k_{-1} \sim k_2$. Here we get from equation 28

$$k = \frac{k_1}{1 + \frac{k_{-1}}{k_2}}$$

The ratio k_{-1}/k_2 is independent of the hydrogen-ion concentration, since k_{-1} and k_2 are independent of the concentrations of the bases, and if we increase the concentrations of all the acids in a certain ratio both k_{-1} and k_2 are increased in the same ratio. Thus, in this case also, the reaction appears as a general basic catalysis. In reality it is composed of a basic catalysis of RH and an acid catalysis of I^-.

We have found that the mechanism expressed in scheme 26 leads to a reaction which will always appear as a unimolecular reaction catalyzed by bases in general, when the hydrogen-ion concentration is so great that $(\mathrm{RH}) >> (I^-)$. If I^- takes up protons to form mainly SH, we measure the velocity of the protolytic reaction between RH and B, that is, the velocity of dissociation of the very weak acid RH. If I^- takes up protons to form mainly RH, the apparent basic catalysis is a disguised acid catalysis of the ion I^-. If neither of the two possibilities is specially favored, we get an apparent basic catalysis which is the result of both a protolytic reaction between RH and the bases and between the acids and I^-. It is impossible to decide from the kinetic experiments under these circumstances which of the three possible cases we have in a given reaction. However, we may do this, if we take a solution which is so alkaline that the prototropic substance is completely ionized, suddenly add an excess of strong acid, and examine how much is formed of each of the two isomerides.

If the mechanism in scheme 25 is analyzed mathematically in the same way as scheme 24 an analogous result is obtained. If the hydrogen-ion concentration is so small that the concentration of the ion IH_2^+ is negligible compared with that of RH, the reaction RH → SH appears as a unimolecular reaction catalyzed by acids in general. If IH_2^+ by giving up a proton to the base B is predominatingly transformed into SH, we have a genuine acid catalysis of RH. In this case we measure the velocity with which RH receives protons from the acids present. If, on the other hand, the transformation of IH_2^+ into RH is highly favored we have a disguised basic catalysis of IH_2^+, whose concentration is proportional to the hydrogen-ion concentration. We here measure that particular protolytic reaction between IH_2^+ and B by which SH is formed. If neither of the two possibilities is specially favored, we get an apparent acid catalysis which is the result of both protolytic reactions.

The results found here for protolytic reactions with bond-shifting should also hold for those with only proton-shifting mentioned on page 589, but it has not yet been possible to measure the velocity in any such system.

In order to study the mechanism of prototropic isomerization in more detail we must consider the question by which of the reactions 20 to 23 the bond-shifting takes place. We denote by one dash the bond configuration of $HX \cdot Y{:}Z$, and by two dashes that of $X{:}Y \cdot ZH$. Hence we may write the tautomeric equilibria 20 to 23 in the following way

$$RH' \rightleftarrows RH'', \qquad SH' \rightleftarrows SH'', \qquad I^{-\prime} \rightleftarrows I^{-\prime\prime} \qquad \text{and } IH_2^{+\prime} \rightleftarrows IH_2^{+\prime\prime}$$

The total isomerization RH′ → SH″ may take place in the ways contained in the following scheme, where we have left out the acids and bases which take part in the protolytic reactions.

$$\begin{tikzcd}
IH_2^{+\prime} \arrow[r, phantom, "\rightleftarrows"] \arrow[d, phantom, "\downarrow\uparrow(23)"] \arrow[rrr, bend left] & RH' \arrow[r, phantom, "\rightleftarrows"] \arrow[d, phantom, "\downarrow\uparrow(20)"] & I^{-\prime} \arrow[r, phantom, "\rightleftarrows"] \arrow[d, phantom, "\downarrow\uparrow(22)"] & SH' \arrow[d, phantom, "\downarrow\uparrow(21)"] \arrow[lll, bend right, shift right=2] \\
IH_2^{+\prime\prime} \arrow[r, phantom, "\rightleftarrows"] \arrow[rrr, bend right] & RH'' \arrow[r, phantom, "\rightleftarrows"] & I^{-\prime\prime} \arrow[r, phantom, "\rightleftarrows"] & SH'' \arrow[lll, bend left, shift left=2]
\end{tikzcd} \qquad (29)$$

One of the tautomeric forms of the equilibria 20 to 23 may often be present only in very small quantity compared with the other. Thus the equilibria 20 and 21 will for electrostatic reasons always be highly displaced in favor of the uncharged forms RH′ and SH″. It is often possible to predict from the constitution which of the tautomers of equilibria 22 and 23 is predominating. Thus in the case of acetone the concentration of $I^{-\prime}$ ($\overset{-}{C}H_2 \cdot CO \cdot CH_3$) will probably be very small compared with that of $I^{-\prime\prime}$ ($CH_2{:}C\overset{-}{O} \cdot CH_3$).

Strictly, we cannot speak in the ordinary sense of concentration of the single tautomerides. However, in a given reaction a certain fraction will behave as if it had one constitution, the rest as if it had the other. If we ascribe to the single members of the above tautomeric equilibria a definite concentration, this therefore implies the assumption that the same fraction of a given tautomeric substance behaves as if it had one of the constitutions in all protolytic reactions concerned.

One or more of the reactions in scheme 29 may be excluded for structural reasons. If the atom X in the original molecule $HX \cdot Y{:}Z$ has a complete octet of shared electrons, a bond-shifting can take place only after X has given off a proton. This is the case when X is a carbon atom. Thus, when RH' is the keto form of acetone, the reactions 20 and 23 are excluded. It has been found by Dawson (17) that the enolization of acetone is catalyzed by both acids and bases. The only possible mechanism for the acid catalysis is that expressed by the scheme

$$\underset{(RH')}{CH_3 \cdot CO \cdot CH_3} \rightleftarrows \underset{(IH_2{}^{+\prime})}{CH_3 \cdot (C{:}\overset{+}{O}H) \cdot CH_3} \rightleftarrows \underset{(SH')}{\overset{-}{C}H_2 \cdot (C{:}\overset{+}{O}H) \cdot CH_3} \rightleftarrows \underset{(SH'')}{CH_2{:}COH \cdot CH_3}$$

There can be no doubt that the ion $CH_3 \cdot (C{:}\overset{+}{O}H).CH_3$ will give off a proton bound to the oxygen atom much more easily than one bound to a carbon atom. Consequently, the reaction denoted by a heavy arrow in the scheme determines the velocity of the prototropic isomerization. Here the apparent acid catalysis is a basic catalysis of the ion $CH_3 \cdot (C{:}\overset{+}{O}H) \cdot CH_3$. If it were possible to follow the opposite reaction, the ketonization of the enol form of acetone, we would also find general acid catalysis. In this case we would have a genuine acid catalysis of the form $\overset{-}{C}H_2 \cdot (C{:}\overset{+}{O}H) \cdot CH_3$, which is, however, present only in extremely small concentration.

If both X and Z in the original molecule have complete octets of shared electrons, the only way of bond-shifting is by reaction 22 in scheme 29. Thus the prototropic isomerization of a pure three-carbon system (that is a system where the only possible prototropy is of the type $C \cdot C{:}C \rightleftarrows C{:}C \cdot C$) proceeds in the following way

$$RH' \rightleftarrows I^{-\prime} \rightleftarrows I^{-\prime\prime} \rightleftarrows SH'' \qquad (31)$$

According to this mechanism the reaction is catalyzed by bases, but not by acids. As far as known, acid catalysis has never been found in such systems. However, it has been found in some three-carbon systems of the type $O:C\cdot C:C\cdot C \rightleftarrows O:C\cdot C\cdot C:C$, e.g., glutaconic acid (18). Here it may be explained as a basic catalysis of the ion $H\overset{+}{O}:C\cdot C:C\cdot C$.

The mechanism expressed in scheme 31 seems to be very common in prototropic reactions. It is the only one which we can never exclude. It is of interest to examine it a little further in order to find which of the single reactions determines the velocity of isomerization. The ordinary (apparent) acid strength of the prototropic system

$$K = (H^+)\frac{(I^{-\prime}) + (I^{-\prime\prime})}{(RH) + (SH)}$$

is no measure of the real strengths of the acids RH and SH. These may formally be defined by the equations

$$K_{RH} = (H^+)\frac{(I^{-\prime})}{(RH)} \quad \text{and} \quad K_{SH} = (H^+)\frac{(I^{-\prime\prime})}{(SH)}$$

where it is assumed that equilibrium 31 is attained. The apparent strength is between the real strengths of the two acids. If the fraction ϵ of the prototropic system is of the form SH when equilibrium is attained, we have

$$\frac{K_{RH}}{K_{SH}} = \frac{(I^{-\prime})(SH)}{(I^{-\prime\prime})(RH)} = \frac{\epsilon}{1-\epsilon}\frac{(I^{-\prime})}{(I^{-\prime\prime})} \tag{32}$$

If the medium contains an acid A the reactions $I^{-\prime} + A \rightarrow RH' + B$ and $I^{-\prime\prime} + A \rightarrow SH'' + B$ will take place with velocities which we denote by v' and v'' respectively. v' and v'' depend upon the concentrations and basic strengths of $I^{-\prime}$ and $I^{-\prime\prime}$. By means of formulas 8 and 32 we get the following approximate expression for the ratio of the velocities

$$\frac{v'}{v''} = \frac{(I^{-\prime})}{(I^{-\prime\prime})}\left(\frac{K_{SH}}{K_{RH}}\right)^{\beta} = \frac{1-\epsilon}{\epsilon}\left(\frac{K_{RH}}{K_{SH}}\right)^{1-\beta}$$

From this equation we get the following rules. When SH is a very much stronger acid than RH and ϵ is not extremely small, we have $v'' >> v'$, that is, the velocity of the prototropic reaction is determined by the protolytic reaction between RH and the bases. If, on the other hand RH is very much stronger than SH and $1-\epsilon$ not extremely small, we have $v' >> v''$, that is, the velocity of the prototropic reaction is determined by the protolytic reaction between $I^{-\prime\prime}$ and the acids.

As an example we shall discuss the basic catalysis of the enolization of acetoacetic ester $CH_3COCH_2COOC_2H_5$ (35, 36). For simplicity we only write $O{:}C{\cdot}CH_2$. From scheme 29 we find the following two possible mechanisms

$$\begin{array}{ccccccc} O{:}C{\cdot}CH_2 & \rightleftarrows & O{:}C{\cdot}\overset{-}{C}H & \rightleftarrows & \overset{-}{O}{\cdot}C{:}CH & \rightleftarrows & HO{\cdot}C{:}CH \\ (RH') & & (I^{-\prime}) & & (I^{-\prime\prime}) & & (SH'') \end{array} \qquad (33)$$

and

$$\begin{array}{ccccccc} O{:}C{\cdot}CH_2 & \rightleftarrows & O{:}C{\cdot}\overset{-}{C}H & \rightleftarrows & H\overset{+}{O}{:}C{\cdot}\overset{-}{C}H & \rightleftarrows & HO{\cdot}C{:}CH \\ (RH') & & (I^{-\prime}) & & (SH') & & (SH'') \end{array} \qquad (34)$$

The acid strength of the enol form SH″ is undoubtedly so much greater than that of the keto form RH′ that, although ϵ is only 0.004, the ion I^- will mainly form SH″ when it reacts with acids. Consequently the reaction denoted by a heavy arrow determines the velocity of the total process 33. However, when we consider scheme 34, the ion $I^{-\prime}$ will undoubtedly take up protons much more quickly at the carbon atom than at the oxygen atom. In other words, the reaction $I^{-\prime} \rightarrow SH'$ will be much slower than $RH' \rightarrow I^{-\prime}$. From this we conclude that the mechanism in scheme 34 is of no importance for the isomerization. This proceeds by reaction 33. We measure the velocity of dissociation of the extremely weak acid, the keto form of acetoacetic ester. If we measured the opposite reaction, the ketonization of the enol form, we would also find general basic catalysis, but this would in reality be a reaction between the ion $I^{-\prime}$ and the acids: $I^{-\prime} + A \rightarrow RH' + B$.

The basic catalysis of the enolization of acetone follows probably the same mechanism, but here the conclusions are less safe, because ϵ is so small that it has been impossible to measure it.

Protolytic reactions between ordinary acids or bases are generally too rapid to be measured. When the acid or base is so weak that we might expect to find a slow reaction, it is generally impossible to measure the rate because equilibrium is attained when too little of the corresponding system is formed. The reason why it is sometimes possible to measure the velocity of protolytic reactions in prototropic systems is to be sought in the tautomerisms 20 to 23. The rate of the protolytic reaction of one of the acids (or bases) in scheme 29 is measurable if the acid (or base) is sufficiently weak and its corresponding base (or acid) is transformed sufficiently completely into its tautomer. It may be measurable even when the acid (or base) is not especially weak, if the concentration of the acid (or base) is kept sufficiently small by a tautomerism. Examples of these two types of protolytic reactions may be found in the discussion of acid catalysis of the isomerization of acetone (scheme 30).

We may add a few words on the pseudo acids. The usual idea of the mechanism of dissociation (Hantzsch (19)) is expressed by the scheme

$$RH \rightleftarrows SH \rightleftarrows S^- + H^+ \qquad (35)$$

RH is called a pseudo acid, and SH the aci-form. This opinion is not supported by the points of view maintained in this paper. The system $RH \rightleftarrows SH$ is an ordinary prototropic system. The mechanism of neutralization follows not scheme 35 but 31. There is no difference in principle between the acid character of the pseudo and aci-form. They are both genuine acids, but the pseudo form is a much weaker acid than the aci-form (cf. the discussion of scheme 31). The so-called pseudo acids are not false acids, but acids with false strength.

SUMMARY

Brönsted's theory of acid and basic catalysis and our knowledge of protolytic reactions have been discussed.

Experiments on the decomposition of nitramide have been compared with the theory.

Some of the main results in the study of prototropic reactions have been pointed out.

Lowry's electrolytic theory of prototropic reactions has been criticized.

Another mechanism of prototropic reactions has been discussed.

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THE VELOCITY OF BROMINATION OF ACETOACETIC ETHYL ESTER. II

THE GENERAL BASIC CATALYSIS

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In Part I (10) the bromination of acetoacetic ethyl ester was studied in pure water and solutions of hydrochloric acid. It was found that the reaction may be expressed by the schemes 1a–1d (Part I, p. 751). Thus four consecutive reactions could be distinguished: (a) the acetoacetic ester is enolized, and (b) brominated to the keto form of α-monobromoacetoacetic ester; (c) this is enolized, and (d) brominated to α,α-dibromoacetoacetic ester. Only reactions 1a and 1c take place with measurable velocity. Hydrogen ions do not catalyze to any perceptible degree.

In this part of the investigation the bromination of acetoacetic ethyl ester is studied in buffer solutions containing a weak acid (HB) and its sodium salt (NaB), or, if we use Brönsted's definition (3) of acids and bases, an acid (HB) and its corresponding base (B^-). The hydrogen-ion concentration was as a rule greater than 10^{-6}. The measurements agree with the mechanism expressed in the schemes 1a–1d when we assume that the enolizations of acetoacetic ester and α-mono-bromoacetoacetic ester are catalyzed by the base B^-.

We use the following symbols in addition to those given in Part I, p. 752.[1]

k_B and h_B, catalytic constants for the catalysis by B^- of the enolization of acetoacetic ester (HR) and α-monobromoacetoacetic ester (HR′), respectively.

a, stoichiometrical initial concentration of the acid HB.

b, stoichiometrical initial concentration of the salt NaB.

It will be shown that the velocity of bromination can be explained by assuming that it is determined by two consecutive reactions with the velocities $[k_0 + k_B\ (B)^-]\ (HR)$ and $[h_0 + h_B(B^-)]\ (HR')$. Owing to the

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[1] In Part I, page 759, line 6, the following misprint occurs:

$$\frac{\sqrt{\Sigma\delta^2}}{n-1} \text{ should read } \sqrt{\frac{\Sigma\delta^2}{n-1}}$$

hydrobromic acid formed by the bromination, the concentration of the catalyst will decrease during the reaction.

From these assumptions we shall first deduce a mathematical expression for the course of the reaction. Then we shall show that the expression agrees with the experiments.

When the subscripts 0 and ∞ denote that the concentration corresponds with $t = 0$ and $t = \infty$, respectively, we have for the concentration of the catalyst

$$(\mathrm{B}^-)_0 = b + (\mathrm{H}^+)_0, \qquad (\mathrm{B}^-) = b + (\mathrm{H}^+) - \frac{x}{2}$$

and

$$(\mathrm{B}^-)_\infty = b + (\mathrm{H}^+)_\infty - 2c \tag{19}$$

(H^+) varies so little during reaction that it is sufficient to assume that its increase is proportional to x. From a rough value of the dissociation constant K_{HB} we calculate $(\mathrm{H}^+)_0$ and the hydrogen-ion concentration $(\mathrm{H}^+)_m$ corresponding to $\frac{x}{2} = c$. We calculate the proportionality factor κ from the equation

$$(\mathrm{H}^+)_m - (\mathrm{H}^+)_0 = \kappa\frac{c}{2}$$

We then have

$$(\mathrm{H}^+) = (\mathrm{H}^+)_0 + \kappa\frac{x}{2}$$

which we introduce into equation 19:

$$(\mathrm{B}^-)_0 = b + (\mathrm{H}^+)_0 \qquad (\mathrm{B}^-) = (\mathrm{B}^-)_0 - (2 - \kappa)\frac{x}{4}$$

and

$$(\mathrm{B}^-)_\infty = (\mathrm{B}^-)_0 - (2 - \kappa)c \tag{20}$$

In some cases the increase in (H^+) is so small that we can disregard it and put $\kappa = 0$.

The course of the reaction is determined by the differential equations

$$-\frac{d(\mathrm{HR})}{dt} = [k_0 + k_{\mathrm{B}}(\mathrm{B}^-)]\,(\mathrm{HR}) \tag{21}$$

and

$$\frac{d(\mathrm{HR'})}{dt} = [k_0 + k_{\mathrm{B}}(\mathrm{B}^-)]\,(\mathrm{HR}) - [h_0 + h_{\mathrm{B}}(\mathrm{B}^-)]\,(\mathrm{HR'}) \tag{22}$$

While the expressions in square brackets are not constant we may with good approximation consider the ratio

$$r = \frac{h_0 + h_B(\mathrm{B}^-)}{k_0 + k_B(\mathrm{B}^-)} \tag{23}$$

as constant. Provided that one of the following conditions holds, r is a constant:

$$(1)\ \frac{h_0}{k_0} = \frac{h_B}{k_B}$$

$$(2)\ h_0 << h_B(\mathrm{B}^-) \text{ and } k_0 << k_B(\mathrm{B}^-)$$

and

$$(3)\ b >> \frac{x}{2}$$

They all hold approximately.

From the equations 21, 22, and 23 we get

$$\frac{\mathrm{d}(\mathrm{HR}')}{\mathrm{d}(\mathrm{HR})} = r\frac{(\mathrm{HR}')}{(\mathrm{HR})} - 1$$

which is identical with expression 9 in Part I, p. 753. By integration we get expression 10. When $r > 1$, equation 10 approaches the following equation as t increases

$$\frac{(\mathrm{HR}')}{(\mathrm{HR})} = \frac{1}{r-1}$$

By introducing this into equation 4, we get

$$c - \frac{x}{4} = (\mathrm{HR})\left(1 + \frac{1}{2(r-1)}\right) \tag{24}$$

If r is sufficiently great, equation 24 will only fail for very small values of t. If we eliminate (HR) from equation 21 and 24 we get

$$\frac{1}{4}\frac{\mathrm{d}x}{\mathrm{d}t} = k_B\left[(\mathrm{B}^-) + \frac{k_0}{k_B}\right]\left(c - \frac{x}{4}\right)$$

By introducing (B^-) from equation 20 we get

$$\frac{1}{4}\frac{\mathrm{d}x}{\mathrm{d}t} = k_B\left[(\mathrm{B}^-)_0 + \frac{k_0}{k_B} - (2-\kappa)\frac{x}{4}\right]\left(c - \frac{x}{4}\right)$$

If we integrate and use equation 20 we obtain

$$k^*t = f(x) + \log_{10} S \tag{25}$$

where we have used the abbreviations

$$k \equiv k_0 + k_B (B^-)_\infty \tag{26}$$

and

$$f(x) \equiv \log_{10} \frac{(B^-) + \frac{k_0}{k_B}}{(B^-)_0 + \frac{k_0}{k_B}} - \log_{10} \frac{c - \frac{x}{4}}{c} \tag{27}$$

and S is an integration constant.

In order to test the agreement between expression 25 and the experiments, we introduce the observed values of x into $f(x)$. (B^-) is calculated from x by means of equation 20. For a first approximation we may use $k_0/k_B = 0$ or a preliminarily estimated value. We now plot $f(x)$ against t. ~~When t is sufficiently great the points fall on a straight line, whose slope~~ determines a preliminary value of k^*. From expression 26 we find the corresponding value of $k_B{}^*$ and of k_0/k_B. We repeat the computation with the new value of k_0/k_B and continue in the same way until a new repetition does not alter the value of k^*. The intercept on the ordinate axis of the straight line is $-\log S$.

Equation 25 does not hold for the observed values of x during the first part of the experiment. Owing to mathematical difficulties we must refrain from testing the explanation for this part of the reaction. If instead of using the observed values of x we use those determined by means of equation 24, equation 25 will hold for the whole experiment. When $t = 0$, we have $(HR) = c\,(1-\epsilon)$, and, consequently, by equation 24 when we use the abbreviation 12

$$c - \frac{x}{4} = c(1-\epsilon)\left(1 + \frac{1}{2(r-1)}\right) = Ac$$

If we introduce this expression together with $t = 0$ into equation 25 we get

$$\frac{A-1}{A} = \frac{S-1}{S} \, \frac{(B^-)_0 + \frac{k_0}{k_B}}{(B^-)_\infty + \frac{k_0}{k_B}} \tag{28}$$

By means of this expression we calculate A from S, determined from the experiment as mentioned above. From A we find r, and, by introducing this and the known values of $k_0{}^*$, $h_0{}^*$, and $k_B{}^*$ into equation 23, we find $h_B{}^*$.

Owing to the approximate character of the calculations we can not expect to get a great accuracy in the determination of the catalytic constant, especially in the case of $h_B{}^*$.

THE HYDROLYSIS OF BROMINE

In an aqueous solution of bromine we have the following equilibria

$$Br_2 + H_2O \rightleftarrows HBrO + H^+ + Br^- \tag{29}$$

and

$$Br_2 + Br^- \rightleftarrows Br_3^- \tag{30}$$

We neglect a possible formation of the ion Br_5^-. The hydrobromic acid formed by scheme 29 will cause a decrease in the concentration of the catalyst. In order to repress the hydrolysis all experiments were done in 0.05 *M* potassium bromide. We shall here see that this is sufficient to make the error negligible.

The equilibrium constants of the reactions in scheme 29 determined by Bray and Connolly (2) and in scheme 30 determined by Jakowkin (7) are

$$(H^+)(Br^-)(HBrO)/(Br_2) = 5.2 \times 10^{-9}$$

and

$$(Br^-)(Br_2)/(Br_3^-) = 0.063$$

The normality of the bromine is $d = 2(Br_2) + 2(Br_3^-)$. We get

$$(HBrO) = \frac{1.6 \times 10^{-10} d}{(0.063 + (Br^-))(H^+)(Br^-)}$$

In the experiments (Br^-) was 0.05, d usually about 0.02, and $(H^+) > 10^{-5}$. For these values we get $(HBrO) < 6 \times 10^{-5}$. The hydrobromic acid formed by the hydrolysis is equivalent to the (HBrO). When $b > 0.01$ the formation of 6×10^{-5} *N* strong acid is without importance.

EXPERIMENTAL

The bromination of acetoacetic ester was examined in the following five solutions: (1) acetic acid + sodium acetate; (2) glycolic acid + sodium glycolate; (3) chloroacetic acid + sodium chloroacetate; (4) phosphoric acid + primary potassium phosphate; (5) acid sodium sulfate + normal sodium sulfate.

Kahlbaum's acetic acid "for analysis" was used without purification. Glycolic acid was purified as described in reference 9. Chloroacetic acid (pure, "Merck") was distilled. The buffer solutions were made by adding sodium hydroxide to solutions of the acids. The phosphate mixtures were made from Kahlbaum's primary potassium phosphate (for Sörensen's buffer solutions) and hydrochloric acid. The sulfate mixtures were made from sulfuric acid and sodium hydroxide. The hydrogen-ion concentration was always so great that it was unnecessary to keep the solutions carbon dioxide-free. Sufficient potassium bromide solution was added to make the solutions 0.05 *M* with respect to this substance during the bromination. The initial concentration of bromine was always about 0.02 *N*, except in experiments carried out in order to show that the concentration of bromine has no influence on the velocity. The volume of the reacting solution was always 200 cc. The experimental procedure was the same as described in Part I.

In computing the catalytic constants k_B^* and h_B^* we have used the values of ϵ, k_0^*, and h_0^* found for the water reaction (the "uncatalyzed" reaction) in 0.05 *M* potassium bromide by the experiments given in table 4 (Part I, p. 761). Other salts present in the catalytic experiments may also have an effect on the water reaction. It has already been shown that the kinetic salt effect of sodium chloride on k_0^* and h_0^* is small, and the effects of the other salts are probably also small. Since, further, the water reaction usually plays a rather insignificant part compared with the catalytic reaction, we have always neglected a possible salt effect on k_0^* and h_0^* in the calculation of k_B^* and h_B^*. The error thus committed is probably insignificant, except in the experiments in sulfate mixtures. Here the salt effect on the water reaction is probably greater than in the other experiments, and it has an especially great influence on the value of the catalytic constant, because the sulfate ion catalysis is only a small part of the total reaction.

Acetate ion catalysis

It was first shown that even a great variation in the concentration of bromine did not affect the velocity of bromination in the acetate buffers. This is seen especially clearly from four series of preliminary experiments in acetate buffers (8). Here an insufficient amount of bromine was added and the moment when the reaction ceased because all bromine had reacted was determined electrometrically by means of the arrangement described in Part I, p. 757. The mean value of k_B^* found here was 7.47 (at 18°C.), while $k_B^* = 7.41$ was found by the experiments with an excess of bromine in this paper.

The velocity is independent of the concentration of undissociated acetic acid (table 1) and thus also independent of the hydrogen- and hydroxyl-ion concentration of the acetate buffer, when the acetate ion concentration is kept constant.

Table 4 gives a summary of ten series of experiments in different mixtures of acetic acid and sodium acetate at the temperatures 0.03, 17.94, and 24.97°C. The results of two of the series are given in more detail in tables 2 and 3.

The constant k^* has been computed by plotting $f(x)$ against t as described above. In the last column of tables 2 and 3 $\delta = f(x) - (k^* t - \log S)$ has been tabulated. The agreement with formula 25 is always good when $0.8 > (c - \frac{x}{4})/c > 0.5$. In the first part of the reaction, when $(c - \frac{x}{4})/c > 0.8$, too great values of $f(x)$ are obtained. This is in qualitative agreement with the theory, but owing to mathematical difficulties we cannot test the agreement quantitatively. Later in the reaction, when $(c - \frac{x}{4})/c < 0.5$, we get greater and greater discrepancies, corresponding to too small values of x. This was also found in experiments in pure water and hydrochloric acid and is probably due to a secondary reaction. In this period of the reaction the solution acquired a peculiar sharp smell and, toward the end of the reaction, it turned cloudy.

TABLE 1

Bromination of acetoacetic ester in acetic acid-sodium acetate mixtures at 18°C.

	$b = 0.04008$			$b = 0.02004$	
	$a = 0.110$	$a = 0.060$		$a = 0.080$	$a = 0.030$
t	$(c - \frac{x}{4})/c$	$(c - \frac{x}{4})/c$	t	$(c - \frac{x}{4})/c$	$(c - \frac{x}{4})/c$
0.250	0.8584	0.8584	1.500	0.6001	0.6009
0.495	0.7246	0.7246	3.000	0.3674	0.3725
1.005	0.5114	0.5117			

TABLE 2

Bromination of acetoacetic ester in a mixture of acetic acid and sodium acetate at 0.03°C.

$a = 0.0600$; $b = 0.04008$; $c = 5.291 \times 10^{-3}$; (KBr) $= 0.050$; $K_{\mathrm{HB}} = 3 \times 10^{-6}$; $(\mathrm{B}^-) = 0.04013 - \frac{x}{2}$; $(\mathrm{B}^-)_\infty = 0.02955$; $k^* = 0.05144$; $\log S = 0.0113$; $k_{\mathrm{B}} = 1.621$; $h_{\mathrm{B}}^* = 23$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
1.003	0.633	0.0421	0.0403	+18
1.997	1.261	0.0915	0.0914	+1
2.497	1.553	0.1177	0.1171	+6
2.997	1.808	0.1426	0.1429	−3
3.497	2.052	0.1688	0.1686	+2
4.000	2.275	0.1947	0.1945	+2
4.502	2.419	0.2199	0.2203	−4
5.003	2.667	0.2460	0.2461	−1
5.997	2.998	0.2950	0.2972	−22

From the summary of all the experiments in acetate mixtures given in table 4 it is seen that the constancy of $k_B{}^*$ at constant temperature is good even when the acetate concentration is varied considerably. The mutual agreement of the values of $h_B{}^*$ is not very good. However, when we remember that we can only obtain a rough value of this constant, we might not expect a better agreement.

TABLE 3

Bromination of acetoacetic ester in a mixture of acetic acid and sodium acetate at 17.94°C. $a = 0.0900$; $b = 0.00012$; $c = 6.275 \times 10^{-3}$; (KBr) $= 0.050$; $K_{HB} = 3 \times 10^{-5}$; $(B^-) = 0.06017 - \frac{x}{2}$; $(B^-)_\infty = 0.04762$; $k^* = 0.3718$; $\log S = 0.0099$; $k_B{}^* = 7.43$; $h_B{}^* = 121$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
0.103	0.514	0.0299	0.0284	+15
0.200	1.049	0.0646	0.0645	+1
0.300	1.552	0.1014	0.1016	−2
0.398	2.003	0.1383	0.1381	+2
0.500	2.411	0.1758	0.1760	−2
0.595	2.759	0.2115	0.2113	+2
0.700	3.084	0.2486	0.2504	−18

TABLE 4

Bromination of acetoacetic ester in mixtures of acetic acid and sodium acetate at 0, 18, and 25°C.

(KBr) = 0.050 in all experiments

TEMPERATURE	$(B^-)_0$	$(B^-)_\infty$	k^*	$k_B{}^*$	$h_B{}^*$	MEAN VALUES	
						$k_B{}^*$	$h_B{}^*$
degrees C.							
0.03	0.04013	0.02955	0.05144	1.621	23	1.620	25
	0.1002	0.08967	0.1488	1.620	27		
17.94	0.02009	0.01381	0.1208	7.46	98	7.41	119
	0.02009	0.00998	0.0912	7.38	121		
	0.04013	0.03385	0.2691	7.42	112		
	0.06017	0.05389	0.4162	7.39	127		
	0.06017	0.04762	0.3718	7.43	121		
	0.08021	0.07393	0.5645	7.39	137		
24.97	0.02009	0.01513	0.2222	12.62	214	12.70	210
	0.04013	0.03020	0.4170	12.77	207		

Glycolate ion catalysis

Table 5 gives the results of a single series of experiments, and table 6 a summary of all the experiments in mixtures of glycolic acid and sodium glycolate. The dissociation constant K_{HB} at different salt concentration has been taken from a yet unpublished determination. The agreement of the kinetic experiments with the theory is as good as in the experiments on acetate ion catalysis.

TABLE 5

Bromination of acetoacetic ester in a mixture of glycolic acid and sodium glycolate at 0.03°C.

$a = 0.0136$; $b = 0.05550$; $c = 3.056 \times 10^{-3}$; $(\mathrm{KBr}) = 0.050$; $k_{HB} = 2.2 \times 10^{4}$; $(\mathrm{B}^-) = 0.05555 - 1.99 \times \frac{x}{4}$; $(\mathrm{B}^-)_\infty = 0.04948$; $k^* = 0.02630$; $\log S = 0.0128$; $k_B^* = 0.460$; $h_B^* = 6.87$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
3.00	0.474	0.0666	0.0661	+5
5.00	0.788	0.1187	0.1187	0
5.00	0.790	0.1189	0.1187	+2
7.00	1.064	0.1710	0.1713	−3
9.00	1.307	0.2241	0.2239	+2
11.00	1.516	0.2764	0.2765	−1

TABLE 6

Bromination of acetoacetic ester in mixtures of glycolic acid and sodium glycolate at 0, 18, and 25°C.

(KBr) = 0.050 in all experiments

TEMPERATURE	$(\mathrm{B}^-)_0$	$(\mathrm{B}^-)_\infty$	k^*	k_B^*	h_B^*	MEAN VALUES	
						k_B^*	h_B^*
degrees C.							
0.03	0.05555	0.04948	0.02630	0.460	6.87	0.462	6.62
	0.09256	0.08645	0.04357	0.463	6.36		
17.94	0.05555	0.04948	0.1197	2.06	29.4	2.06	28.4
	0.09256	0.08645	0.1958	2.06	27.3		
24.97	0.05555	0.04948	0.2032	3.48	53.6	3.48	53.4
	0.09256	0.08645	0.332	3.48	53.2		

Monochloroacetate ion catalysis

Table 7 gives the results of a single series of experiments, and table 8 a summary of all the experiments in mixtures of monochloroacetic acid and sodium monochloroacetate. The dissociation constant of monochloroacetic acid at 20°C. and in infinite dilution $K_{HB}^{\circ} = 1.41 \times 10^{-3}$ has been determined by Grove (6). From this value and the assumption that the relative increase of K_{HB} by addition of salt is the same as for glycolic acid, it is estimated that the value $K_{HB} = 2.3 \times 10^{-3}$ is sufficiently accurate

TABLE 7

Bromination of acetoacetic ester in a mixture of monochloroacetic acid and sodium monochloroacetate at 17.94°C.

$a = 0.1018$; $b = 0.1002$; $c = 3.382 \times 10^{-3}$; $(\mathrm{KBr}) = 0.050$; $K_{HB} = 0.0023$; $(\mathrm{B}^-) = 0.1024 - 1.92 \times \frac{x}{4}$; $(\mathrm{B}^-)_\infty = 0.0959$; $k^* = 0.0709$; $\log S = 0.0145$; $k_B = 0.554$; $h_B{}^* = 7.8$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
1.000	0.446	0.0586	0.0564	+22
2.000	0.893	0.1276	0.1273	+3
2.500	1.092	0.1626	0.1627	−1
3.000	1.274	0.1974	0.1982	−8
3.500	1.447	0.2335	0.2337	−2
4.000	1.601	0.2685	0.2691	−6
5.000	1.880	0.3408	0.3400	+8
6.000	2.098	0.4046	0.4109	−63

TABLE 8

Bromination of acetoacetic ester in mixtures of monochloroacetic acid and sodium monochloroacetate at 0, 18, and 25°C.

$(\mathrm{KBr}) = 0.050$ in all experiments

TEMPERATURE	$(\mathrm{B}^-)_0$	$(\mathrm{B}^-)_\infty$	k^*	$k_B{}^*$	$h_B{}^*$	MEAN VALUES	
						$k_B{}^*$	$h_B{}^*$
degrees C.							
0.03	0.06226	0.05597	0.01001	0.1158	1.71	0.1162	1.62
	0.1024	0.0959	0.01470	0.1165	1.54		
17.94	0.06226	0.05597	0.0488	0.554	8.0	0.554	7.9
	0.1024	0.0959	0.0709	0.554	7.8		
24.97	0.04218	0.03611	0.0669	0.989	11.6	0.983	12.0
	0.1024	0.0959	0.1250	0.978	12.3		

for calculation of (H^+) in all the experiments. Also here the agreement is good.

Primary phosphate ion catalysis

Table 9 gives the results of a single series of experiments, and table 10 a summary of all the experiments in mixtures of phosphoric acid and primary potassium phosphate. The values of the first dissociation constant of phosphoric acid used for the calculation of (H^+) have been calculated from the measurements of Bjerrum and Unmack (1) at 18°C. and 25°C. These measurements have been carried out in solutions containing sodium

TABLE 9

Bromination of acetoacetic ester in a mixture of phosphoric acid and primary potassium phosphate at 24.97°C.

$a = 0.01520$; $b = 0.06085$; $c = 3.056 \times 10^{-4}$; (KBr) $= 0.050$; (KCl) $= 0.015$; $K_{HB} = 0.0089$; $(B^-) = 0.06274 - 1.69 \times \frac{x}{4}$; $(B^-)_\infty = 0.05758$; $k^* = 0.0817$; $\log S = 0.0160$; $k_B^* = 0.877$; $h_B^* = 10.6$

t	$\frac{x}{4} \times 10^1$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
1.253	0.0575	0.0863	0.0864	−1
2.000	0.0914	0.1475	0.1474	+1
2.752	0.1206	0.2089	0.2088	+1
3.500	0.1456	0.2701	0.2700	+1
4.253	0.1672	0.3314	0.3315	−1

TABLE 10

Bromination of acetoacetic ester in mixtures of phosphoric acid and primary potassium phosphate at 0, 18, and 25°C.

(KBr) = 0.050 in all experiments

TEMPERATURE	$(B^-)_0$	$(B^-)_\infty$	TOTAL SALT CONCENTRATION s	k^*	k_B^*	h_B^*	MEAN VALUES	
							k_B^*	h_B^*
degrees C.								
0.03	0.06311	0.05807	0.126	0.00907	0.0954	0.88		
17.94	0.03596	0.03122	0.094	0.03320	0.493	5.9	0.488	5.6
	0.04716	0.04214	0.114	0.03882	0.499	5.6		
	0.07003	0.06468	0.145	0.0491	0.484	5.6		
	0.09259	0.08705	0.170	0.05944	0.478	5.4		
24.97	0.06274	0.05758	0.126	0.0817	0.877	10.6	0.876	11.2
	0.05641	0.05143	0.125	0.07616	0.874	11.7		

ions instead of potassium ions and at salt concentrations $\leqq 0.1\ N$, while the solutions for the catalytic experiments were usually somewhat more concentrated. Nevertheless, the values obtained from the interpolation formulas given by Bjerrum and Unmack are considered to be accurate enough for the rather rough calculation of (H^+). For the experiments at 0°C. the values of $-\log K_{HB}$ at 25°C. and 18°C. have been extrapolated to 0°C. It is assumed that the concentration of the secondary phosphate ion is always negligible.

Formula 25 holds well within the single series of experiments. The part of the total reaction which is caused by the catalysis is only one to two times as great as the part caused by the water reaction. Nevertheless, the constancy of k_B^* when the concentration of primary phosphate ion is varied is good. Naturally, the accuracy of h_B^* is much smaller, but also here the constancy is fairly good.

The second dissociation constant of sulfuric acid

For the calculation of the experiments on the bromination of acetoacetic ester in mixtures of acid and normal sodium sulfate it is necessary to have some knowledge of the second dissociation constant of sulfuric acid at different salt concentrations. Sherrill and Noyes (13) have calculated this constant K at 25°C. from measurements of the electric conductivity of solutions of sulfuric acid and of acid sodium sulfate. By extrapolation to infinite dilution they find the activity dissociation constant $K^0 = 0.0115$.

Here we shall compute K^0 from their determinations of K in a slightly different way. According to the theory of Debye and Hückel the activity coefficient f_i of an ion in dilute solution may be expressed by the formula

$$-\log f_i = z^2\alpha\sqrt{\mu} - \beta_i\mu$$

where z is the number of electric charges on the ion, μ the ionic strength of the solution, α is a constant, the same for all ions (at 25°C. in water $\alpha = 0.504$), and β_i approaches a constant value, when $\mu \rightarrow 0$. By means of this formula we may express the second dissociation constant of sulfuric acid as follows

$$-\log K = -\log K^0 - 2.016\sqrt{\mu} + \beta\mu$$

We now plot $-\log K + 2.016\sqrt{\mu}$, calculated from the values of Sherrill and Noyes, against μ. The points fall on a straight line which determines the constants $-\log K^0$ and β. We thus find for the solutions of sulfuric acid

$$-\log K = 1.988 - 2.016\sqrt{\mu} + 0.62\mu \qquad (\mu \leqq 0.0844) \qquad (31)$$

and for the solutions of acid sodium sulfate

$$-\log K = 1.984 - 2.016\sqrt{\mu} + 1.27\mu \qquad (\mu \leqq 0.1056) \qquad (32)$$

The agreement is seen from table 11 where the dissociation constants K found by Sherrill and Noyes are given in the third column, while those calculated from the formulas 31 and 32 are given in the last column. By this extrapolation we get $K^0 = 0.0103$ at 25°C.

In order to get an idea of the variation of K^0 with temperature we make the following considerations. Thorvaldson, Brown and Peaker (14) have found calorimetrically that the heat evolved by mixing 1 N H_2SO_4 and an equivalent amount of NaOH, 100 H_2O at 20°C. is 16.984 kg-cal. per equivalent H_2SO_4. Richards and Hall (12) have determined the heats of neutralization of different strong acids and sodium hydroxide. They found for HCl, 100 H_2O + NaOH, 100 H_2O at 20°C. 13.924 kg-cal. and for HBr, HJ, and HNO_3 nearly the same value. Thus sulfuric acid in approximately the same molar concentration gives 3 kg-cal. more per equivalent than the strong acids. We may assume that the first dissociation of 1 N H_2SO_4 is practically complete. The difference in the heat of neutralization is probably caused by the second dissociation $HSO_4^- + H_2O \rightarrow SO_4^{--} + H_3O^+$. If the second dissociation constant of sulfuric acid is not many times as great in 1 N H_2SO_4 as by infinite dilution, only few per cent of the acid is present in form of the normal sulfate ion. We thus get from the above measurements that the heat of dissociation of the ion HSO_4^- is approximately 3 kg-cal. per ½ mole or 6 kg-cal. per mole. If we use this value also at infinite dilution and in all the temperature interval 0–25°C. we get from K^0 at 25°C. by means of the formula

TABLE 11

Second dissociation constant of sulfuric acid at 25°C.

SOLUTIONS OF SULFURIC ACID				SOLUTIONS OF ACID SODIUM SULFATE			
$-\log K = 1.988 - 2.016\sqrt{\mu} + 0.62\mu$				$-\log K = 1.984 - 2.016\sqrt{\mu} + 1.27\mu$			
Stoichiometric concentration of H_2SO_4	μ	K (exp.)	K (calcd.)	Stoichiometric concentration of $NaHSO_4$	μ	K (exp.)	K (calcd.)
0.00025	0.0007	0.0118	0.0116	0.000391	0.0011	0.0107	0.0121
0.001	0.0027	0.0130	0.0130	0.000781	0.0022	0.0121	0.0128
0.005	0.0116	0.0168	0.0167	0.001562	0.0044	0.0135	0.0139
0.00625	0.0141	0.0175	0.0175	0.003125	0.0084	0.0153	0.0155
0.0125	0.0225	0.0208	0.0208	0.00625	0.0160	0.0178	0.0178
0.0250	0.0461	0.0260	0.0260	0.0125	0.0302	0.0213	0.0213
0.0500	0.0844	0.0352	0.0352	0.0250	0.0564	0.0265	0.0265
				0.0500	0.1056	0.0348	0.0344

$$U = 4.575 \times 10^{-3} \frac{d \log K^0}{d\,(T^{-1})}$$

where U is the heat of dissociation in kilogram-calories per mole per liter and T is the absolute temperature, the following values of K^0:

25°C.	$-\log K^0 = 1.99$	$K^0 = 0.0103$
18°C.	$-\log K^0 = 1.88$	$K^0 = 0.013$
0°C.	$-\log K^0 = 1.58$	$K^0 = 0.026$

Sulfate ion catalysis

Experiments on the bromination of acetoacetic ester were carried out in solutions of sodium sulfate containing a little acid sodium sulfate and 0.050 M potassium bromide ($0.16 < \mu < 0.34$). K was found from equation 32. For experiments at 18°C. and 0°C. the values of $-\log K^0$ found at these temperatures were substituted for 1.984 in equation 32. Owing to the great ionic strength of the solution we can only get very rough values of K in this way. However, we consider the accuracy sufficient for the following reasons. Firstly, the correction for the variation of (H^+) is here very small, and secondly, there is, as we shall see, another source of error which makes it of no use to attempt to determine the concentration of the catalyst with great accuracy.

TABLE 12

Bromination of acetoacetic ester in a mixture of acid and normal sodium sulfate at 24.97°C.

$a = 0.00035$; $b = 0.07644$; $c = 3.039 \times 10^{-3}$; (KBr) $= 0.050$; $K_{HB} = 0.053$; $(B^-) = 0.07658 - 1.16 \times \frac{x}{4}$; $(B^-)_\infty = 0.07306$; $k^* = 0.03785$; $\log S = 0.0164$; $k_B{}^* = 0.091$; $h_B{}^* = 1.2$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
1.00	0.189	0.0277	0.0214	+63
3.00	0.616	0.0976	0.0972	+4
4.00	0.817	0.1350	0.1350	0
5.00	1.002	0.1725	0.1728	−3
6.00	1.175	0.2109	0.2107	+2
7.00	1.330	0.2484	0.2486	−2
8.00	1.475	0.2867	0.2864	+3
9.00	1.603	0.3235	0.3242	−7

As seen from table 12 the agreement with formula 25 is as good as in experiments with other catalysts. In table 13 is given a summary of all the experiments in sodium sulfate. It is seen that k^* is only 11 to 24 per cent greater than $k_0{}^*$. Thus the velocity is not much increased by the presence of the sodium sulfate. The kinetic salt effect on $k_0{}^*$ is probably not negligible compared with the increase. However, the increase can not be explained only by the salt effect. We have found in Part I, that 0.1 M

sodium chloride or potassium chloride gives a decrease of the velocity of 1 to 2 per cent. It is therefore most unlikely that the salt effect of 0.1 *M* sodium sulfate can give an increase of 24 per cent. However, the effect of the salt being unknown, it is disregarded. In the other catalytic experiments the error thus introduced is probably of no importance. Here it makes the values of k_B^* less reliable. In addition, the experimental error in k^* is of greater importance here, where the water reaction is 80 to 90 per cent of the total reaction. In spite of these possible errors, the values of k_B^* at different catalyst concentrations agree fairly well among themselves. Naturally, the values of h_B^* are only very rough.

We have now examined the bromination of acetoacetic ester in solutions containing one of the following bases,—acetate, glycolate, monochloroacetate, primary phosphate, and sulfate ions—together with the corresponding acid. We have always found agreement with formula 25 for the part of the reaction where a comparison was possible. From this we conclude that the mechanism is as given in scheme 1 (Part I, p. 751), and that the enolization of acetoacetic ester and of α-monobromoacetoacetic ester is catalyzed by bases in general. The theory of general acid and basic catalysis and of prototropic isomerization has recently been discussed in another paper (11), where references to the literature on the subject will be found.

TABLE 13

Bromination of acetoacetic ester in mixtures of acid and normal sodium sulfate at 0, 18, and 25°C.

(KBr) = 0.050 in all experiments

TEMPERATURE	$(B^-)_0$	$(B^-)_\infty$	μ	k^*	k_B^*	h_B^*	MEAN VALUES	
							k_B^*	h_B^*
degrees C.								
0.03	0.0767	0.0744	0.28	0.004012	0.0065	0.09		
17.94	0.0486	0.0455	0.195	0.02012	0.0510	0.4	0.047	0.5
	0.0766	0.0734	0.28	0.02111	0.0452	0.6		
	0.0961	0.0928	0.34	0.02205	0.0458	0.4		
24.97	0.0383	0.0355	0.16	0.03475	0.100	1.9	0.096	1.5
	0.0766	0.0731	0.28	0.03785	0.091	1.2		

The water reaction studied in part I is explained as the result of the basic catalysis of the water. If we neglect the effect of the association of the water molecules, the concentration of water is $(H_2O) = 55.5$, its basic strength 55.5^{-1} and the catalytic constants $k_{H_2O} = k_0/55.5$ and $h_{H_2O} = h_0/55.5$.

The catalytic constants for the six bases examined are given in table 14 together with the strengths of the acids which correspond to the bases. In the paper (11) mentioned above we have discussed the formula

$$\frac{1}{q}k_B = G\left(\frac{p}{q}K_B^{\circ}\right)^{\beta} \tag{33}$$

where K_B^0 is the strength of the catalyzing base at infinite dilution, p and q are statistical factors, and β and G are constants for a given reaction at a given temperature ($0 < \beta < 1$). In order to test the validity of this formula for the reaction examined here we plot log $(\frac{1}{q}k_B^*)$ and log $(\frac{1}{q}h_B^*)$ against log $(\frac{p}{q}K_B^0)$ (figure 1 and 2). The points for acetate, glycolate, and monochloroacetate ions fall very close to a straight line. If we draw the line through the points for acetate and glycolate ions we get in the case of acetoacetic ester the following values of β: 0.602, 0.605, and 0.599 at 0, 18, and 25°C., respectively. β is here independent of the temperature. In figure 1 we have drawn all the straight lines with the slope $\beta = 0.60$. This value has also been used for the calculation of G^* from formula 33 (see table 14). For α-monobromoacetoacetic ester, where the accuracy is

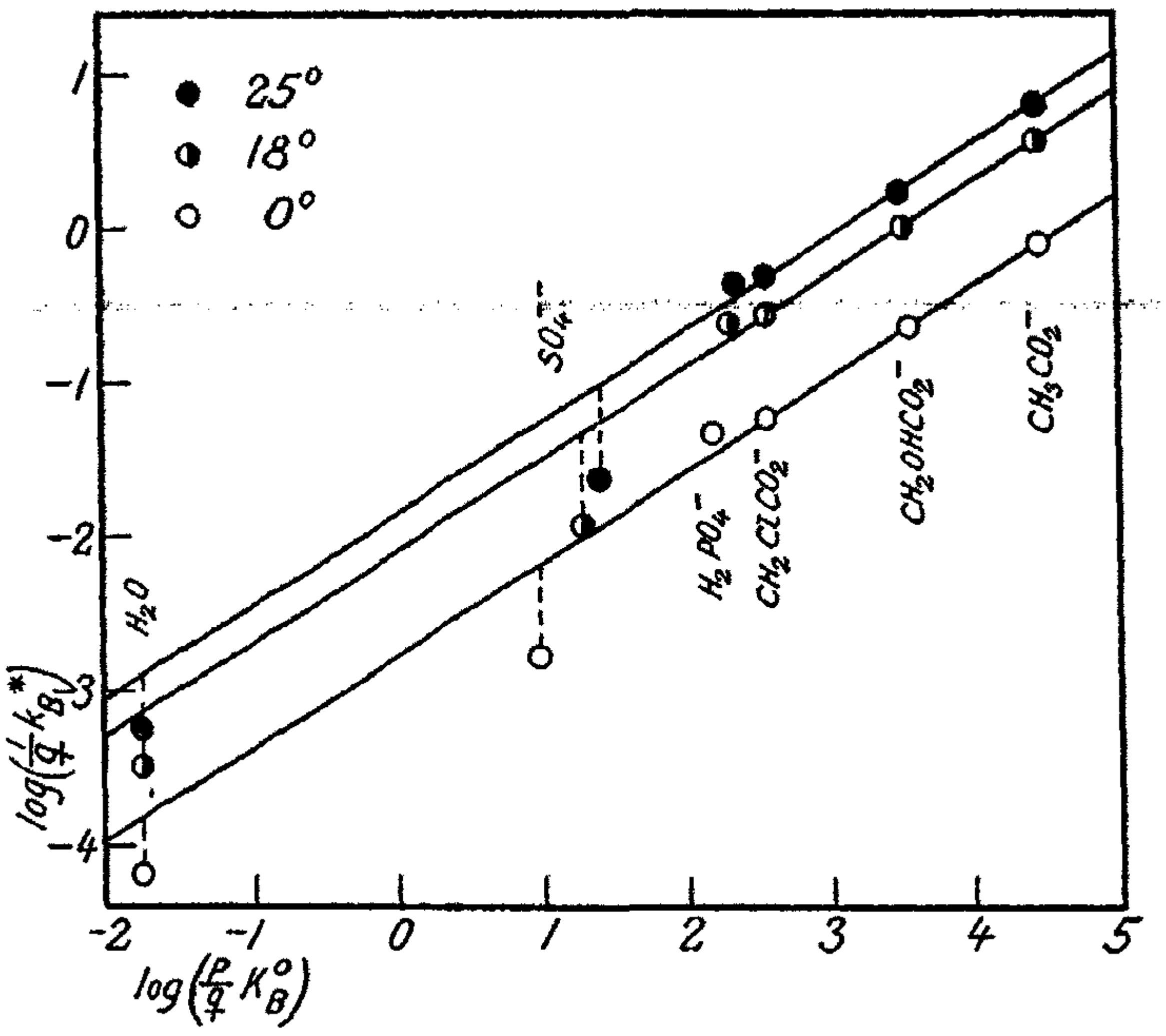


FIG. 1. BASIC CATALYSIS OF THE ENOLIZATION OF ACETOACETIC ESTER
The dependence of catalytic constant upon basic strength

much smaller, we get from the catalytic constants of acetate and glycolate ions $\beta = 0.64$, 0.68, and 0.63 at 0, 18, and 25°C., respectively. We have used the value $\beta = 0.64$ for drawing the straight lines in figure 2 and for calculating G^* (table 14). While the agreement with formula 33 is always good for the three carboxylate bases, the catalysis of the primary phosphate ion is a little too strong, and that of the sulfate ion much too weak. This latter deviation of the base with two negative charges is qualitatively in agreement with the theory (11). The points for water fall below the lines. However, the deviation is not unreasonably great when we remember that we have neglected the effect of the association. As seen both from the figures and the table, the deviation from formula 33 for a given base is approximately independent of the temperature.

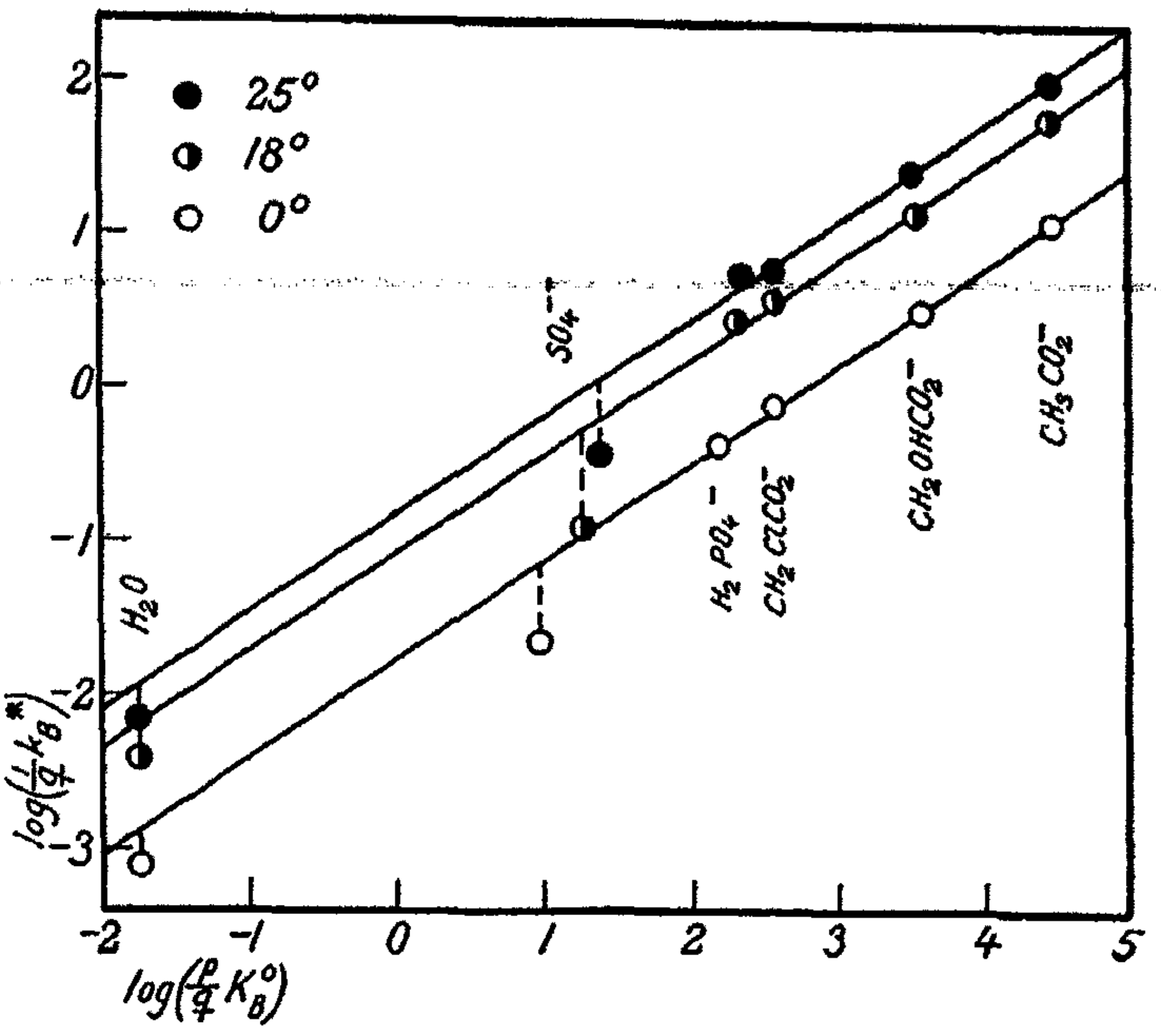


FIG. 2. BASIC CATALYSIS OF THE ENOLIZATION OF α-MONOBROMOACETOACETIC ESTER
The dependence of catalytic constant upon basic strength

From the experimental values of k_B^* at the three temperatures we get the expressions for log k_B^* given in table 15. This table also contains the heats of activation Q in kg-cal. calculated from the formula

$$Q = -4.575 \times 10^{-3} \frac{d \log k_B}{d\,(T^{-1})}$$

The basic strength of a catalyst generally varies with the temperature. The increase in velocity when the temperature rises may therefore formally

TABLE 14

Basic catalysis of the enolization of acetoacetic and α-monobromoacetoacetic ester at 0, 18, and 25°C.

TEMPERATURE	CATALYST					ACETOACETIC ESTER $\beta = 0.60$			α-MONOBROMOACETOACETIC ESTER $\beta = 0.64$		
		p	q	K_{HB}°	$\log\left(\frac{p}{q}K_{B}^{\circ}\right)$	k_{B}^{*}	$\log\left(\frac{1}{q}k_{B}^{*}\right)$	$G^{*} \times 10^{3}$	k_{B}^{*}	$\log\left(\frac{1}{q}k_{B}^{*}\right)$	$G^{*} \times 10$
degrees C.											
0.03	$CH_3CO_2^-$	1	2	$1.70 \times 10^{-5(a)}$	4.469	1.620	0.908–1	1.69	25	1.097	1.73
	$CH_2OHCO_2^-$	1	2	$1.36 \times 10^{-4(a)}$	3.566	0.462	0.364–1	1.68	6.62	0.520	1.74
	$CH_2ClCO_2^-$	1	2	$1.41 \times 10^{-3(b)}$	2.55	0.1162	0.764–2	1.72	1.62	0.909–1	1.90
	$H_2PO_4^-$	3	2	$1.00 \times 10^{-2(d)}$	2.18	0.0954	0.678–2	2.35	0.88	0.643–1	1.77
	SO_4^{--}	1	4	$2.6 \times 10^{-2(e)}$	0.98	0.0065	0.211–3	0.42	0.09	0.35 –2	0.5
	H_2O	1	1	55.5	−1.74	0.637×10^{-4}	0.804–5	0.70	0.766×10^{-3}	0.884–4	1.00
17.94	$CH_3CO_2^-$	1	2	$1.79 \times 10^{-5(a)}$	4.447	7.41	0.569	7.96	119	1.775	8.5
	$CH_2OHCO_2^-$	1	2	$1.48 \times 10^{-4(a)}$	3.528	2.06	0.013	7.87	28.4	1.153	7.9
	$CH_2ClCO_2^-$	1	2	$1.41 \times 10^{-3(b)}$	2.55	0.554	0.442–1	8.17	7.9	0.597	9.2
	$H_2PO_4^-$	3	2	$7.58 \times 10^{-3(c)}$	2.296	0.488	0.387–1	10.23	5.6	0.447	9.5
	SO_4^{--}	1	4	$1.3 \times 10^{-2(e)}$	1.28	0.047	0.073–2	2.02	0.5	0.097–1	1.9
	H_2O	1	1	55.5	−1.74	3.21×10^{-4}	0.506–4	3.55	3.89×10^{-3}	0.590–3	5.0
24.97	$CH_3CO_2^-$	1	2	$1.77 \times 10^{-5(a)}$	4.450	12.70	0.803	13.6	210	2.021	15.0
	$CH_2OHCO_2^-$	1	2	$1.54 \times 10^{-4(a)}$	3.511	3.48	0.241	13.6	53.4	1.426	15.2
	$CH_2ClCO_2^-$	1	2	$1.41 \times 10^{-3(b)}$	2.55	0.983	0.692–1	14.5	12.0	0.779	14.0
	$H_2PO_4^-$	3	2	$6.90 \times 10^{-3(c)}$	2.337	0.876	0.642–1	17.4	11.2	0.748	18.0
	SO_4^{--}	1	4	$1.03 \times 10^{-2(e)}$	1.39	0.096	0.380–2	3.52	1.5	0.57 –1	4.8
	H_2O	1	1	55.5	−1.74	5.62×10^{-4}	0.750–4	6.22	6.92×10^{-3}	0.840–3	9.0

(a) Unpublished electrometric measurements. (b) At 20°C., Grove (6). (c) Bjerrum and Unmack (1). (d) As (c). Extrapolation to 0°C. (e) This paper, page 614.

be divided in two parts: (1) the increase in velocity at constant basic strength, (2) the change in velocity owing to the change in basic strength. It may be of some interest to consider the first part separately. From formula 33 we find, when we assume that β and K_B^0 are constant, the "heat of activation"

$$Q_G = -4.575 \times 10^{-3} \frac{d \log G}{d\,(T^{-1})}$$

The values of Q_G calculated from this formula are given in table 15. For monochloroacetic acid we have assumed that the dissociation constant is independent of the temperature. Q_G is approximately constant for all the bases. When we compare bases which have at constant temperature the same G^* this must naturally be so. However, Q_G has nearly the same value also for the last three bases, although G^* here varies considerably. It is interesting that the sulfate ion, which has an especially great heat of activation (Q), has the same Q_G as the other bases.

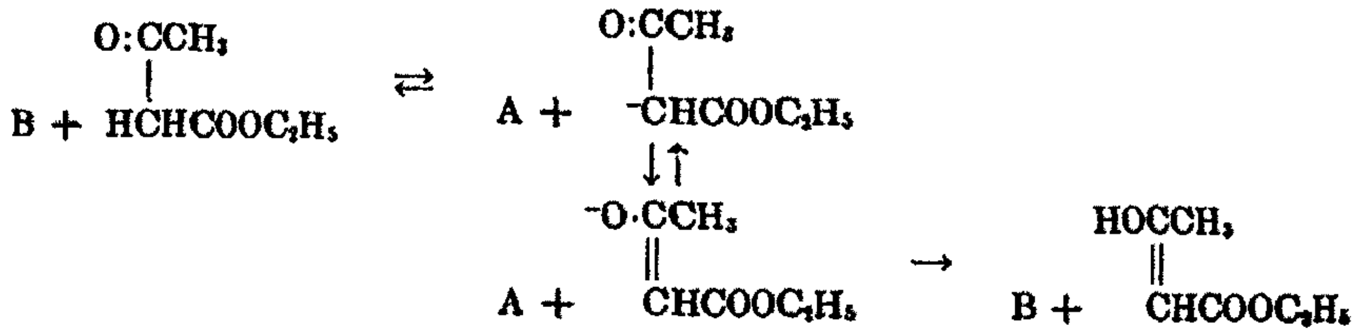
TABLE 15

Basic catalysis of the enolization of acetoacetic and α-monobromoacetoacetic ester

The dependence upon temperature; the heat of activation

CATALYST	ACETOACETIC ESTER			α-MONOBROMO-ACETOACETIC ESTER
	$\log k_B^*$ (0°C. – 25°C.)	Q	Q_G	Q
$CH_3CO_2^-$	$10.905-2.921 \times 10^3/T$	13.4	13.5	14
$CH_2OHCO_2^-$	$10.166\ 2.868 \times 10^3/T$	13.1	13.6	13.5
$CH_2ClCO_2^-$	$10.125-3.021 \times 10^3/T$	13.8	(13.8)	13
$H_2PO_4^-$	$10.487-3.143 \times 10^3/T$	14.4	13.0	16
SO_4^{--}	$11.788-3.817 \times 10^3/T$	17.5	13.7	
H_2O	$7.130-3.093 \times 10^3/T$	14.2	14.2	14

The mechanism of prototropic isomerization was discussed at length in the theoretical paper (11). As shown there the enolization of acetoacetic ester follows the scheme



where the equilibrium between the two forms of the ion is attained practically instantaneously. It follows from the theory that the transference of protons from the keto-ester to the base determines the velocity of the total reaction, if the tautomeric ion by taking up a proton from an acid forms predominatingly the enol-ester. It was shown that this is probably the case here, because the enol form is a much stronger acid than the keto form. However, we may also test this condition experimentally in the following way.

The apparent dissociation constant of acetoacetic ester at 25°C. is 2.0 $\times$ 10^{-11} (Goldschmidt and Oslan (4)). It is therefore easy to prepare a solution which is so alkaline that the ester is completely ionized. To this solution we suddenly add a mixture containing an excess of hydrochloric acid and bromine water. If only enol is formed this will instantaneously react with bromine (one mole per mole ester). After this the α-monobromoacetoacetic ester formed will react slowly with more bromine. The excess of bromine was removed by adding allyl alcohol immediately after the hydrochloric acid, and the solution was titrated in the ordinary way. It was always found that about one mole of bromine had reacted per mole of ester. However, the experiments were not quite reproducible. When the excess of bromine was small, less than the theoretical amount was used. Similar experiments have been carried out by Grossmann (5). He also finds that acetoacetic ester in sufficiently alkaline solution behaves as if it were exclusively the enol form of the ion. From these considerations we conclude that the velocity of enolization which we have measured in this work is actually the velocity of transference of protons from the keto form to the bases, or, in other words, the velocity of dissociation of the keto form, which is an extremely weak acid.

SUMMARY

This paper contains an experimental study of the rate of bromination of acetoacetic ester in solutions of weak bases and their corresponding acids.

It has been shown that the velocity of bromination is determined by the consecutive enolizations of acetoacetic and α-monobromoacetoacetic ester, which reactions are catalyzed by bases in general.

The catalytic constants of the six bases acetate, glycolate, monochloroacetate, primary phosphate, sulfate ions, and water at 0, 18, and 25°C. have been determined and compared with the strengths of the bases.

Evidence has been given in favor of the view that the velocities of enolization are determined by the velocities of dissociation of the keto forms, which are extremely weak acids.

I wish to thank the head of the laboratory, Professor Niels Bjerrum, for valuable advice and kind interest in my work.

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ADSORPTION OF HYDROGEN BY PALLADIUM BLACK UNDER HIGH PRESSURE

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Among the great number of authors who studied the system "Pd-H_2," many considered the question of the influence of hydrogen pressure upon the adsorptive capacity of palladium, but actual study of the influence of high pressure of hydrogen on its adsorption by palladium occupied the attention of very few investigators. The first work in which high hydrogen pressure was applied to the system "Pd-H_2" is the work of Dewar (1), who wanted to clear up the question as to whether a critical temperature exists at which palladium will not adsorb hydrogen at an optional pressure. For this purpose Dewar carried out experiments at temperatures from 360°C. to 600°C. and under hydrogen pressures of 60, 80, and 120 atmospheres.

The results of Dewar's experiments might be summarized in table 1. He found that at 420°C. and 80 atmospheres of hydrogen pressure, the amount of hydrogen adsorbed by palladium is of a magnitude of the order of 225–200 mg. per 100 grams of palladium. Mond, Ramsay, and Shields (6) come to an opposite conclusion as to the rôle of pressure, on the basis of their experiments on the occlusion of hydrogen and oxygen by palladium.[1] They indicate that increase of hydrogen pressure up to 4.6 atmospheres at room temperature does not influence the amount of hydrogen adsorbed by palladium.

Reviewing the results of the recent investigations on the state of hydrogen adsorbed in palladium, in particular the results of investigations by Holt (4), Sieverts, Firth (2), McBain (5) and Müller and Schwabe (7), one may come to the conclusion that all data bespeak the fact that in all platinum metals hydrogen is primarily adsorbed, that at least in the case of palladium a solid solution is formed, and that no chemical composition occurs with any of the metals of this group.

In the case of adsorption of hydrogen by palladium, however, there is reason to assume a direct solubility of hydrogen, and therefore the adsorptive capacity of palladium must depend upon the pressure.

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[1] The amount of oxygen present in palladium is less than the experimental error.

von Samson-Himmelstern (9), recalculating the data of Hoitsema (3) and Roseboom (8), comes to the conclusion that the relationship between the amount of hydrogen adsorbed by palladium and the pressure may be expressed by the following formula:

$$x = a \log p + b$$

where x = concentration of hydrogen dissolved, p = pressure, and a and b are constants. This equation he applied to the data of Roseboom, extended up to 1000 mm. of pressure. Extrapolating by his formula up to 1000 atmospheres of pressure, he obtains 0.787 gram-atom of hydrogen adsorbed per gram-atom of palladium If the extrapolation is made based on a linear relationship between the adsorptive capacity and the pressure, then 9 gram-atoms of hydrogen adsorbed per gram-atom of palladium are obtained at 1000 atmospheres and 25°C.

Experiments of von Samson-Himmelstern, who saturated palladium with hydrogen electrolytically, under a pressure of 1000 atmospheres, showed that almost no difference exists in the amount of hydrogen adsorbed by palladium at 1 and 1000 atmospheres. Thus, if at 1 atmosphere 1 gram-atom of palladium adsorbs 0.7 gram-atom of hydrogen, then at 1000 atmospheres the amount of hydrogen adsorbed again did not exceed 0.007 gram-atom of hydrogen per gram-atom of palladium. As we will see further, the part of pressure in the hydrogen adsorption by palladium is considerably greater than follows according to von Samson-Himmelstern.

TABLE 1

Adsorption of hydrogen by palladium

TEMPERATURE	PRESSURE OF HYDROGEN	HYDROGEN ADSORBED BY 119 G. OF PALLADIUM
degrees C.	*atmospheres*	*cc.*
420	80	2980
500	80	1900
420	120	3000

Thus the survey of a small number of opinions on the question of the rôle of pressure in hydrogen adsorption by palladium permits the conclusion that there is no opinion in the literature actually based on experiments involving the application of high pressure. When the question arose, in connection with the work on displacement of noble metals from solutions of their salts by hydrogen under pressure, as to how much hydrogen might be adsorbed by palladium black and the state of this adsorbed hydrogen, we could find no answer in the literature and had to carry out a series of experiments under conditions which were to be used in further experiments on the displacement of palladium from solutions, namely, at intervals of pressure from 1 to 25–50 atmospheres and at temperatures from 15°C. to 150°C.

EXPERIMENTAL PART

After a search for a suitable method for the determination of the adsorptive capacity of palladium for hydrogen under high pressure, a very simple equipment was adopted, which was essentially the ordinary Ipatieff's bomb, but of a diminished size (see figure 1).

The bomb was provided with an accurately controllable valve and with a manometer for accurate measurements up to 0.1 of an atmosphere.

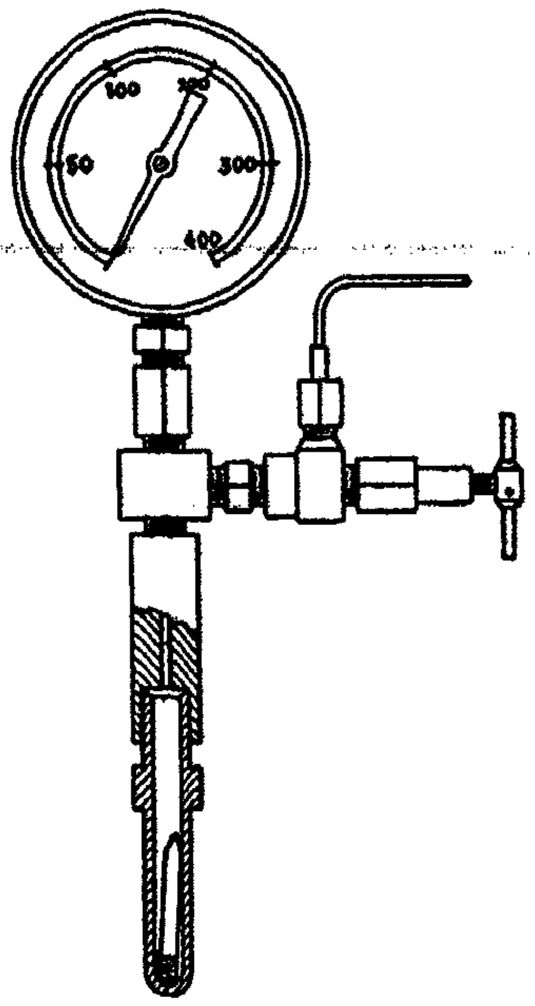

Fig. 1. Ipatieff Bomb

Palladium was placed in the bomb in a sealed ampulla; hydrogen was pumped into the apparatus until a definite pressure was reached, then when the whole system was shown to be tight, the ampulla was broken by a slight shaking of the bomb. The contact of palladium with hydrogen pumped into the bomb resulted in a drop of pressure in the bomb, and in certain cases this drop reached a remarkable magnitude. The difference in readings before and after the experiment gave the total drop in pressure, and from the original volume of gas present in the bomb and the volume of the bomb itself, subtracting the volume of palladium and the glass of the ampulla, the amount of hydrogen adsorbed by the palladium was calculated.

The amount of gas pumped into the bomb by a given pressure was determined as follows: A definite pressure was produced in the bomb, for example, 20 atmospheres, and after testing the tightness for a day, the gas was discharged to a gasometer, a gas buret, or a gas meter. The volume of gas in cubic centimeters thus obtained by direct measurement corresponds to 19 atmospheres; from this the number of cubic centimeters corresponding to 1 atmosphere may be determined. A repeated determination of the number of cubic centimeters corresponding to 1 atmosphere, made at 5, 10, 15, and 20 atmospheres initial pressure, gave nearly an absolute check (the difference amounted to tenth parts of a centimeter), and thus indicated the correctness of readings of the measuring apparatus and the insignificant deviation of hydrogen from the ideal gas law.

Palladium black was prepared from a carefully purified palladium, according to Willstätter (10). The experiments were carried out as follows: After the sealed test tube containing the palladium was placed in the bomb and hydrogen pumped in, the bomb was tested for a while for tightness. In case the bomb was tight, the amount of hydrogen present in the bomb was determined by direct discharge. Afterwards hydrogen was pumped in again up to the former pressure and the tightness tested again.

After these preliminary tests the ampulla was broken by carefully inclining the bomb. Immediately after this, observation of the readings of the indicator on the manometer was started. The indicator moved rapidly at first, and then slowly in the direction of diminished pressure. In most cases the equilibrium was reached after two to three hours, while at low pressures, the equilibrium was established much more slowly.

The amount of gas adsorbed by palladium was determined by two methods: (1) By the difference in readings of pressure before the experiment and after. (2) By the difference between the amount of hydrogen pumped in the bomb and the amount of hydrogen discharged from the bomb after the experiment.

In the determination of the adsorptive capacity of palladium by the second method the question arises as to how fast the hydrogen, adsorbed at increased pressure, is given off at a decreased pressure. It was found that hydrogen, adsorbed by palladium under high pressure, was liberated extremely slowly after the pressure was decreased to 1 atmosphere. This is proved not only by direct observations, but also by a good correspondence in the results obtained by determination of the hydrogen adsorption by the first and second methods.

The following detailed description of one of the experiments is given as an example: 3 g. of palladium black were placed in a sealed ampulla having a volume of 16 cc. and an internal volume of 9.5 cc., and 10 atmospheres of hydrogen were pumped in. The amount of hydrogen taken corresponded to 440 cc. After testing for tightness the ampulla was broken. The drop in pressure with time is shown in table 2. Calculation of the amount of hydrogen adsorbed by 3 g. of palladium at 3.5 atmospheres pressure gives 251 cc. according to the first method and 250 cc. according to the second method. Thus, the results practically coincide. The calculation of hydrogen adsorbed per gram-atom gives the following figures: 1 gram-atom of palladium adsorbs 0.79 gram-atom of hydrogen at 3.5 atmospheres pressure.

In further preliminary experiments according to the method described, various weights of palladium black (from 3 to 10 g.) and also various initial pressures of hydrogen from 7 to 40 atmospheres were applied, in order that the equilibrium hydrogen pressure would be established for such weights in the intervals of from 1 to 30 atmospheres.

TABLE 2

TIME AFTER BREAKING THE AMPULLA	PRESSURE
minutes	*atmospheres*
0	10
5	4.2
15	4.1
30	4.0
45	3.9
60	3.8
90	3.6
120	3.5
150	3.5
48 hours	3.5

Depending upon the weight of palladium and the initial hydrogen pressure, the pressure during the experiments decreased by from 10 to 20 atmospheres. The results of experiments carried out at 150°C. are shown in table 3.

It is seen from table 3 that under pressures above 1 atmosphere the solubility of hydrogen in palladium changes extremely slowly. Increasing the pressure twenty-seven times increases the solubility only 1.34 times. Thus the chief adsorptive capacity of pallladium lies within pressure limits of 1 atmosphere.

Attempts to apply the method used above for the determination of the adsorptive capacity at higher pressures failed, because the ampulla did not stand the high pressures and burst before the beginning of the experiment. Great difficulties were also encountered when working at high temperatures.

Thus the method had to be modified as follows (see figure 2): Instead of one bomb, two bombs with accurately measured volumes were used. Both

TABLE 3

Adsorption of hydrogen by palladium

EXPERIMENT NO.	WEIGHED AMOUNT OF PALLADIUM	INITIAL PRESSURE OF HYDROGEN	HYDROGEN PRESSURE AT THE END OF THE EXPERIMENT (EQUILIBRIUM)	HYDROGEN ADSORBED BY 1 CC. OF PALLADIUM	HYDROGEN ADSORBED BY 1 GRAM-ATOM OF PALLADIUM
	grams	*atmospheres*	*atmospheres*	*cc.*	*gram-atoms*
5	10.2	20	1.0	900	0.74
2	3	8	2.0	930	0.76
1	3	10	3.5	958	0.79
3	3	15	7.0	1000	0.82
4	10	30	8.5	1030	0.82
6	3.5	20	10.0	1055	0.83
7	10	40	14.0	1100	0.93
8	3.15	30	19.0	1160	0.96
9	3.10	40	27.0	1210	1.00

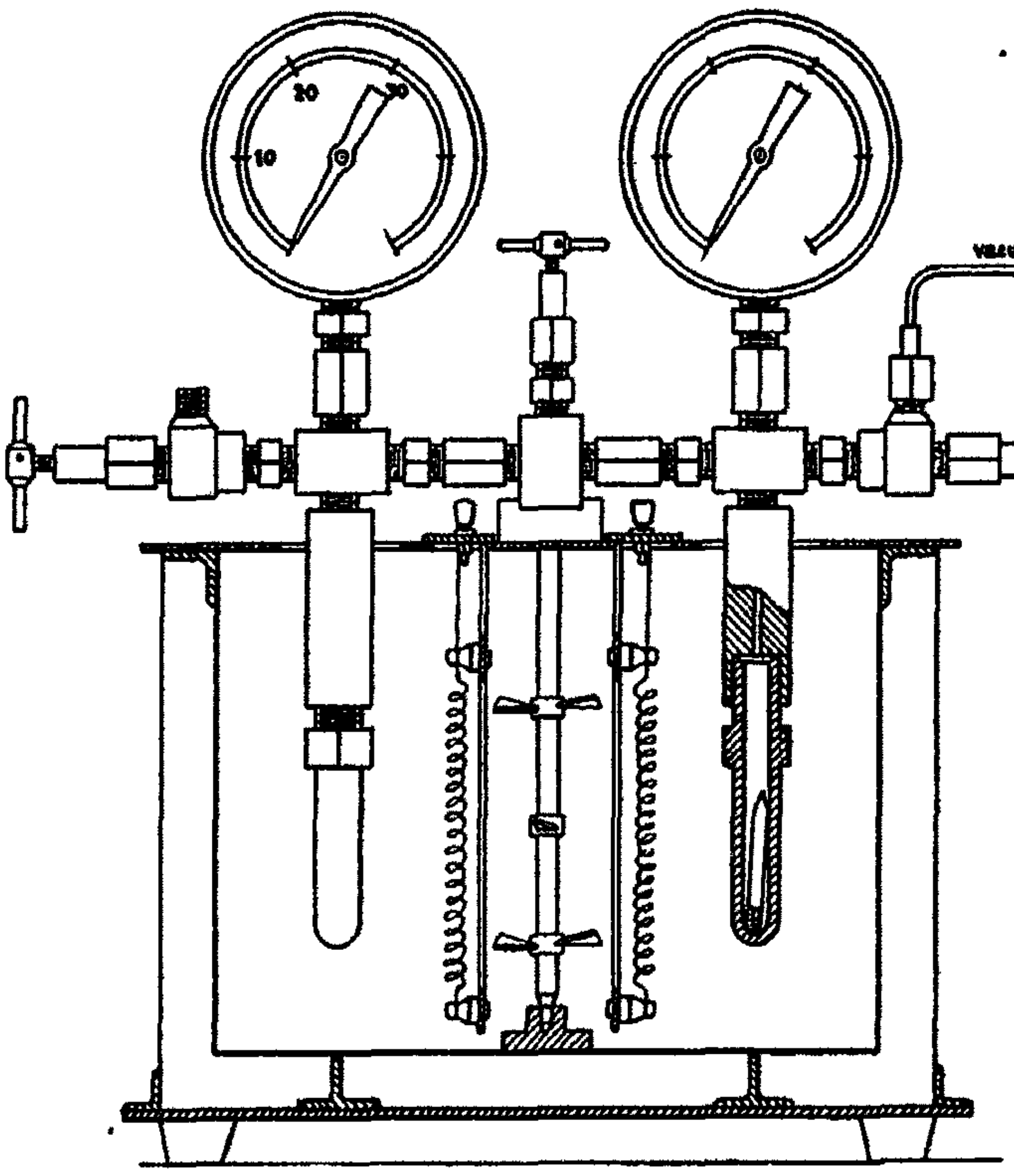

FIG. 2. BOMBS FOR ADSORPTION AT HIGH PRESSURES

bombs were connected with each other, so that by means of a proper turn of the valve, the pressure in one bomb could be controlled as desired, and in the other one a vacuum could be created, or by connecting both bombs, a constant pressure could be maintained in them for any desired time, without loss of gas. For the determination of the adsorptive capacity of palladium, the latter, accurately weighed and purified, was placed in a test tube in one of the bombs; after this the bomb was heated up to the required temperature (100–300°C.), connected with the vacuum pump, and maintained under a pressure of 1–2 mm. for 1 hour. If the bomb held the vacuum, then by a proper turn of the valve it was connected with the other bomb, which contained a definite amount of hydrogen under a definite pressure.

The amount of hydrogen was determined on the basis of the manometer readings, considering the free volumes of both bombs; at increased pressures, proper corrections for the deviation of hydrogen from the gas laws were introduced.

Applying the method described, determinations of the solubility of hydrogen in palladium were carried out at 25, 100, 150, 200, and 300°C. at pressures from 0.5 to 25 atmospheres.

Experiments at 25°C. were carried out in an isothermic room in which the temperature was maintained constant to within 0.1°C. The weight of palladium used was 9.2 g. The pressure of hydrogen in the bomb in which palladium was not present was 20 atmospheres. After testing the whole for tightness and after the vacuum of 1–2 mm. was observed to be constant in the bomb in which palladium was present, by opening the valve the first bomb was connected with the second, containing the palladium. The pressure in the first bomb was established at 10 atmospheres. After 24 hours a constant hydrogen pressure of 0.5 atmospheres was established in the second bomb containing palladium. The calculation shows that the amount of hydrogen adsorbed by 1 cc. of palladium equals 730 cc., or 1 gram-atom of palladium adsorbs 0.6 g. of hydrogen at 0.5 atmosphere.

Experiments at low pressures of hydrogen were carried out with the intention of checking the correctness of the method used and also to check data already existing in the literature for lower pressures. As the readings of the high pressure manometer could not be made accurately enough for the measurements of low pressures, after the pressure dropped in the bomb containing the palladium an ordinary mercury manometer was connected to it by means of a valve. As may be seen from the data and curve (table 4 and figure 3), the results obtained by us at low pressures agree with results obtained by other investigators.

Experiments at 100°C. and 150°C. were carried out in the same bombs in an oil thermostat with accurately regulated temperature. Thanks to the high temperatures the equilibrium became established within a few hours (see tables 5 and 6).

The results of experiments at 25°, 100°, and 150°C. are illustrated in figure 3 in the form of curves.

TABLE 4

Solubility of hydrogen in palladium at 25°C. and various pressures

EXPERIMENT NO.	PRESSURE AT EQUILIBRIUM	AMOUNT OF HYDROGEN ADSORBED BY 1 CC. OF PALLADIUM	HYDROGEN ADSORBED BY 1 GRAM-ATOM OF PALLADIUM
	atmospheres	*cc.*	*gram-atoms*
1	0.5	730	0.60
2	1.0	785	0.65
3	2.0	845	0.70
4	4.5	860	0.71
5	10.0	940	0.77
6	20.0	1050	0.87

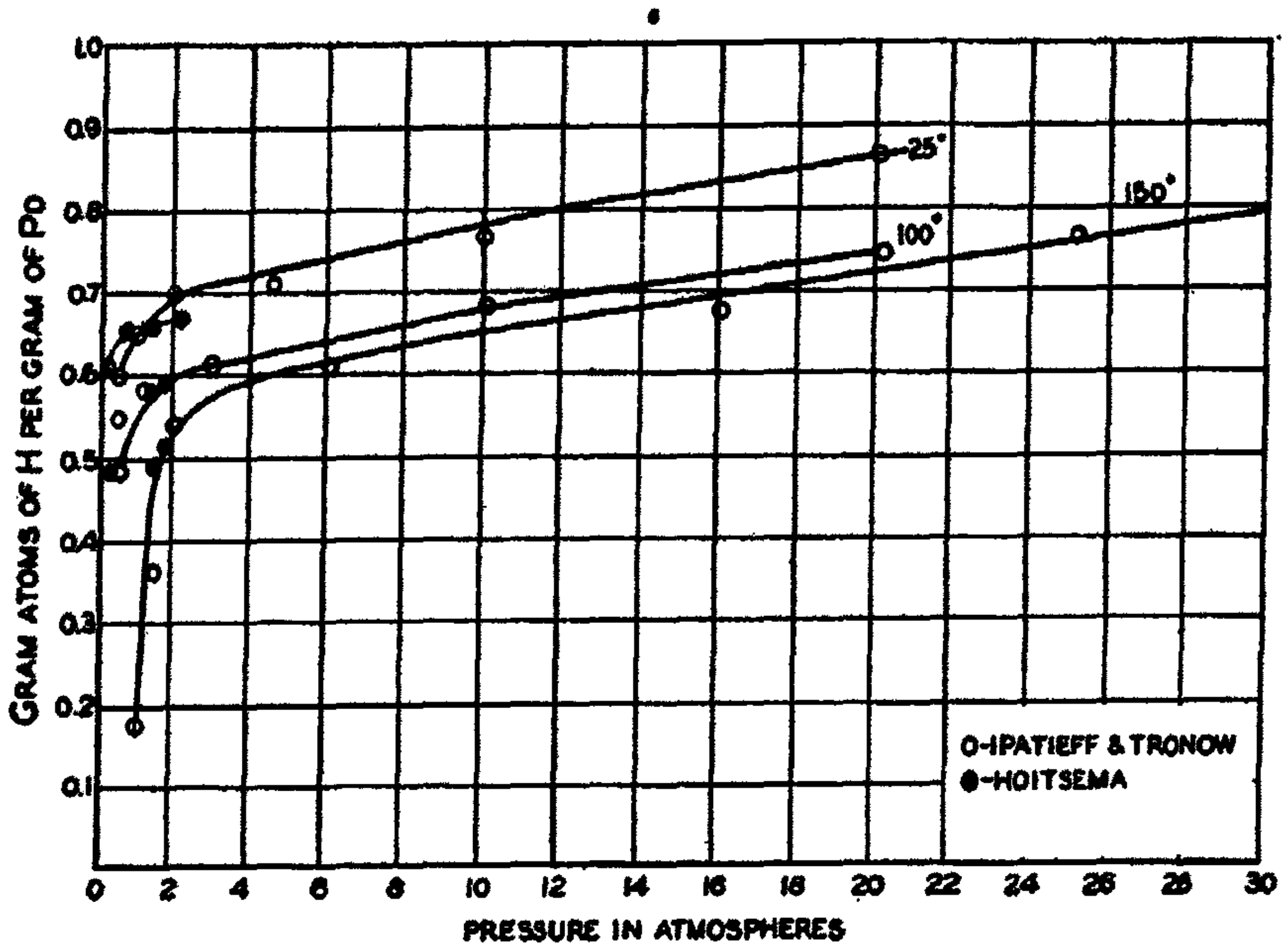

FIG. 3. RESULTS AT 25, 100, AND 150°C.

In these curves solid points correspond to the results of Roseboom, and circles show results obtained by us. As will be seen, the results agree well, also at low pressure. The curves have a peculiar character at each temperature with a sharp break at a pressure of about 1 atmosphere.

If the solubility of hydrogen in palladium is expressed not as a direct function of pressure, but as a function of the logarithm of pressure, then for the curve at 25°C. and 100°C. we obtain a straight line. The curve at 150°C. gives a straight line only beyond 2 atmospheres, because when passing from low pressures to high pressures, too sharp an increase in solubility occurs.

If we follow the curves in the direction of low pressures, obtained on the basis of results of other investigators, then three sections of the curves are observed, as follows: The first section at very low pressures, in which a proportionality between solubility and pressure exists. These sections pass into the following, in which a sharp ascent of the curves is observed. This ascent might be explained either by the formation of a compound between palladium and hydrogen or by the formation of immiscible solid solutions.

TABLE 5

Solubility of hydrogen in palladium at 100°C.

EXPERIMENT NO.	PRESSURE DURING THE EQUILIBRIUM	HYDROGEN ADSORBED PER 1 CC. OF PALLADIUM	HYDROGEN ADSORBED PER 1 GRAM-ATOM OF PALLADIUM
	atmospheres	*cc.*	*gram-atoms*
1	0.5	580	0.48
2	1.2	700	0.58
3	3.0	740	0.61
4	10.0	820	0.68
5	22	906	0.75

TABLE 6

Solubility of hydrogen in palladium at 150°C.

EXPERIMENT NO.	PRESSURE DURING THE EQUILIBRIUM	HYDROGEN ADSORBED PER 1 CC. OF PALLADIUM	HYDROGEN ADSORBED PER 1 GRAM-ATOM OF PALLADIUM
	atmospheres	*cc.*	*gram-atoms*
1	1	210	0.17
2	1.5	435	0.36
3	2	600	0.54
4	6.0	740	0.61
5	16	824	0.68
6	25	940	0.77

Both these sections were studied in detail, and their study did not give a satisfactory explanation of the abnormal solubility of hydrogen in palladium. Neither did study of the third section, which is illustrated at each temperature by a logarithmic curve, give a final explanation of the question that interested us.

But even if a solid palladium hydride exists, then the stability of this compound should decrease with increase of temperature, and at a certain temperature no pressure could force hydrogen to combine with palladium. However, we know that two immiscible solutions may merge into one solution with the increase of temperature. Thus we may draw the conclusion that in this and the other case a temperature will be reached at which the vertical sections of the curves of solubility of hydrogen in palladium disappear.

TABLE 7

Solubility of hydrogen in palladium at 200°C.

HYDROGEN PRESSURE	HYDROGEN ADSORBED PER 1 GRAM-ATOM OF PALLADIUM
atmospheres	*gram-atoms*
1	0.002
3	0.042
4	0.077
5	0.183
6	0.32
7.5	0.40
17.5	0.44
26	0.56

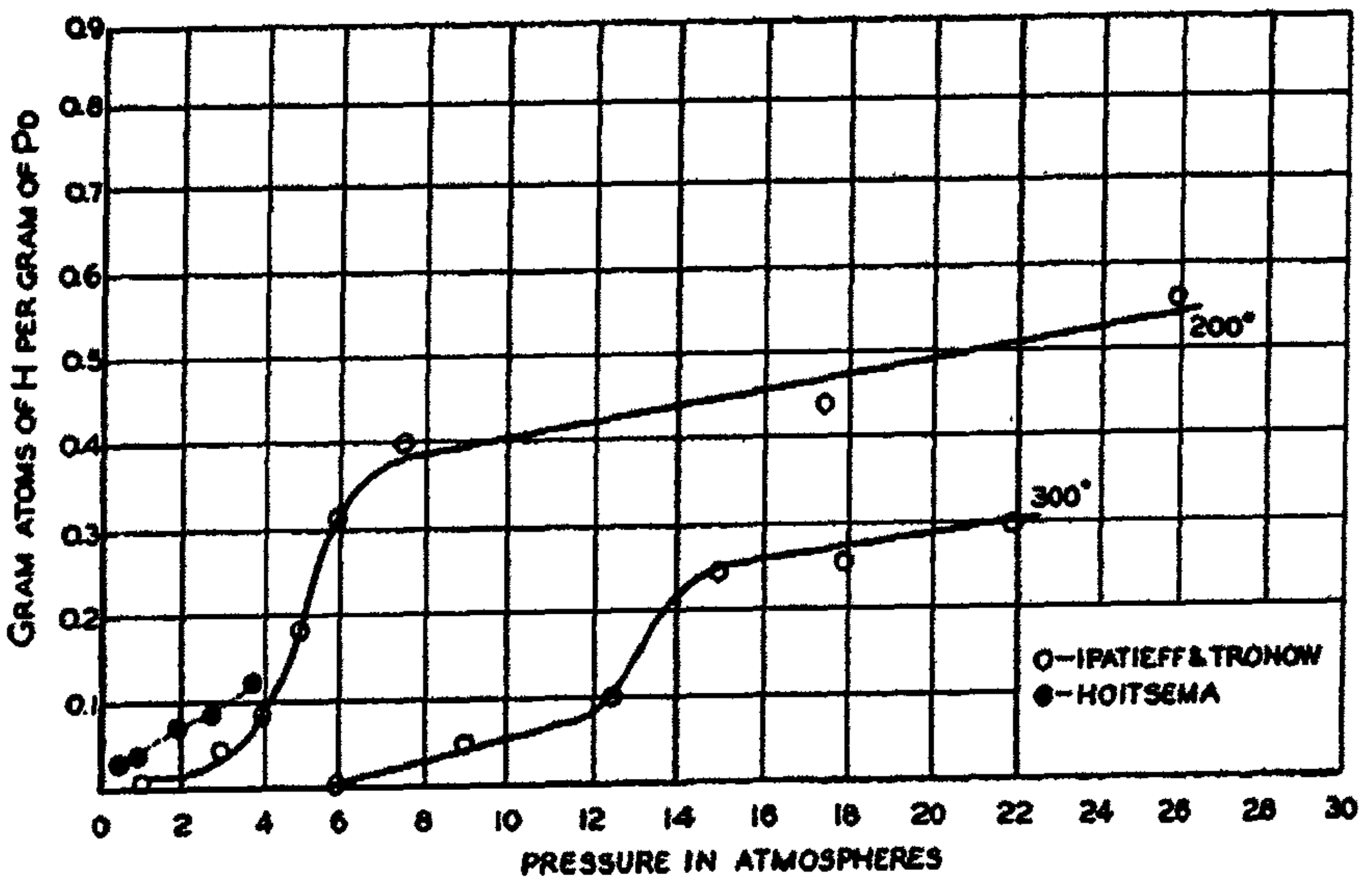

FIG. 4. RESULTS AT 200 AND 300°C.

From the experiments of other writers we know that with increase of temperature the parallel, vertical sections are displaced in the direction of an increased pressure and the length of the sections themselves decreases each time. For example, at 100°C. the break in the curve is observed at a pressure of less than 1 atmosphere, at 150°C. at a pressure of 1 to 2 atmospheres, and at 180°C. at 2 to 3 atmospheres.

At 200°C. Hoitsema did not reach a break because the pressure had to be elevated about 4 atmospheres and he did not have the necessary apparatus at his disposal. We succeeded in carrying out experiments at 200°C. and 300°C., and in this connection it should be noted that at 300°C. experiments were carried out in an air thermostat and therefore the data cannot be as accurate as at lower temperatures; probably this curve must be considered as corresponding to a lower temperature. The character of the curves for 200°C. and 300°C. is exactly the same as at lower temperatures (see table 7 and figure 4).

In all curves obtained at increased temperatures, the breaking point displaces in the direction of higher pressures. The so-called vertical part of the curve deviates more and more from the vertical. Considering further experiments at higher temperatures, it is evident that the curve of the relation between the solubility of hydrogen in palladium and pressure will change to a straight line.

Phenomena observed in the solubility of hydrogen in palladium recall the concept of gases at their critical temperature.

SUMMARY

1. The solubility of hydrogen in palladium black was determined at 15°, 25°, 100°, 150°, 200°, and 300°C. at pressures of from 1 to 27 atmospheres.

2. In agreement with data of Hoitsema, isotherms obtained are characterized by the presence of peculiar parallel parts, distinguishing hydrogen adsorption in palladium from other adsorption isotherms.

3. It is shown that with increase of temperature these parallel parts displace themselves in the direction of high pressures and begin to incline from the vertical; at 300°C. this tends to disappear and the whole curve becomes straightened out.

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THE INSERT GAS EFFECT IN THE RADIOCHEMICAL POLYMERIZATION OF ACETYLENE

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A recent paper on carbon dioxide as a radiochemical catalyst by Rosenblum (6) includes a few experimental results supplied by Lind and Bardwell concerning the rate of polymerization in a mixture of acetylene and carbon dioxide irradiated by alpha rays.

These results are found to agree with two formulas which I have deduced in 1931 and which were tested at first by means of the then available data on the catalytic effect of nitrogen in the same reaction (2).

In the case of the acetylene polymerization, the theory is very simple and may be summarized as follows. When acetylene is irradiated by β rays, every pair of ions produced in the gas causes the condensation of twenty-six molecules (3). This confirms the suggestion made by Rideal (5) that one layer of (n) neutral acetylene molecules clusters around every ion $C_2H_2^-$ or $C_2H_2^+$. The somewhat lower value $M/N = 20$, that has been found (1, 4) when acetylene is irradiated by α particles, may be explained by the increased rate of recombination which is to be anticipated in the case of intense and columnar ionization.

Let τ be the time required for the completion of a 13-molecular cluster, n_0 the initial number of ions per unit volume, n the ionization still remaining at the time τ. The bimolecular law that applies to ionic recombination, $dn/dt = -\alpha n^2$, yields the integrated formula

$$\frac{n}{n_0} = \frac{1}{1 + n_0 \alpha \tau}$$

Now, the time τ required for complete clustering varies as the inverse of the acetylene concentration, while n_0 depends on the total pressure. Let p_1 and p_2 be the partial pressures of acetylene and of inert gas, let i_1 and i_2 be the respective molecular ionizations (i.e., total ionization times stopping power). Putting

$$Q_1 = i_1 p_1 \quad \text{and} \quad Q_2 = i_2 p_2$$

$$Y_1 = \frac{Q_1}{Q_2 + Q_1} \quad \text{and} \quad Y_2 = \frac{Q_2}{Q_1 + Q_2}.$$

we shall write

$$\frac{n}{n_0} = \frac{1}{1 + A/Y_1}$$

The constant A is easily found if the lowering of M/N from 26 (β rays) to 20 (α rays) is ascribed entirely to the fact that a part of the recombination occurs before completion of the clusters. This assumption leads to the relations

$$\frac{M}{N} = 26\frac{n}{n_0} = \frac{26}{1+A} = 20$$

$$A = 0.3$$

since, for pure acetylene, $Y_1 = 1$.

TABLE 1

p_1	p_2	M/N (experimental)	M/N (theoretical)
mm.	*mm.*		
557.5	561.5	16.39	16.0
460.3	550.5	16.38	15.4
436.1	547.8	15.15	15.2
413.5	545.2	13.82	15.1
349.9	538.0	13.02	14.4
304.9	533.0	12.82	13.9
200.3	521.3	10.78	12.1
171.1	517.9	10.78	11.4
133.0	517.6	10.08	10.2
95.9	509.5	8.6	8.6
25.4	501.5	3.1	3.3

Using this value of A and putting $i_1 = 1.4$ and $i_2 = 1.52$, the formula that should apply in the case of the polymerization of acetylene mixed with carbon dioxide can be written as follows

$$\frac{M}{N} = \frac{26}{1 + 0.3\,\frac{1.4p_1 + 1.52p_2}{1.4p_1}}$$

The first three columns of table 1 give p_1, p_2, and the corresponding experimental values of M/N (calculated by Lind and Bardwell for 100 per cent ionic efficiency of the catalyst). The fourth column gives the theoretical values of M/N from the above formula.

There is still another feature of interest about the polymerization of acetylene mixed with carbon dioxide. A small amount of the latter disappears from the gaseous phase, but can be partially recovered on heating the solid. In the experiment of Lind and Bardwell the amount of missing carbon dioxide that was not recovered corresponded to a partial pressure of 63 − 35 = 28 mm. Nitrogen shows a similar behavior, which has been explained (3) by the assumption that a nitrogen ion may be found in the center of a cluster just as well as a positive or negative acetylene ion.

It is easy to calculate the amount of carbon dioxide that should disappear if among the positive ions the percentage of carbon dioxide were equal to $Y_2 = Q_2/(Q_1 + Q_2)$ and if among the negative ions the percentage of CO_2^- were equal to $Z_2 = R_2/(R_1 + R_2)$. In the latter expression, $R_1 = 28.5 \times 10^{-16} p_1$ and $R_2 = 24.4 \times 10^{-16} p_2$, where 28.5×10^{-16} and 24.4×10^{-16} are the squares of the critical radii that may be obtained from the dielectric constants 1.00134 and 1.00098. The small variation of pressure of carbon dioxide is then expressed by the equation

$$-\mathrm{d}p_2 = \frac{p_2}{26}\left(\frac{1.52}{1.40}\ln\frac{1}{Y_2} + \frac{24.4}{28.5}\ln\frac{1}{Z_2}\right)$$

Y_2 and Z_2 being calculated from initial conditions. (For the deduction of the formula see reference 3). Using the numerical values quoted by Rosenblum we find $-\mathrm{d}p_2 = 29.3$ mm.

The agreement with the experimental value of 28 mm. is quite satisfactory. It might have been improved by taking into account the variability of p_2 when calculating Y_2 and Z_2.

SUMMARY

A theory previously developed is shown to be consistent with recently published data concerning the inert gas effect in the radiochemical polymerization of acetylene.

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THE SOLUBILITIES OF CALCIUM HYDROXIDE, CALCIUM IODATE, AND AMMONIUM PERCHLORATE IN DILUTE AMMONIACAL SOLUTIONS

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In a previous paper (6) it has been mentioned that the effect of ammonia upon the adsorption of calcium hydroxide from aqueous medium by silica gel and hydrous oxides is not to be attributed to a complex formation between calcium hydroxide or calcium ions and ammonia. More definite proof of this statement was obtained from solubility measurements of calcium hydroxide in solutions having a concentration up to 2 N in ammonia. Since ammonia appeared to have a marked lowering affect upon the solubility of calcium hydroxide, it was decided to determine the solubilities of calcium iodate and of ammonium perchlorate in the same media.

MATERIALS USED

Calcium oxide. A hot solution of c.p. calcium chloride was treated with a slight excess of a solution of ammonium oxalate. The precipitate was digested, filtered, washed until free from chloride, dried and ignited in an electric furnace.

Calcium iodate, $Ca(IO_3)_2 \cdot 6H_2O$. A hot solution of c.p. calcium chloride was treated with a slight excess of potassium iodate. The precipitate, after washing, was twice recrystallized from conductivity water. Upon drying at 110°C. the monohydrate is formed. On shaking with water or dilute ammonia solution it is quickly transformed into the hexahydrate.

Ammonium perchlorate. A Kahlbaum product recrystallized from water was used.

Ammonia. A solution of carbonate-free ammonia was obtained by distillation of 20 per cent ammonia in the presence of an excess of barium hydroxide. The distillate was kept in a paraffined container and protected from carbon dioxide of the air.

SOLUBILITY DETERMINATION

Solubilities were determined in a thermostat at 25.00°C. ± 0.02°C. Paraffined containers were used throughout this work, although with glass-stoppered Pyrex bottles the same results were found. In all cases equilibrium was attained after fourteen to twenty hours of shaking. The precipitates were then allowed to settle in the thermostat and samples of the supernatant liquids analyzed.

TABLE 1

Solubility of calcium oxide in ammoniacal solutions at 25°C.

CONCENTRATION OF NH_3	DENSITY OF SATURATED SOLUTION AT 25°C.	CONCENTRATION OF CALCIUM HYDROXIDE		
		Moles per liter	CaO per 100 cc. of solution	CaO per 100 solution
N			*grams*	*grams*
0	0.998	0.02128	0.1194	0.1196
0.496	0.994	0.01993	0.1117	0.1124
0.981	0.989	0.01850	0.1038	0.1049
1.475	0.985	0.01700	0.0953	0.0967
1.955	0.982	0.01571	0.0881	0.0896

TABLE 2

Solubility of calcium iodate hexahydrate in ammoniacal solutions at 25°C.

CONCENTRATION OF NH_3	DENSITY OF SATURATED SOLUTION AT 25°C.	CONCENTRATION OF $Ca(IO_3)_2$		
		Moles per liter	$Ca(IO_3)_2$ per 100 cc. of solution	$Ca(IO_3)_2$ per 100 g. of solution
N			*grams*	*grams*
0	0.999	0.00785	0.306	0.306
0.489	0.995	0.00779	0.304	0.305
0.986	0.991	0.00756	0.295	0.298
1.422	0.987	0.00733	0.285	0.289
1.966	0.983	0.00715	0.279	0.284

TABLE 3

Solubility of ammonium perchlorate in ammoniacal solutions at 25°C.

CONCENTRATION OF NH_3	DENSITY OF SATURATED SOLUTION AT 25°C.	CONCENTRATION OF NH_4ClO_4		
		Moles per liter	NH_4ClO_4 per 100 cc. of solution	NH_4ClO_4 per 100 g. of solution
N			*grams*	*grams*
0	1.095	1.830	21.50	19.64
0.443	1.092	1.841	21.63	19.81
0.876	1.089	1.871	21.98	20.16
1.303	1.088	1.915	22.50	20.68
1.731	1.086	1.954	22.96	21.14
2.59	1.084	2.049	24.08	22.23

ANALYSES

In the solubility determinations of calcium hydroxide the calcium and hydroxide content was determined. After removing the excess ammonia, the calcium was precipitated from weakly acid solution as oxalate, and titrated according to standard procedures with potassium permanganate. Other samples were evaporated to dryness, the residues treated with an excess of standard hydrochloric acid, carbon dioxide driven off by boiling, and the acid back-titrated with sodium hydroxide, using methyl red as indicator. The results obtained in both procedures agreed within 0.5 per cent, the oxidimetric method always yielding higher values than the acidimetric one. The solubility of calcium iodate was found from iodometric titrations of the iodate. The ammonium perchlorate content of the solutions was determined by evaporating known volumes to dryness and weighing after drying to constant weight at 110°C. All analyses have been made in duplicate or triplicate. Duplicate analyses with samples from the same bottle agreed within 0.1 per cent in the case of ammonium perchlorate; with samples from different bottles discrepancies of the order of 1 per cent were sometimes noticed. Therefore the solubility data given for ammonium perchlorate do not seem to be as exact as those of the other two substances. The highest values obtained are reported in table 3. In all cases the densities of the supernatant liquids were determined at 25°C. Correspondingly the solubilities found are expressed in moles per liter and in grams per 100 g. and per 100 cc. of solution.

RESULTS

The results are given in tables 1, 2, and 3.

DISCUSSION OF THE RESULTS

1. *Solubilities in water.* Data reported in the literature on the solubility of calcium oxide in water vary from 0.115 to 0.125 g. of CaO per 100 cc. at 25°C. (cf. Seidell, 1928). In a recent paper Johnston and Grove (5) gave results obtained with crystalline calcium hydroxide, which are 7.5 per cent lower than the figure obtained with our product. The difference is probably due to the difference in the nature of the saturating phases used.

The values obtained with our product of calcium oxide were quite reproducible and independent of the amount of solid taken. The solubility of calcium iodate hexahydrate agrees exactly with the figure determined by Hill and Brown (3). Their paper was published after this work had been finished. There is a wide divergency in the literature on the solubility of ammonium perchlorate in water; expressed in grams of NH_4ClO_4 per 100 g. of solution the following data at 25°C. are reported 21.1 (Carlson (1), by interpolation); 19.8 (Mazzuchelli and Rosa (8) by interpolation), 20.02 (Freeth (2), at 25°C.); 19.95 (Willard and Smith (10), at 25°C.). The figure of 19.64 determined in this study is lower than any of the previous values reported, but was found to be consistent with various times of shaking and different amounts of solid body.

2. The effect of ammonia upon the solubilities of the three substances investigated is quite different. The solubility of ammonium perchlorate increases regularly with increasing ammonia concentration in the solution, that of calcium iodate hexahydrate decreases slightly, and that of calcium hydroxide very markedly. Konowalow (7) at 20°C. found 0.1017 g. of calcium oxide per 100 cc. of water, and 0.0610 g. per 100 cc. of solution containing 5.2 per cent of ammonia (about 3 *N*).

From the results given in table 1 it may be concluded that up to a concentration of 2 *N* in ammonia the solubility of calcium oxide decreases linearly.

$$S = 0.1194 - 0.016\,C_{NH_3}$$

S is solubility expressed in grams of CaO per 100 cc. of solution at 25°C.; C_{NH_3} is the normality of ammonia.

The decrease of the solubility of calcium hydroxide in the presence of ammonia cannot be attributed to a common ion effect. For example, in a solution 1 *N* with respect to ammonia and saturated with lime, the concentration of the hydroxyl ions contributed by the ammonia is only 1.3 per cent of that formed by dissociation of the calcium hydroxide. The decrease of the solubility of calcium hydroxide in the presence of ammonia therefore has to be attributed to a specific medium effect. Ammonia at 24.5°C. has a dielectric constant (4) of 14.9 and is therefore expected to decrease markedly the dielectric constant of aqueous solutions, and consequently the dissociation of electrolytes. It should be remembered that the second dissociation of calcium hydroxide is far from being complete; in the presence of ammonia it is still further decreased and consequently the solubility also. Qualitatively speaking, ammonia has here the same effect as organic solvents, such as methanol, ethanol, etc., have on the dielectric constant of aqueous solutions. It is beyond the scope of this paper to investigate in further detail the striking effect of ammonia upon the solubility of calcium oxide.

3. The results obtained confirm the primary object of this investigation, namely, to prove that the effect of ammonia on the adsorption of calcium hydroxide by hydrous oxides and silica gel is not to be attributed to a complex formation. The linear decrease of the solubility with the ammonia concentration and the constant composition of the solid show definitely that up to concentrations of 2 *N* in ammonia no complexes are formed in the solution.

SUMMARY

1. The solubilities of calcium hydroxide, calcium iodate, and ammonium perchlorate at 25°C. in water and in solutions containing concentrations of ammonia up to 2 N have been determined.

2. The solubility S (in grams of CaO per 100 cc. of solution at 25°C.) of calcium hydroxide decreases linearly with increasing ammonia concentration:

$$S = 0.1194 - 0.016\, C_{NH_3}$$

3. No complex compounds between calcium hydroxide or calcium ions and ammonia are formed in the solution at ammonia concentrations smaller than 2 N.

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THE OSMOTIC PROPERTIES OF COLLOIDAL ELECTROLYTES AND THE HAMMARSTEN EFFECT

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I. NATURE OF THE PROBLEM

The vast literature on colloidal electrolytes suffers, more perhaps than most chapters of physical chemistry, from a lack of correlation in the light of exact theories. Thermodynamic concepts such as activity and osmotic coefficients are often misused and, whenever the ideas of the interionic attraction theory are applied, the reasonings are of an entirely qualitative nature. We refer the reader to the book of Pauli and Valkò (8) where most papers on the subject are discussed, briefly reviewed, or at least quoted. Theoretical treatments so far proposed are either too specialized or too vague. On the other hand, the general mathematical treatment of Scatchard and Kirkwood (9), which implicitly includes the case of colloidal electrolytes, is prohibitively complicated for most physically significant cases. The so-called "Hammarsten effect" gave rise to a qualitative theoretical treatment by E. and H. Hammarsten (4, 5) and to a general theory by Linderström-Lang (7). According to Pauli and Valkò (8) a colloidal electrolyte exhibits the Hammarsten effect when its osmotic pressure is smaller than that calculated for a concentration equal to the activity of the simple ions, i.e., when, in the case of an acid for instance,

$$P < a_{\mathrm{H}^+} \cdot RT \tag{1}$$

P is the measured osmotic pressure, a_{H^+} the activity of the hydrogen ion, R, the molar gas constant, and T the absolute temperature.

Let us recall in this connection that activities do not bear a direct relation to the osmotic pressure, except for the fact that there are thermodynamic differential relations between activity and osmotic coefficients. If g_0 is the osmotic coefficient of the solvent and f_s the activity coefficient of the solute, we have

$$N_0 d\left\{(1 - g_0) \log \frac{1}{N_0}\right\} = - N_s d \log f_s \tag{2}$$

N_0 and N_s being the mole fractions of the solvent and the solute, respectively.

In the case of dilute solutions we may define the osmotic coefficient as the ratio between the observed osmotic pressure P and that calculated according to the formula

$$P_e = mRT \tag{3}$$

m being the concentration in moles per liter. We have then

$$P = gP_e = gmRT \tag{4}$$

The abnormality corresponding to the Hammarsten effect is that g defined as above is often of the order of 1 or less when, on account of dissociation, one would expect much higher values.

The low osmotic pressures exhibited by many colloidal electrolytes suggest immediately the presence of ions of very high valence such as those which would result from the association of a large number of simple ions into colloidal micelles. It is then natural to investigate the properties of these systems by means of the theory of electrolytes. We shall assume that all micelles have the same charge $z\epsilon$, ϵ being the elementary quantum of electricity. We thereby overlook the possible presence of micelles of different charges or that of neutral aggregates. The charge and size of the micelle should then be considered as averages. Furthermore, we shall restrict our reasoning to cases where the oppositely charged particles are monovalent single ions. Supposing that in dilute solutions the cohesive forces have no appreciable effect once the micelles are formed, our problem is reduced to a study of the properties of an electrolyte of valence type 1-z according to the Debye-Hückel theory.

II. OSMOTIC PROPERTIES OF AN ELECTROLYTE OF VALENCE TYPE 1-z ACCORDING TO THE DEBYE-HÜCKEL THEORY

The solution contains n free monovalent ions and n/z ions of valence z per cubic centimeter. The charge $z\epsilon$ of the latter is supposed to be concentrated in such a way that the distance of closest approach between the monovalent ions and the ions of valence z is a A.U. The electric fields of both kinds of ions are supposed to possess spherical symmetry.

The Debye-Hückel theory (2, 6) defines as follows the "characteristic length" or radius of the ionic atmosphere $1/\kappa$:

$$\kappa = \sqrt{\frac{4\pi\epsilon^2}{DkT}\cdot\Sigma n_r z_r^2} \tag{5}$$

D is the dielectric constant, k is Boltzmann's constant, n_r the number of ions r per cubic centimeter, and z_r the valence of these ions. Here we have

$$\Sigma n_r z_r^2 = n + \frac{n}{z}\cdot z^2 = n(z + 1) \tag{6}$$

The ionic strength I of the solution is

$$I = \frac{1}{2} \cdot \frac{1000}{N_A} \cdot \Sigma n_r z_r^2 \tag{7}$$

N_A being Avogadro's number.

In our case,

$$I = \frac{1}{2} \cdot \frac{1000}{N_A} \cdot n(z + 1) \tag{8}$$

Calling C the concentration of the monovalent ions in moles per liter, we have

$$I = \frac{1}{2} C(z + 1) \tag{9}$$

It will be sufficiently accurate for our purpose to suppose that the product DT, in the case of water, is constant in the range of temperature in which most experimental data are obtained (0 to 25°C). We have then

$$\kappa = 0.23 \sqrt{C(z + 1)} \cdot 10^8 \tag{10}$$

Defining the osmotic coefficient g of the solvent as the ratio between the actual osmotic pressure and that of an ideal solution of concentration $C\ (1 + \frac{1}{z})$ we have

$$1 - g = 0.26\omega \sqrt{C\left(1 + \frac{1}{z}\right)} \cdot \sigma(\kappa a) \tag{11}$$

with

$$\omega = \left(\frac{\Sigma \nu_r z_r^2}{\nu}\right)^{3/2} \tag{12}$$

ν_r being the number of ions r into which one molecule of salt dissociates, and ν the total number of ions. Here we have

$$\omega = \left(\frac{1 + \frac{1}{z} z^2}{1 + \frac{1}{z}}\right)^{3/2} = z^{3/2} \tag{13}$$

$\sigma(\kappa a)$ is a function of the product κa defined as follows:

$$\sigma(\kappa a) = \frac{3}{(\kappa a)^3} \left[1 + \kappa a - \frac{1}{1 + \kappa a} - 2 \log (1 + \kappa a)\right] \tag{14}$$

In the first paper of Debye and Hückel (2) a table of the numerical values of σ is given.[1]

The ratio between the actual (or observed) osmotic pressure and that of the corresponding ideal undissociated solute is usually given in experimental papers. A definite formula is then assumed for the solute and the concentrations are expressed in moles per liter in terms of that formula. It is more logical to express the concentrations in moles or gram equivalents of the simple ion (Na^+, Cl^-, . . .) per liter (C in our notation).

From equations 11 and 13 we deduce for the osmotic pressure

$$P = gP_{\mathrm{id.}} = P_{\mathrm{id.}}[1 - 0.26z\sqrt{C(1+z)}\cdot\sigma(\kappa a)] \tag{15}$$

The ideal osmotic pressure $P_{\mathrm{id.}}$ is given by

$$P_{\mathrm{id.}} = C\cdot\frac{1+z}{z}\cdot RT \tag{16}$$

Combining formulas 15 and 16 we find

$$P = CRT\cdot\frac{1+z}{z}[1 - 0.26z\sqrt{C(1+z)}\cdot\sigma(\kappa a)] \tag{17}$$

Formulas analogous to formula 15 could of course be obtained for the freezing point lowering, the dew point lowering, etc.

III. INTERPRETATION OF SOME TYPICAL EXPERIMENTAL DATA

On the basis of the foregoing considerations it is possible to attempt an interpretation of experimental data. Two parameters have to be chosen: z and a. It is quite likely that both these parameters change appreciably with concentration. We shall however show that if z is supposed to be constant, it is possible to find a particular value of z such that the corresponding values of a do not change too much with concentration.

Our procedure is the following: The values of g are computed at the various concentrations for which data are available. It is then shown that the lowest value of z compatible with the probable formula of the compound under consideration (2 for Congo red, 4 for sodium thymonucleate) yields too high values of g and that association of ions of one sign has to be assumed. Various successive values of z, all multiples of the lowest (4, 6, ... for Congo red, 8, 12, ...for sodium thymonucleate) are used until a value is found which gives a $\sigma(\kappa a)$ smaller than one at the lowest concentration at which data are available. The values of $\sigma(\kappa a)$ at the various concentrations are then deduced from the calculated values of g, using formula 15 and the corresponding values of κa are obtained from a smooth curve

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[1] The value 0.855 given in the table for $x = 0.1$ is wrong and should be replaced by 0.866.

drawn by means of the values of κa and $\sigma(\kappa a)$ given by Debye and Hückel (2). κ is calculated by means of formula 10 and a is then obtained. There seems to be one particular value of z for which a is sufficiently constant and such that $\sigma(\kappa a)$ is smaller than 1 at the lowest concentration. (Values of $\sigma(\kappa a)$ larger than 1 correspond to negative values of a.)

These calculations are only of an approximate nature for the following reasons:

1. They are based on a rather crude model (spherical symmetry of the electric field due to the charges).
2. The values of κa become larger than 1 already at very low concentrations. The model and calculations of the Debye-Hückel theory of course lose much of their plausibility when the distance of closest approach of two ions of opposite signs becomes larger than the radius of the ionic atmosphere of either one.
3. The higher terms of the Poisson-Boltzmann equation are neglected.

TABLE 1

Osmotic pressure of Congo red (Donnan and Harris)

$T = 290°$

C EQUIVALENT OF Na^+ PER LITER	$P_{\text{calcd.}}$ (calculated)	P (measured)	$P/P_{\text{calcd.}}$
0.17324	1567.0	1363	0.869
0.14404	1304.0	1139	0.873
0.04742	676.0	603	0.890
0.03664	331.8	310	0.934
0.02170	196.0	185.5	0.950
0.01112	100.5	97	0.965

We now give the results obtained in two typical cases: aqueous solutions of Congo red (Donnan and Harris (3)) and of sodium thymonucleate (E. Hammarsten (4)).

A. Congo red

Table 1 gives the concentration C of Congo red in equivalents of sodium ion per liter, the osmotic pressure calculated for an ideal solution of the compound Na_2Co (molecular weight, 696) in millimeters of mercury, the observed osmotic pressure P in millimeters of mercury, the ratio $P/P_{\text{calcd.}}$. The table is taken from Zsigmondy (10). This table shows that the observed osmotic pressure is smaller than that corresponding to an undissociated solute of formula Na_2Co and hence that highly charged micelles are probably present.

For $z = 2, 4$, and 6 the value of $\sigma(\kappa a)$ corresponding to the lowest concentration is larger than 1. We have calculated $\sigma(\kappa a)$, κa, κ and a for $z = 8$, 10, 12, and 14, respectively. The values of a are plotted against the concentration on figure 1 for these four values of z. The curve corresponding to $z = 10$ seems the most satisfactory. The small values of a obtained at the lower concentrations may be due to the neglect of the higher terms. We feel justified however in concluding that the anions of Congo red solutions consist of four or five simple double-charged anions $Co^{=}$.

B. Sodium thymonucleate

The osmotic properties of this salt were carefully studied by E. Hammarsten (4). The results are particularly suitable for an interpretation according to our method: all the data were obtained at extremely low concentrations, the range being 0.33×10^{-3} to 9×10^{-3} moles per liter (empirical formula of the salt, Na_4T), hydrolysis is apparently negligible, and dissociation is probably very high. Our interpretation will be based, as in the case of Congo red, on the assumption that all the sodium ions are unbound. The molecular weight corresponding to the formula Na_4T is 1545. Table 2 gives the concentrations C of the sodium ion in equivalents per liter, the osmotic pressure $P_{\text{calcd.}}$ calculated for an ideal solution of molality $C/4$ in centimeters of water, the observed osmotic pressure P in centimeters of water, the ratio $P/P_{\text{calcd.}}$.

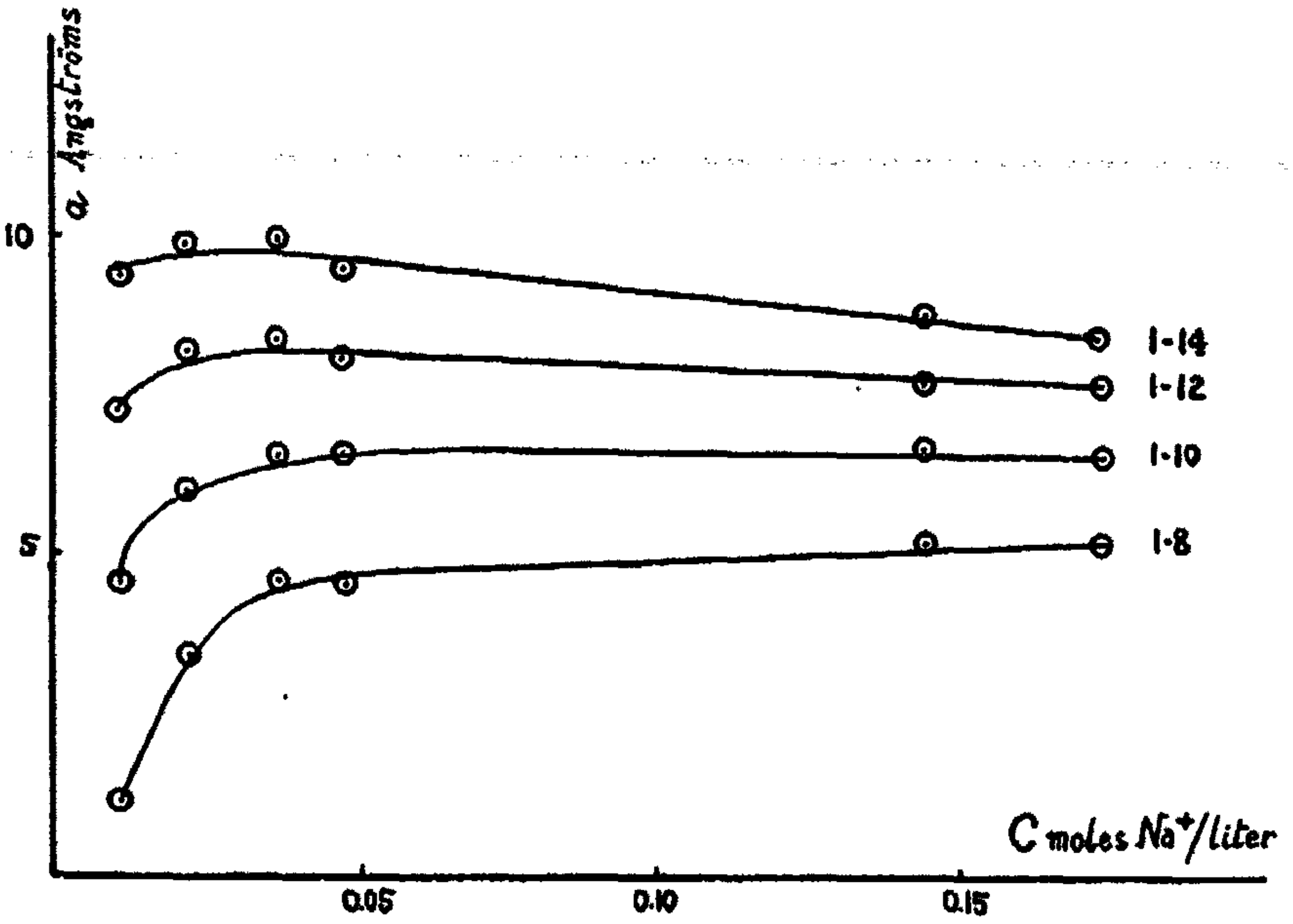

FIG. 1. MEAN IONIC DIAMETERS OF CONGO RED FOR DIFFERENT CHARGES OF THE MICELLES

TABLE 2

Osmotic pressure of aqueous solutions of sodium thymonucleate (E. Hammarsten)
$T = 293°$

C EQUIVALENT OF Na^+ PER LITER	$P_{calcd.}$ (calculated)	P (observed)	$P/P_{calcd.}$
	cm. H_2O	*cm.* H_2O	
1.32	8.1	6.5	0.80
2.52	15.6	13.0	0.83
5.12	31.7	25.0	0.79
6.32	39.2	31.0	0.79
9.68	59.9	47.7	0.79
14.28	88.5	69.0	0.78
17.12	106.1	82.5	0.78
17.20	106.6	83.1	0.78
17.52	108.5	83.5	0.77
16.40	101.4	82.0	0.81
18.08	111.8	85.6	0.77
18.00	111.3	85.8	0.77
18.00	111.3	86.5	0.78
36.00	222.7	173.2	0.78

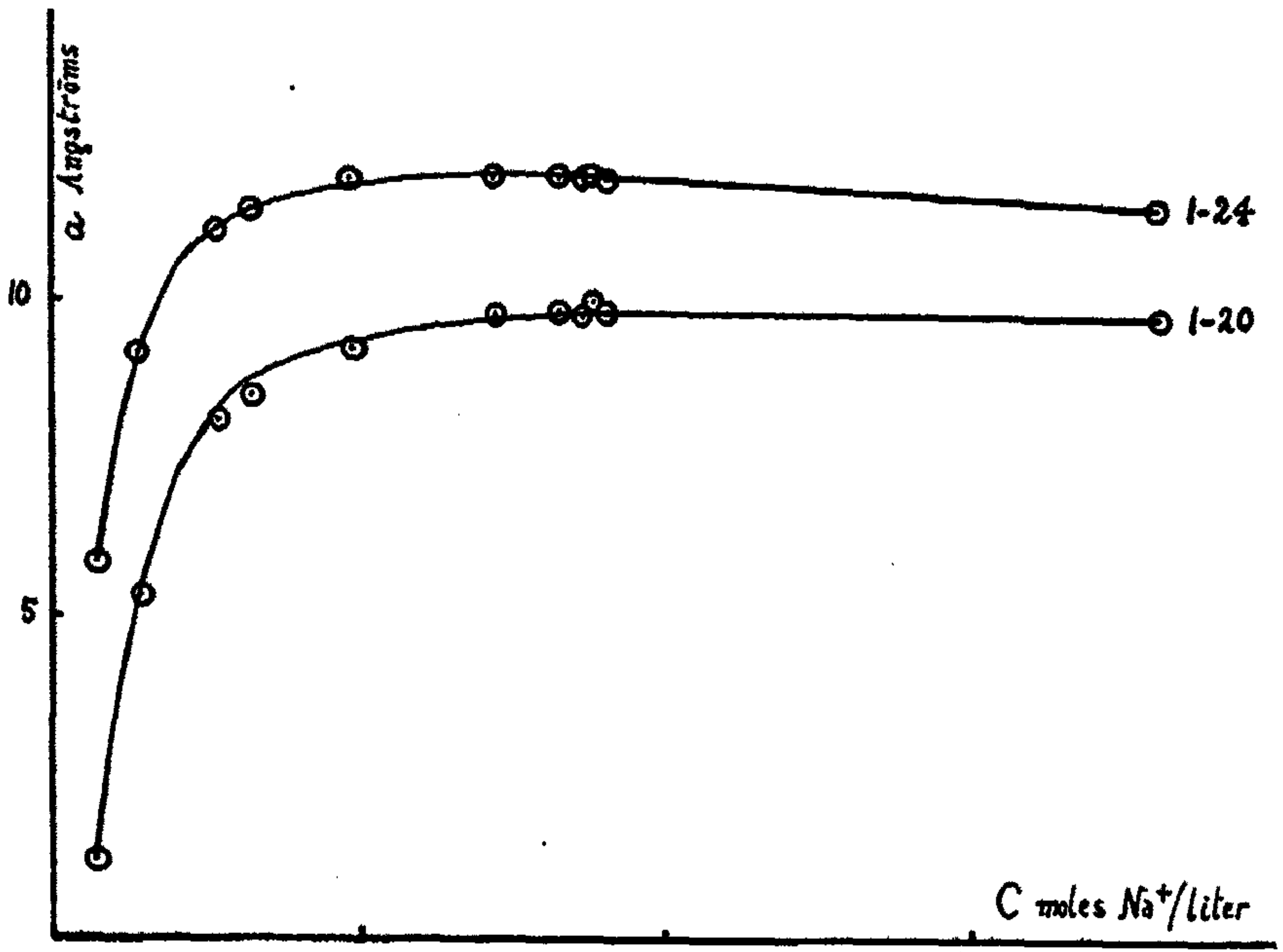

FIG. 2. MEAN IONIC DIAMETERS OF SODIUM THYMONUCLEATE FOR TWO DIFFERENT CHARGES OF THE MICELLES

The ideal osmotic pressure $P_{\text{id.}}$ of a completely dissociated salt of concentration $C\ (1 + \frac{1}{z})$ is given by formula 16.

We have here

$$P_{\text{calcd.}} = \frac{1}{4} CRT \tag{19}$$

and

$$P_{\text{id.}} = 4P_{\text{calcd.}} \frac{1 + z}{z} \tag{20}$$

The other formulas to be used in the calculations are the same as those used in the case of Congo red (formulas 15, 16, 17, 10, etc.).

The ratios $P/P_{\text{calcd.}}$ fluctuate irregularly but are practically constant. We are hence justified in considering that, at all concentrations investigated, the ratio $P/P_{\text{calcd.}}$ is equal to the average value 0.78.

We have to go to as high as $z = 20$ before obtaining a value of $\sigma(\kappa a)$ smaller than 1 at the lowest concentration. We have calculated $\sigma(\kappa a)$, κa, κ and a for $z = 20$ and 24. The values of a are plotted against the concentration on figure 2. The curve for $z = 20$ is a little more satisfactory than that for $z = 24$. The small values of a obtained at the lower concentrations and the large values of κa (which become already larger than 1 at concentrations of the order of 10^{-2} moles per liter) show that we are far from the ideal conditions where the Debye-Hückel theory can be considered as correct. It is however reasonable to conclude that the anions of sodium thymonucleate consist of at least five simple quadruple-charged ions.

We have also made calculations of the same type for the other thymonucleates studied by E. Hammarsten and for certain colloidal dyes studied by Biltz (1). The results were analogous to those presented here.

SUMMARY

It is shown that, if the proper amount of association into micelles is taken into account, the low osmotic pressures observed for several colloidal electrolytes are qualitatively explained by the Debye-Hückel theory. The Hammarsten effect is not an unexpected "abnormality."

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IONIZATION BY ALPHA PARTICLES IN GASEOUS MIXTURES

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INTRODUCTION

Two methods of calculation of the ionization by alpha particles from radon have been developed,—the average path method of Lind (5) and a method due to Mund (6). These calculations have been the subject of former studies (3, 4). Whereas the average path method which involves the molecular ionization is directly applicable to the case of gaseous mixtures, it is necessary to develop a method of computing the relative total ionization for mixtures before the Mund method can be applied to them. Such calculations are presented in this paper. The following symbols are used:

I_T = total ionization (number of ion pairs) produced by an alpha particle from radon in its range (r_0) in air at standard conditions (1.55×10^5 ion pairs).
$\bar{I}$ = average intensity of ionization in air at N.T.P.
I_i = total ionization produced by an alpha particle on gas i in the mixture.
N = number of alpha particles formed in time t.
F' = Mund's correction factor (see references 3 and 4).
r_0 = range of the alpha particle from radon in air at N.T.P. (concordant range = 3.45 cm.; references 3 and 4).
r_i = range of alpha particle in gas i at the temperature of the experiment and at a pressure P equal to the total pressure of the mixture.
x_i = distance traversed by the alpha particle.
y_i = x_i/r_i = reduced distance.
$\bar{x}$ = average path of the alpha particle.
ρ = ratio of r_m to radius of reaction vessel.
E_T = total kinetic energy of the alpha particle.
E_i = energy of the alpha particle at the point x_i.
g_i = total ionization relative to air (N.T.P.) in gas i due to one alpha particle.
P_i = partial pressure of gas i.

P = total pressure of the gaseous mixture.
S_i = stopping power of gas i.
t = temperature of the experiment (°C.).
m = as subscript refers to the gaseous mixture.

I. ENERGY LOSS AND TOTAL IONIZATION PER CENTIMETER PATH

These two quantities are given by

$$dE_i = \frac{2E_T}{3r_i}\left(1 - \frac{x_i}{r_i}\right)^{-1/3} dx_i \tag{1}$$

$$dI_i = \frac{2}{3}\frac{g_i I_T}{r_i}\left(1 - \frac{x_i}{r_i}\right)^{-1/3} dx_i \tag{2}$$

The integrated forms of these equations as a function of the reduced path (x_i/r_i) are:

$$E_i = E_T\left(1 - \frac{x_i}{r_i}\right)^{2/3} = E_T(1 - y_i)^{2/3} \tag{3}$$

$$I_i = g_i I_T\left(1 - \frac{x_i}{r_i}\right)^{2/3} = g_i I_T(1 - y_i)^{2/3} \tag{4}$$

From equations 3 and 4 it is seen that at the same value of the ratio "y" the alpha particle has lost the same fraction of its energy, and similarly the same fraction of its total ionization has been produced when it has travelled the distance x_i in the separate gases. The alpha particle travels in the gaseous mixture, however, and in order to deal with this situation it is convenient to consider the case in the following manner.

II. THE STRIATED GAS

For convenience of discussion a differential element of the gaseous mixture may be thought to consist of i layers of gas which are traversed by the alpha particle in succession. These i layers have together the elementary length dx_m. All of the molecules of type i are separated into the layer dx_i such that

$$\frac{P_i}{P} dx_m = dx_i \tag{5}$$

and

$$\sum \frac{P_i}{P dx_m} = \Sigma dx_i = dx_m \tag{6}$$

This means that each of the individual gases has the pressure P in dx_i. This separation of dx_m into elements dx_i is very helpful in studying the problem. In order to be certain that the treatment below is satisfactory, a graphical study was made for the case of two components. The gas was divided into alternating layers of gas 1 and gas 2, and it became clear that the following discussion adequately represents the case of mixtures.

III. THE RANGE AND STOPPING POWER OF A GAS MIXTURE

The loss of energy by the alpha particle in a gaseous mixture of length dx_m is the sum of the losses (dE_i) due to the ionization of the various gases. This loss is also represented by an expression similar to equation 1 with *the range in the mixture* r_m replacing the range r_i. Using equation 1:

$$\sum \frac{2}{3}\cdot\frac{E_T}{r_i}\left(1-\frac{x_i}{r_i}\right)^{-1/3}\cdot\frac{P_i}{P}\,dx = \frac{2}{3}\frac{E_T}{r_m}\left(1-\frac{x_m}{r_m}\right)^{-1/3}\cdot dx \tag{7}$$

But this comparison must be made at the same point on the reduced path

$$\frac{x_1}{r_1} = \frac{x_2}{r_2} = \ldots \frac{x_i}{r_i} = \frac{x_m}{r_m} \tag{8}$$

Therefore

$$r_m = \frac{P}{\sum \frac{P_i}{r_i}} \tag{9}$$

But

$$r_i = \frac{r_0}{S_i P} \qquad \text{and} \qquad r_m = \frac{r_0}{S_m P} \tag{10}$$

therefore

$$S_m = \frac{\Sigma P_i S_i}{P} \tag{11}$$

The last result is equivalent to the usual statement that stopping powers are additive in the case of mixtures.

IV. THE RELATIVE TOTAL IONIZATION IN A GAS MIXTURE

By a similar argument the total relative ionization (g_m) in a mixture may be defined. The sum of the ionizations (dI_i) in each layer (dx_i) must be equal to the ionization in the layer dx_m. Using equation 2:

$$\sum \frac{2}{3}\frac{g_i I_T}{r_i}\left(1-\frac{x_i}{r_i}\right)^{-1/3}\cdot\frac{P_i}{P}\,dx = \frac{2}{3}\frac{g_m I_T}{r_m}\left(1-\frac{x_i}{r_m}\right)^{-1/3}\cdot dx \tag{12}$$

and with equation 8

$$\sum \frac{g_i P_i}{r} = \frac{g_m P}{r_m} \tag{13}$$

substituting from equation 9 and 10

$$g_m = \frac{\Sigma g_i S_i P_i}{\Sigma P_i S_i} \tag{14}$$

The only case where this result can be checked with experiment is that of air where the proper values of the components are known (5),

$$g_{air} = \frac{1.03 \times 1.064 \times 0.209 + 0.96 \times 0.989 \times 0.791}{1.064 \times 0.209 + 0.989 \times 0.791} = 0.98$$

while the experimental value is 1.0. There is quite a variation in the experimental data from various sources (7), and a better check cannot be expected until more experimental material is at hand.

V. AVERAGE PATH LAW FOR MIXTURES

It has been shown (3, 4) that the average path method of calculating ionization in spherical vessels holds for large values of the ratio ρ. In these former calculations the case of mixtures was not considered. It should be pointed out how the considerations presented here affect the average path method. It is only necessary to consider the gaseous mixture as a fictitious gas with properties g_m and S_m, and the average path law states

$$I_m = 3NI \cdot r \cdot g_m S_m \cdot \frac{P}{760} \cdot \frac{273}{273 + t} \tag{15}$$

where

$$g_m \cdot S_m = \frac{\Sigma g_i S_i P_i}{P} \tag{16}$$

VI. TOTAL RELATIVE IONIZATION IN HYDROGEN-BROMINE MIXTURES

It should be of interest to make a sample calculation of the relative total ionization (g_m) for gaseous mixtures of hydrogen and bromine as a function of their partial pressures. The stopping powers of hydrogen and bromine are 0.24 and 2.80, respectively. The latter value was obtained from Glasson's rule (2). Their relative total ionizations[1] are, respectively, 1.00 and 1.35. Then

$$g_m = \frac{g_1 S_1 P_1 + g_2 S_2 P_2}{S_1 P_1 + S_2 P_2} = \frac{0.24 P_1 + 3.78 P_2}{0.24 P_1 + 2.80 P_2} \tag{17}$$

$$S_m = \frac{S_1 P_1 + S_2 P_2}{P} = \frac{0.24 P_1 + 2.80 P_2}{P} \tag{18}$$

and

$$r_m = \frac{r_0}{S_m} \cdot \frac{760}{P} \cdot \frac{273 + t}{273} \tag{19}$$

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[1] The value for bromine was calculated by the method of R. D. Kleeman (Proc. Roy. Soc. London 79A, 220 (1907)).

These equations have been applied to a set of hydrogen and bromine mixtures, where $P = 760$ mm., $t = 100$°C., and the radius of the spherical vessel is 2.153 cm. The values of g_m for these mixtures are shown in figure 1 as a function of composition. The respective total ionizations in these mixtures are shown in figure 2, where the individual ionizations falling on the hydrogen and the bromine are also shown. The method of calcula-

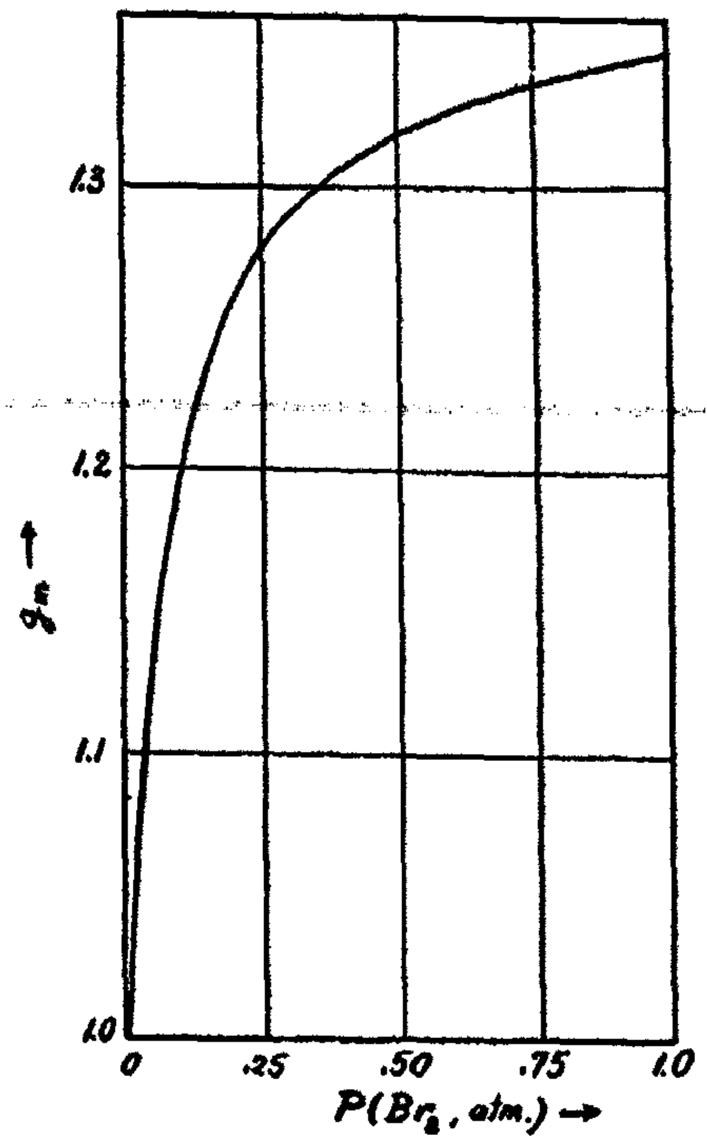

Fig. 1

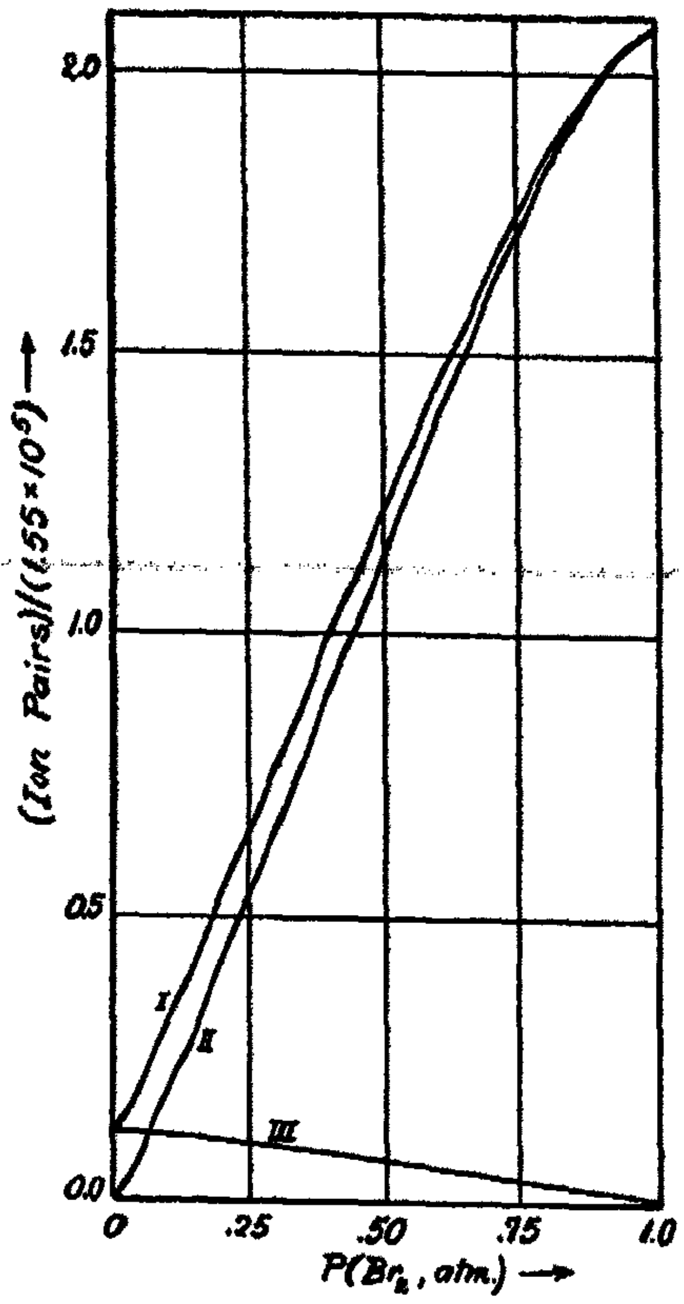

Fig. 2

Fig. 1. Total Relative Ionization of Hydrogen-Bromine Mixtures as a Function of the Partial Pressure of Bromine

Fig. 2. Number of Ion Pairs Per Alpha Particle as a Function of the Partial Pressure of Bromine

The total pressure is 1 atmosphere, the temperature is 100°C., and the radius of the spherical vessel is 2.153 cm.

I, The total number in the mixture; II, the partial ionization on bromine; III, the partial ionization on hydrogen.

tion is indicated in section VII. The individual ionizations are proportional to their respective $(gSP)_i$ products, as follows from equation 2:

$$\frac{I_1}{I_2} = \frac{g_1S_1P_1}{g_2S_2P_2} \qquad \text{or} \qquad I_1 = \frac{g_1S_1P_1}{\Sigma g_iS_iP_i}\cdot I_m \tag{20}$$

VII. CALCULATION OF TOTAL IONIZATION IN HYDROGEN–BROMINE MIXTURES

The use of the foregoing results can best be illustrated by the calculation of a pertinent case. Consider a gaseous mixture of hydrogen and bromine at a total pressure of one atmosphere and partial pressures $P(H_2) = 684$ mm. and $P(Br_2) = 76$ mm. at 25°C. in a vessel of 2.153 cm. radius:

(a) The stopping power of the mixture (equation 11) is 0.50.

(b) The concordant range in the mixture is

$$r_m = \frac{3.45}{0.50} \times \frac{760}{760} \times \frac{298}{273} = 7.53 \text{ cm.} \tag{21}$$

(c) The value of $\rho = 3.5$ and $F' = 0.342$.

(d) g_m for the mixture is 1.20 (by equation 14).

(e) The total ionization in the mixture is

$$\begin{aligned} I_m &= N \times g_m \times I_T \times F' \\ &= N \times 1.20 \times 1.55 \times 10^5 \times 0.342 \\ &= N \times 0.636 \times 10^5 \end{aligned} \tag{22}$$

The average path law of Lind yields in this case the following result: $\bar{x} = 0.5833 \times 2.153 = 1.25$ cm.; $\bar{I} = 2.86 \times 10^4$ ion pair cm.$^{-1}$ (3, 4). Equation 15 yields

$$\begin{aligned} I_m &= N \times 3 \times 2.86 \times 10^4 \times 1.25 \times 1.20 \times 0.50 \times 0.984 \\ &= N \times 0.634 \times 10^5 \end{aligned} \tag{23}$$

VIII. TOTAL RELATIVE IONIZATION OF COMPOUNDS

For the purpose of calculation of g_m a compound might be considered as a mixture of its component atoms, ignoring the effect of bonding forces. This case has been adequately treated by Kleeman (footnote 1 and reference 1).

SUMMARY

The calculation for the ionization by alpha particles from radon in spherical vessels containing gaseous mixtures has been studied. The range of an alpha particle in the mixture is $r_m = P/\Sigma(P/r)_i$. The stopping power of the gas mixture is $S_m = \Sigma\,(PS)_i/P$. The total ionization relative to air (N.T.P.) is $g_m = \Sigma\,(gSP)_i/\Sigma\,(SP)_i$. The molecular ionization of the gas

mixture is given by $(gS)_m = (1/P)\,\Sigma\,(gSP)_i$. There are i components in the mixture and P is its total pressure.

It is a pleasure to thank Dr. S. C. Lind and Dr. G. B. Heisig for discussing these questions with us.

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STUDIES ON SILICIC ACID GELS. IV

The Effect of the Hydrogen-Ion Concentration upon the Time of Set[1]

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INTRODUCTION

In a recent study in this laboratory, Hurd and Miller (5) have obtained data upon the effect of temperature on the time of set of gels of hydrated silica or silicic acid gels, as they are commonly called. The data were later examined and were found to indicate the possibility of a relation between the hydrogen-ion concentration and time of set. A further study of this possible relation has been made. The results are incorporated in this article.[2]

HISTORICAL

Numerous investigators have studied the effects of various factors upon the time of set of silicic acid gels, among such factors being the concentration of silica, the concentration of acid, salts, or foreign materials, and the temperature. The effect of the hydrogen-ion concentration has not been thoroughly studied. The effect of the acid was noted by Holmes (2) and later by Hurd and Letteron (4). The hydrogen ion specifically was noted by Glixelli and Wiertelak (1) and by Prasad and Hattiangadi (8). Ray and Ganguli (10) determined the optimum limits of pH within which setting occurred in their experiments.

To cite merely three opinions[3] concerning the setting of these gels of silicic acid, Holmes has stated that the acid molecules have a dehydrating effect upon the silicic acid, while Laskin (7) believes that certain ions in solution possess a dehydrating effect. Kröger (6) believes that the sodium ions in solution have a peptizing effect upon the silicic acid. However, from the results to be cited in this article, it seems almost certain that the peptizing action in alkaline mixtures containing silicic acid is due to the hydroxyl ion.

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[1] This research was supported by a Grant-in-Aid of the National Research Council.

[2] A report was made on the first half of these results before the Colloid Division of the American Chemical Society at the meeting held in Washington, March, 1933.

[3] In the interests of economy, the bibliography has been practically omitted from this article and the article itself greatly condensed.

EXPERIMENTAL

As previously stated, Hurd and Miller have made a study of the effect of temperature upon the time of set of various mixtures of solutions of sodium silicate and acetic acid. Five commercial brands of silicate were used, known by their maker, the Philadelphia Quartz Company, as brands "S," "N," "K," "U," and "C."[4] Six different mixtures of each brand with acetic acid were used. Every mixture used contained the same concentration of silica, namely, 0.645 gram-mole silica per liter. From these data the time

TABLE 1

Time of set of sodium silicate–acetic acid mixtures at 25°C. in minutes

MIXTURE	BRAND				
	"S"	"N"	"K"	"U"	"C"
	Soda-silica ratio				
	1:3.99	1:3.33	1:2.94	1:2.52	1:2.06
	Time of set				
0	100.0	114.0	81.3	117.5	42.2
1	153.2	158.5	120.2	158.5	79.4
2	206.6	219.0	164.0	205.6	117.5
3	257.0	266.0	209.0	247.2	149.7
4	298.6	298.6	248.4	283.8	182.0
5	355.0	342.8	282.0	320.0	221.4

TABLE 2

Excess acetic acid in the mixtures whose time of set is tabulated in table 1

MIXTURE	BRAND				
	"S"	"N"	"K"	"U"	"C"
	Soda-silica ratio				
	1:3.99	1:3.33	1:2.94	1:2.52	1:2.06
	Excess acetic acid				
0	0.177	0.237	0.185	0.242	0.127
1	0.302	0.362	0.310	0.367	0.252
2	0.427	0.487	0.435	0.492	0.377
3	0.522	0.612	0.560	0.617	0.502
4	0.677	0.737	0.685	0.742	0.627
5	0.802	0.862	0.810	0.869	0.752

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[4] The writers wish to thank the Philadelphia Quartz Company for their kindness in supplying the silicates used in this and other research.

of set of each mixture at 25°C. was determined, the figures being given below in table 1. Also from the concentrations may be obtained what we call "excess acetic acid," namely, the difference in equivalents of the total acetic acid and the sodium of the sodium silicate, expressed as sodium hydroxide. It is thus the excess of acetic acid over that equivalent to the total sodium in the sodium silicate. These data are given in table 2.

The time of set for each mixture of table 1 has been plotted as ordinate against the concentration of excess acetic acid of table 2 as abscissa. The curve is shown in figure 1. These isothermal curves show, apparently, a linear relation between time of set and concentration of excess acid. Extrapolation to the left indicates a minimum time of set with slightly less than enough acetic acid to be equivalent to the sodium of the sodium silicate. It is well known that minimum time of set occurs in mixtures which are slightly alkaline.

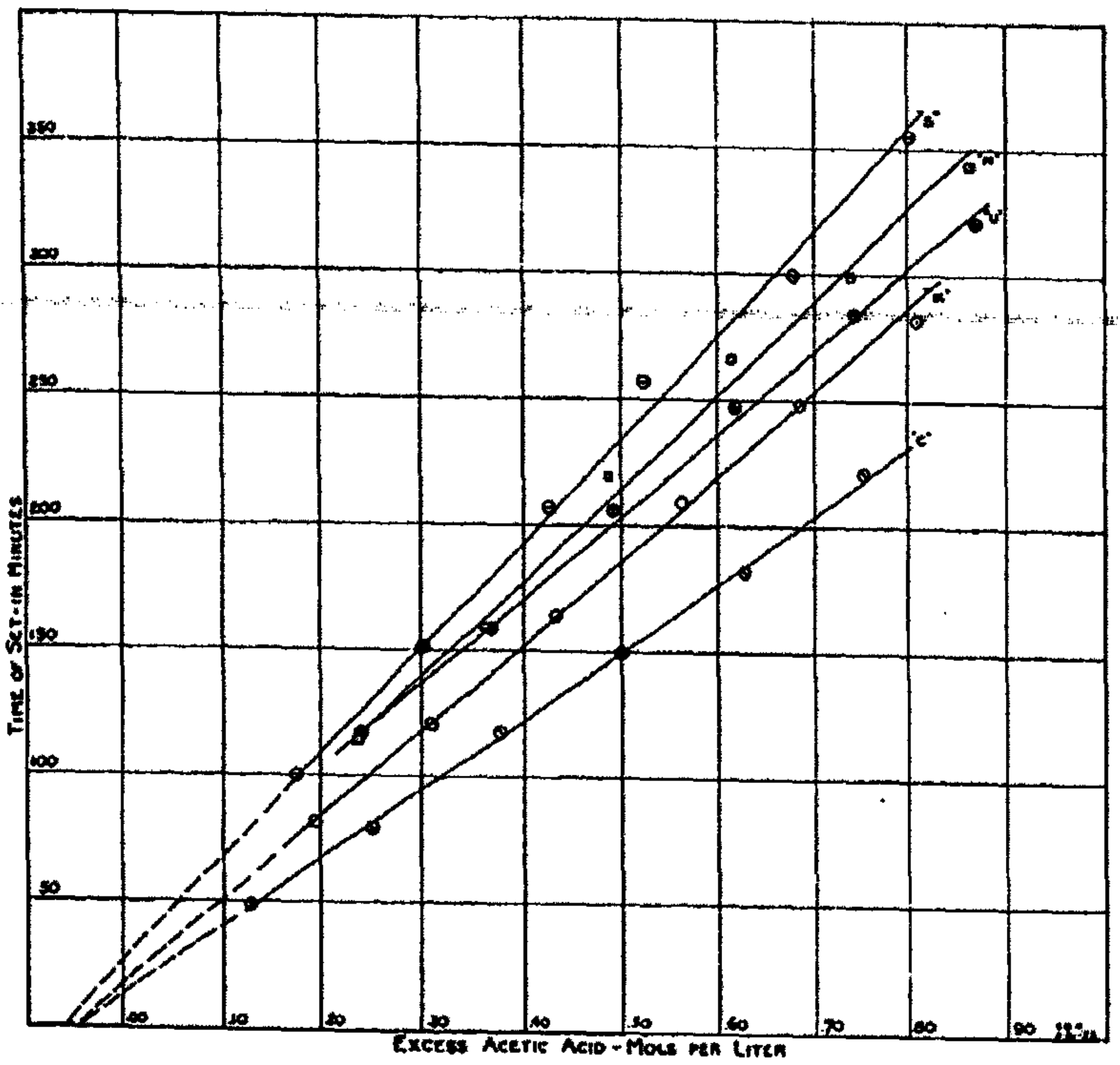

Fig. 1. Time of Set in Relation to Concentration of Excess Acetic Acid

This linear relation between time of set and concentration of excess acetic acid might well be taken to point toward a linear relation between the time of set and the hydrogen-ion concentration since, in solutions containing an excess of weak acid, acetic acid, in the presence of a fixed concentration of sodium acetate, the hydrogen-ion concentration will be very nearly proportional to the acetic acid concentration.

To test the hypothesis that a linear relation exists between the time of set and the hydrogen-ion concentration, the following series of experiments were made. A series of mixtures of solutions of "E" brand sodium silicate and acetic acid were made. This silicate is particularly clear and suitable. It was used in the form of a solution, 1.23 normal with respect to sodium hydroxide. All water used in any of these solutions was distilled water which had been freshly boiled.

The mixtures were made by placing the solution of sodium silicate and the acetic acid solution in small beakers in a 23.5°C. thermostat. The amount of sodium silicate was fixed, 50 cc. of sodium silicate 1.23 normal with respect to sodium hydroxide. The relative amounts of acetic acid and water were varied, although the total volume was fixed. The silicate was poured quickly into the acid, the result mixed thoroughly by pouring back and forth several times and then divided into two 80-cc. portions. One portion was poured into a 100-cc. beaker in a 25°C. thermostat, where the time of set was determined by the tilted rod method. The other half was placed in an electrically insulated 25°C. thermostat where the pH was determined by the quinhydrone method, using a platinum wire electrode and solid quinhydrone. The whole technique for this method using quinhydrone had been carefully tested in this laboratory by an elaborate series of tests and found to be reliable.

Particular attention should be called here to the care used to keep the mixture steadily at 25°C. We have not found this mentioned elsewhere. In all cases, the rise in temperature upon mixing, due to the neutralization of sodium hydroxide by acetic acid, was measured previously. In the case just mentioned it was 1.5°C. The thermostat in which the two solutions were kept before mixing was then adjusted to that interval below 25°C., in this case, to 23.5°C.

The results of this series of experiments are given in table 3. All concentrations are in gram-moles per liter.

The relation between time of set and concentration of hydrogen ions and the logarithmic relation, namely, between logarithm of time of set and pH are shown in figure 2. Between concentrations of hydrogen ion of 1.0×10^{-6} and 7.24×10^{-6} the relation between time of set and concentration of hydrogen ion is seen to be very nearly linear. As the concentration of hydrogen ions increases, however, the time of set is seen to be slightly less than would be indicated for a linear relation. Table 3 shows, however, a large excess of acetic acid required to produce increase in the hydrogen-ion concentration.

In order to try a mixture where the hydrogen-ion concentration could be greatly increased without any appreciable increase in the amount of excess acid, the same type of experiment was carried out using hydrochloric instead of acetic acid. Owing to the rapid change in hydrogen-ion concentration with excess hydrochloric acid, mixtures were made containing

TABLE 3

Time of set and pH data for mixtures of sodium silicate and acetic acid at 25°C.

TOTAL CH_3COOH	EXCESS CH_3COOH	pH	CONCENTRATION OF H^+	TIME OF SET	LOG TIME OF SET
				minutes	
1.363	0.975	4.14	7.24×10^{-5}	331.0	2.520
1.240	0.852	4.21	6.17×10^{-5}	299.0	2.476
1.053	0.665	4.32	4.79×10^{-5}	247.0	2.393
0.942	0.554	4.42	3.80×10^{-5}	213.0	2.328
0.855	0.467	4.48	3.31×10^{-5}	185.0	2.267
0.744	0.356	4.61	2.45×10^{-5}	143.5	2.157
0.683	0.294	4.69	2.04×10^{-5}	114.0	2.057
0.620	0.232	4.78	1.66×10^{-5}	97.0	1.987
0.583	0.195	4.87	1.35×10^{-5}	86.0	1.935
0.558	0.170	4.92	1.20×10^{-5}	74.0	1.869
0.496	0.108	5.09	0.813×10^{-5}	48.5	1.686
0.459	0.071	5.29	0.513×10^{-5}	33.5	1.525
0.434	0.046	5.46	0.347×10^{-5}	21.5	1.332
0.422	0.034	5.60	0.251×10^{-5}	16.0	1.204
0.409	0.021	5.75	0.178×10^{-5}	11.2	1.049
0.397	0.009	6.00	0.100×10^{-5}	6.2	0.792

TABLE 4

Time of set and pH data for mixtures of sodium silicate and hydrochloric acid at 25°C.

pH	CONCENTRATION OF H^+	TIME OF SET	LOG TIME OF SET
		minutes	
4.21	6.17×10^{-5}	75.0	1.875
4.29	5.13×10^{-5}	55.0	1.740
4.32	4.79×10^{-5}	51.0	1.708
4.35	4.47×10^{-5}	49.0	1.690
4.45	3.55×10^{-5}	40.0	1.602
4.49	3.24×10^{-5}	34.5	1.538
4.63	2.34×10^{-5}	29.5	1.470
4.82	1.51×10^{-5}	21.0	1.322
4.90	1.26×10^{-5}	16.5	1.217
5.03	0.933×10^{-5}	14.0	1.146
5.06	0.871×10^{-5}	10.9	1.037
5.44	0.363×10^{-5}	5.5	0.740

as nearly as possible the same amount of acid with a fixed amount of silicate solutions. Checks, of course, could not be made. The excess of hydrochloric acid could not be measured, being less than 0.001. The data are given in table 4 and plotted on figure 2. The linear relation between the time of set and the hydrogen-ion concentration is evident. In fairness, it should be pointed out here that the variation in hydrogen-ion concentration is only about twentyfold, from pH = 4.21 to 5.44. A study over a wider range is contemplated in the future.

The range with acetic acid mixtures from pH = 4.14 to pH = 6.00 represented the limits for the experiment. Higher hydrogen-ion concentrations could not be reached because of curdling of the mixture. Lower hydrogen-ion concentrations could not be reached because the mixture set too rapidly to allow accurate measurements to be made.

To investigate further the effect of the hydrogen-ion concentration upon time of set, the following series of experiments was devised. A series of mixtures was made in which the amount of sodium silicate ("E" brand) was fixed. The amount of acetic acid was varied, but with it was added sufficient sodium acetate so that the pH of the final mixture remained fixed. The proper quantities were determined by preliminary experiments. The proper quantities of solutions were thermostated at 23.5°C. and mixed as before. The time of set was determined with half of the mixture and the pH with the other half, each at 25°C. The solutions used were sodium silicate 1.23 normal, acetic acid 2.007 normal, and sodium acetate 2.225 molar. In all, six different series of runs were made, each at a fixed pH. The data are tabulated in table 5 and in figure 3 the time of set for each sample is plotted against the concentration of excess acetic acid.

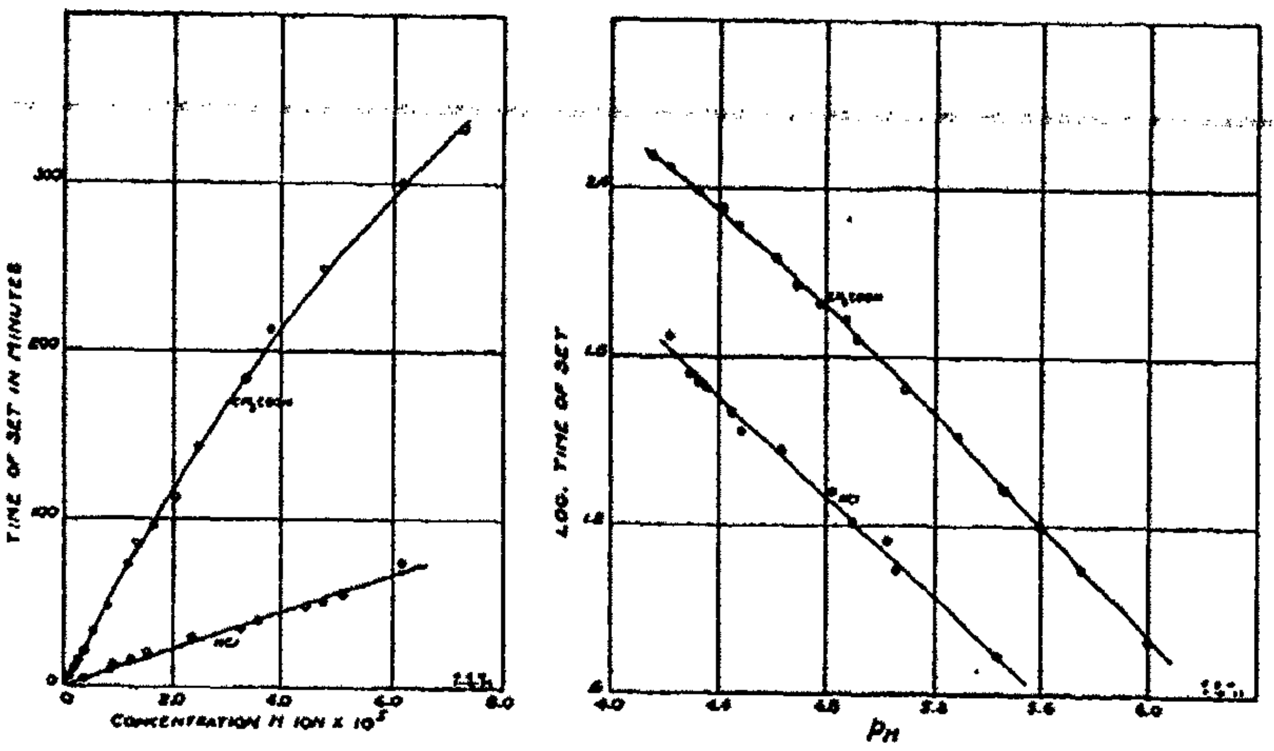

FIG. 2. RELATION BETWEEN TIME OF SET AND HYDROGEN-ION CONCENTRATION

The curves of figure 3 show that while in Series I with pH = 4.22, the time of set remains practically constant as the excess acetic acid and sodium acetate are increased, the effect of these substances is greater and greater

TABLE 5

Time of set of six series of mixtures each with a constant pH

CONCENTRATION OF EXCESS CH_3COONa	TOTAL Na	CONCENTRATION OF TOTAL CH_3COOH	CONCENTRATION OF EXCESS CH_3COOH	TIME OF SET
Series I. pH = 4.22; $H^+ = 6.03 \times 10^{-5}$				
				minutes
0.000	0.385	1.253	0.868	296.
0.047	0.432	1.319	0.934	295.
0.074	0.459	1.380	0.995	296.
0.100	0.485	1.442	1.057	296.5
0.122	0.507	1.506	1.121	297.
Series II. pH = 4.48; $H^+ = 3.31 \times 10^{-5}$				
0.000	0.385	0.880	0.495	189.
0.061	0.446	0.943	0.558	190.
0.097	0.482	1.007	0.622	190.
0.136	0.521	1.068	0.683	193.
0.175	0.560	1.131	0.746	199.5
Series III. pH = 4.79; $H^+ = 1.62 \times 10^{-5}$				
0.000	0.385	0.628	0.243	101.
0.101	0.486	0.691	0.306	103.
0.213	0.598	0.754	0.369	106.
0.309	0.694	0.816	0.431	109.5
0.394	0.779	0.879	0.494	116.
Series IV. pH = 4.92; $H^+ = 1.20 \times 10^{-5}$				
0.000	0.385	0.565	0.180	78.
0.153	0.538	0.628	0.243	82.
0.288	0.673	0.691	0.306	87.
0.404	0.789	0.754	0.369	91.
0.515	0.900	0.816	0.431	97.
Series V. pH = 5.09; $H^+ = 8.13 \times 10^{-6}$				
0.000	0.385	0.502	0.117	53.
0.188	0.573	0.565	0.180	58.
0.369	0.754	0.628	0.243	64.
0.543	0.928	0.691	0.306	71.
0.713	1.098	0.754	0.369	77.5
Series VI. pH = 5.44; $H^+ = 3.63 \times 10^{-6}$				
0.000	0.385	0.439	0.054	24.5
0.390	0.775	0.502	0.117	31.2
0.700	1.085	0.565	0.180	39.2
1.030	1.415	0.628	0.243	45.0

All concentrations are in gram-moles per liter. Constant are NaOH, 0.385, and SiO_2, 0.645.

the higher the pH. It should also be noticed that in series I the first sample, which contains no excess sodium acetate, already contains excess acetic acid, 0.868 gram-mole per liter. In series VI, on the other hand, the first sample, which contains no excess sodium acetate, contains only 0.054 gram-mole per liter excess acetic acid. The shape of the family of curves is suggestive.

The curves and data show clearly, however, that the time of set is increased by the presence of excess acetic acid and excess sodium acetate, and is not alone a function of the hydrogen-ion concentration. We have not been able to distinguish between the effect of the sodium acetate and that of the acetic acid.

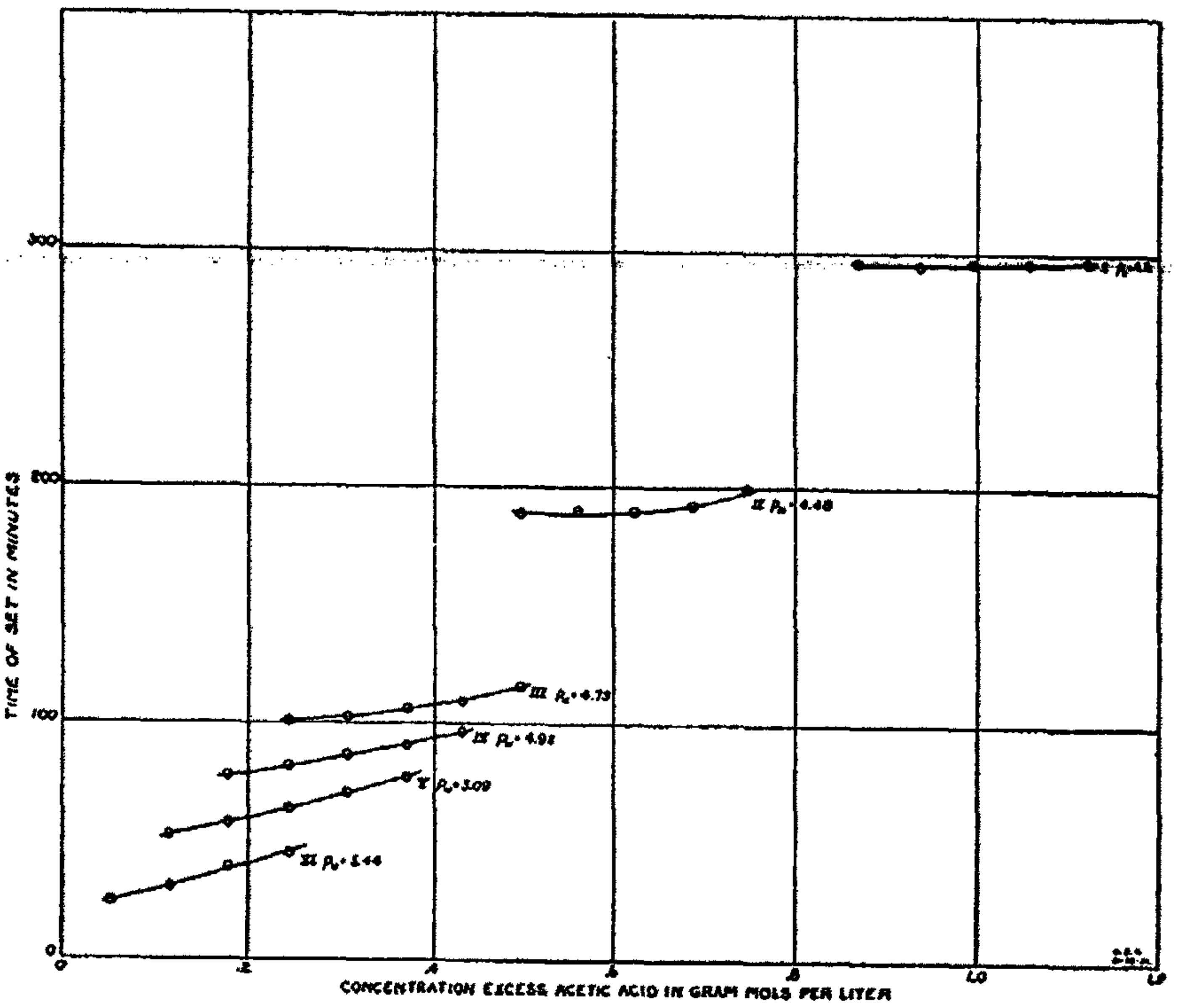

FIG. 3. TIME OF SET OF MIXTURES WITH CONSTANT pH AS A FUNCTION OF EXCESS ACETIC ACID

To test further the effects of sodium salts in considerable amounts upon the time of set, three series of determinations of the time of set and pH of the mixture were made, using increasing amounts of three different salts, sodium chloride, sulfate, and nitrate. The concentrations of sodium silicate and acetic acid were kept constant. The effects of electrolytes have been studied by other investigators, especially Prasad and Hattiangadi (9). Too little attention has been paid to the simultaneous effect of variation of the pH, however, as was pointed out by Hurd and Carver (3).

The results of these three runs are given in table 6 and are plotted in figure 4. It is apparent that increasing amounts of sodium chloride show no effect upon the pH. The effect upon the time of set is marked, namely, a decrease of over 50 per cent in time of set in a mixture containing approximately 1 gram-mole per liter. The sodium sulfate caused an appreciable decrease in pH, while the sodium nitrate caused a smaller decrease. Each of the pH changes should cause an increase in the time of set, estimated at about nine minutes in the case of the highest concentration of sodium sulfate. The effect of each of these three salts is to cause a marked decrease in the time of set. The sodium ion, therefore, in company with its anion,

TABLE 6

The effect of certain sodium salts upon the time of set of silicic acid gels and upon the pH of the mixtures

SALT	CONCENTRATION	pH	TIME OF SET *minutes*
$NaCl$	0.000	5.09	52.5
	0.063	5.09	48.0
	0.188	5.09	40.0
	0.312	5.09	36.5
	0.468	5.09	31.3
	0.625	5.09	28.0
	0.845	5.09	25.6
	0.938	5.09	23.9
Na_2SO_4	0.000	5.09	53.0
	0.062	5.09	51.0
	0.124	5.09	48.5
	0.188	5.08	48.0
	0.250	5.08	47.5
	0.376	5.04	45.3
	0.500	5.03	44.5
	0.625	5.03	43.7
$NaNO_3$	0.000	5.09	52.5
	0.062	5.09	46.7
	0.124	5.08	43.0
	0.188	5.08	40.8
	0.250	5.08	38.8
	0.376	5.07	34.0
	0.500	5.07	31.6
	0.625	5.06	29.5

shows no net peptizing effect, such as might be expected from the interpretations of Kröger.

The assumption may be made, therefore, in the interpretation of the data of table 5 that the sodium acetate, in addition to its function of keeping the pH constant in the presence of increasing amounts of acetic acid, would contribute materially toward decreasing the time of set. The net increase might, therefore, be due to the increasing amounts of acetic acid.

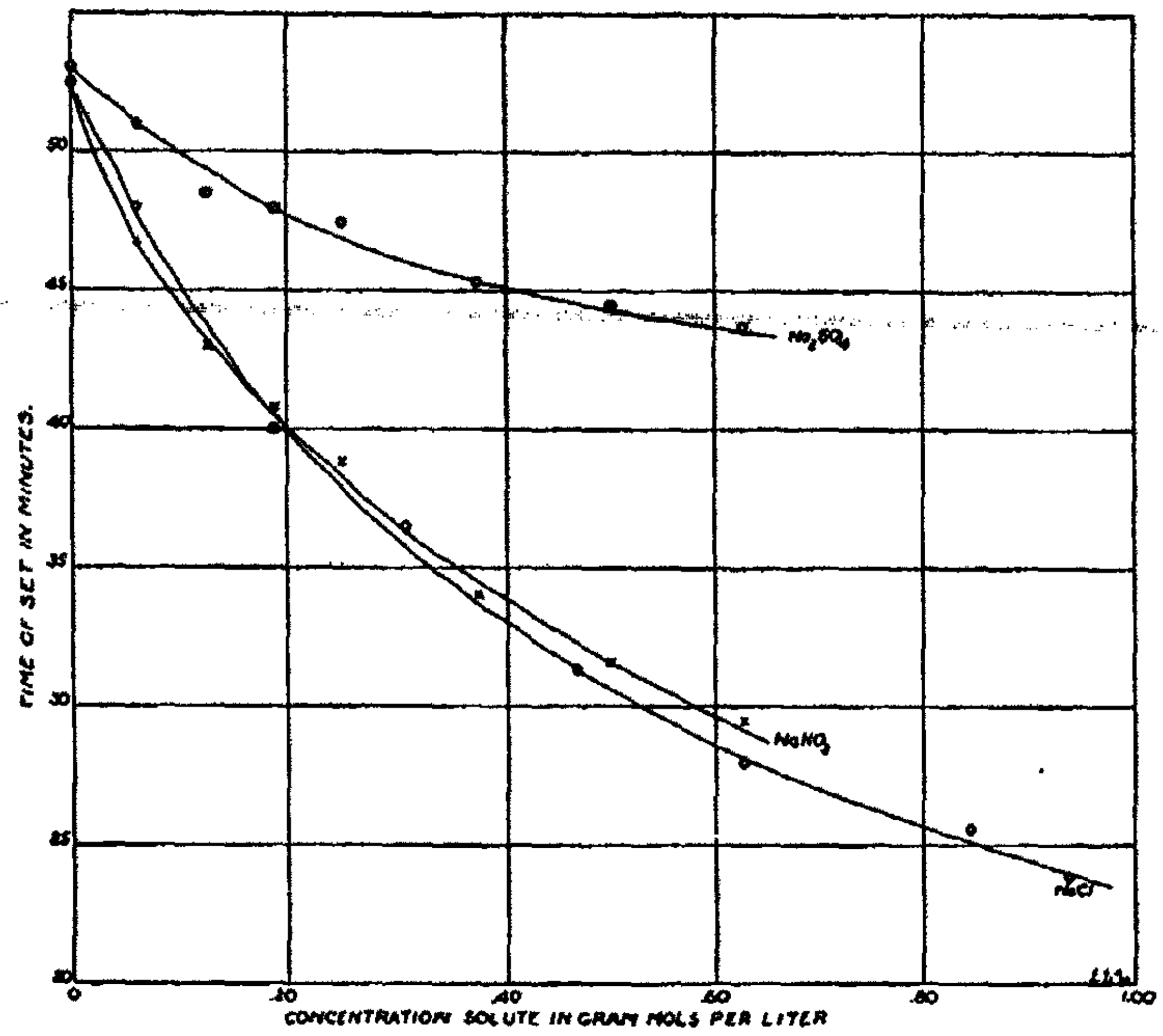

FIG. 4. EFFECT OF CERTAIN SODIUM SALTS ON TIME OF SET

DISCUSSION OF RESULTS

In this paper an attempt has been made to study so far as possible the effect, on the time of set, of the hydrogen-ion concentration, the concentration of excess acid, and of certain salts. The precautions taken to isolate these variables so far as possible have been explained. The description of details has been necessarily limited. The concentration of silica and the temperature have been kept constant throughout.

In the case of gels made from sodium silicate and acetic acid, the time of set appears to be a nearly linear function of the concentration of hydrogen ion from pH = 4.14 to 6.00. The presence of considerable excess acetic acid confuses the interpretation, however. In the case of gels made with hydrochloric acid, the excess acid required to produce the same change in hydrogen-ion concentration is so small that it may be neglected. Here the time of set appears as a linear function of the hydrogen-ion concentration, as shown by figure 2.

We may admit the assumptions first proposed by Hurd and Letteron, namely, (1) that in dealing with the mechanism involved in the setting of a silicic acid gel we are dealing with a process which follows the laws of an ordinary chemical reaction, so far as its velocity is concerned, and (2) that for a given silica content, the time of set measures the time when a certain fixed proportion of the silica, in whatever form, in solution has reacted.

Then it may be shown easily that the specific reaction rate, k, is inversely proportional to the time of set, t'. It is not necessary that we know the order of the reaction, n. From the curve of figure 2 for the hydrochloric acid gel, the time of set appears to be not only a linear function of the hydrogen-ion concentration, but to be actually proportional to the hydrogen-ion concentration.

Since the specific reaction rate, k, is inversely proportional to the time of set, t', and since the hydroxyl-ion concentration is inversely proportional to the hydrogen-ion concentration, it would appear that the specific reaction rate, k, is proportional to the hydroxyl-ion concentration. This may suggest the idea that in silicic acid gel mixtures in this pH range, the hydroxyl ion plays the part of a catalyst.

From other work it appears, however, that in mixtures containing silicic acid of pH greater than 8, the hydroxyl ion peptizes the silica.

SUMMARY

Several series of experiments are described in which an attempt has been made to determine the effect on the time of set of silicic acid gels of the hydrogen-ion concentration and the concentrations of excess acid and of certain salts.

With gels from sodium silicate and hydrochloric acid from pH = 4.2 to 5.5, the time of set appears to be a linear function of the hydrogen-ion concentration.

With gels from sodium silicate and acetic acid from pH = 4.14 to 6.0, a nearly linear relation is evident between time of set and concentration of hydrogen ions.

With gel mixtures of constant pH, the time of set is increased by increasing amounts of acetic acid and sodium acetate.

Three salts, sodium chloride, sodium sulfate, and sodium nitrate were found to decrease the time of set considerably without causing any considerable change in the pH.

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THE REACTION OF SODIUM WITH DRY OXYGEN

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Bonnsdorff (1) stated that sodium and potassium were not oxidized by dry oxygen, and later Holt and Sims (4) published a paper on the oxidation of the alkali metals in which they announced: "Potassium and sodium (and probably lithium) are not attacked by dry oxygen and may be distilled in it without undergoing oxidation."

The truth of this statement has apparently never been questioned. Work done in this laboratory, however, has indicated that the statement is only partially correct. In the absence of moisture, sodium is coated with a film of oxide which protects it from further oxidation. In the presence of moisture, the film is unstable and, because of this fact, sodium is slowly but completely oxidized in ordinary air. The experiments upon which this belief is based will be described in detail, and it will be shown that the earlier workers either overlooked this surface film or else observed it, but failed to realize its significance.

THE EXPERIMENTS

All of the observations reported here were made upon liquid sodium–mercury amalgams. The mercury was purified by washing carefully with acid mercuric nitrate solution and then distilling under reduced pressure in a current of air. The amalgams were prepared by electrolysis of specially purified sodium chloride solutions. A platinum anode was used.

It was first observed that such amalgams could be preserved in vacuo indefinitely, but when they were stored under dry hydrogen, obtained from a cylinder in the laboratory, they behaved in an abnormal manner. If the flask holding such an amalgam was rocked, the amalgam would wet the walls and would not drain back completely. A thin mirror-like film was left adhering to the glass. The experiments reported in this paper were performed in order to explain the formation of these mirror films.

Experiment 1

A bulb was blown on the end of a glass tube and then partially filled with sodium amalgam (0.5 per cent). The bulb was then connected to a Cenco Hyvac pump and evacuated. After several minutes, the bulb and the tube were heated until the mercury was boiling freely. The tube was then sealed off, leaving the amalgam in an evacuated bulb with a tube several inches long. A similar bulb was prepared containing pure mercury. The bulb containing the amalgam was corroded on the inside by the sodium oxide fused into the glass, but when the amalgam and the pure mercury were run into the clean tubes attached to their respective bulbs, it was not possible to distinguish between the two. Such tubes containing amalgam and mercury have been kept for three years without any visible changes.

Experiment 2

When one of the bulbs containing amalgam was sealed off and cooled, a minute crack appeared in the glass. This bulb was watched to determine the effect of the slow admission of air. Before the appearance of the crack, the amalgam could not be distinguished from mercury of the highest purity. Afterwards the amalgam became coated with a thin film which was made visible only by the wrinkles which appeared when the surface was agitated. At the same time, the amalgam acquired the property of wetting the glass to form mirrors. At first the surfaces exhibited a brilliant metallic luster, but this slowly became tarnished and dull.

Experiment 3

A bulb containing amalgam was evacuated and heated as described previously, but before sealing it off, a small amount of air was admitted. In this bulb, the surface films appeared at once. There was no tarnishing; the surfaces remained bright.

Experiment 4

Previously experiments had shown that some material present in the air caused the formation of the mirror films, and that an excess of air caused the films to tarnish. It was suspected that moisture was responsible for these effects. In order to eliminate the effect of moisture, the apparatus shown in figure 1 was constructed. Bulb C was partially filled with phosphorus pentoxide. Its capacity was approximately 35 cc. Amalgam was placed in bulb A and the apparatus was then sealed at D. The entire system was then evacuated through E and F. About 1 cc. of mercury was distilled over into B, and then all of the apparatus to the left of stopcock E was heated as uniformly as possible. Mercury distilled over into C sweeping out the last traces of air from the amalgam bulbs. The stopcocks were then closed and the apparatus was allowed to cool. The bulb C was then allowed to fill with air by opening F momentarily. The apparatus was then shaken to coat the walls of the drying chamber with the pentoxide and thereby hasten the drying process.

After 44 hours, the amalgam was transferred to bulb B. At that time, the amalgam resembled pure mercury. The dried air was then admitted to the amalgam chamber. No change could be observed until the bulbs were tilted. Then the amalgam was found to be coated with a rigid surface film, and a mirror film was left on the glass. It should be noted in particular that neither of these phenomena could have been detected if solid sodium had been exposed to dry air. The brilliance of the surface was not impaired.

Experiment 5

Experiment 4 was repeated using hydrogen from a cylinder instead of air. The gas was admitted to the amalgam after drying for 4 days. A film was formed over the surface as in the previous experiments. However, it did not appear instantly. Several seconds were required for its formation.

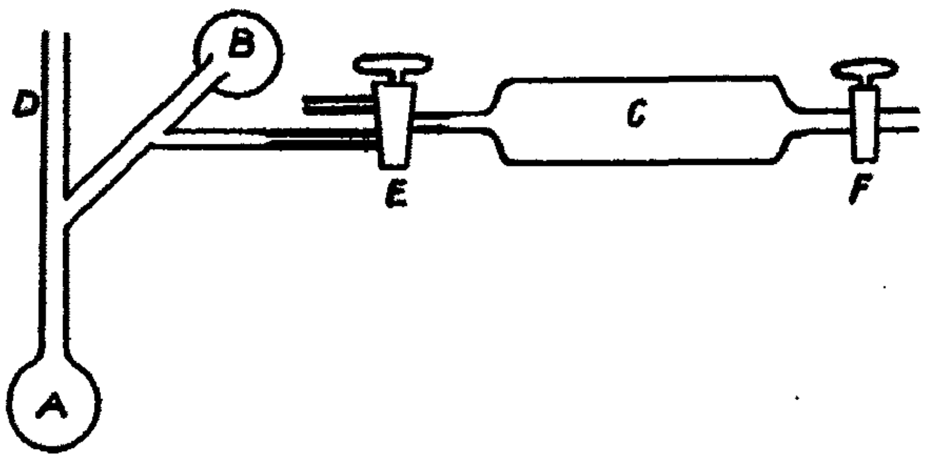

FIG. 1. APPARATUS USED TO ELIMINATE THE EFFECT OF MOISTURE

Experiment 6

The hydrogen used in the previous experiment had been obtained from an experimental plant and was suspected of containing traces of oxygen, though this has never been proved directly. Experiment 5 was repeated in duplicate using hydrogen which had been passed through freshly prepared alkaline pyrogallol solution. After intervals of 6 and 4 days, the gas was admitted to the amalgam chamber. No change could be detected. The purified hydrogen was without effect.

Experiment 7

Experiments 5 and 6 had shown that there was a small amount of the substance responsible for film formation in the hydrogen used, and that this could be removed by alkaline pyrogallol. In this experiment, carbon dioxide dried for 14 days was found to have no action upon the sodium amalgams.

Experiment 8

Nitrogen dried for 14 days over phosphorus pentoxide had no action upon a sample of sodium amalgam.

Experiment 9

Oxygen was dried for 14 days over phosphorus pentoxide, using the apparatus shown in figure 1. Before admitting the gas to the bulbs containing the amalgam, a globule of amalgam was transferred to the tube leading to the stopcock. When the oxygen was admitted, this globule was shot down the tube by the inrushing gas, leaving the tube coated with a mirror-like film, proving that the formation of the film was practically instantaneous. No change could be observed in the appearance of the amalgam in the bulbs until the apparatus was tilted. The surface crumpled like tinfoil.

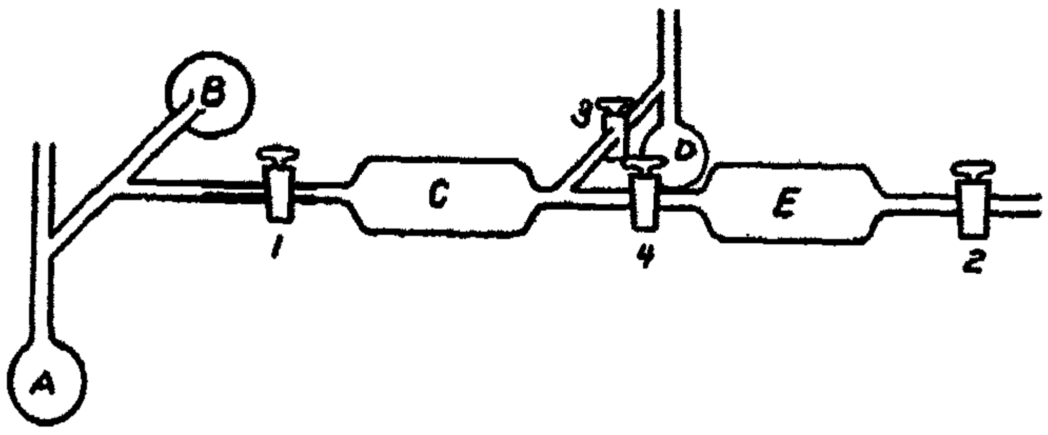

Fig. 2. Apparatus Used to Determine the Effect of Pure Water Vapor upon a Sodium Amalgam

Experiment 10

The apparatus shown in figure 2 was constructed in order to determine the effect of pure water vapor upon a sodium amalgam. An alkaline solution of stannous chloride was placed in bulb D and a few pieces of tin were added. It was believed that this would fix any oxygen which might remain in that bulb, and that no volatile substance except water would be introduced into the system. This bulb was then heated until the solution boiled vigorously, and then the inlet was sealed off. Bulb E was partly filled with solid sodium amalgam to remove oxygen, and liquid sodium amalgam was placed in bulb A. This compartment was boiled out as usual before closing stopcocks 1 and 2. A small amount of moisture was then admitted to the solid amalgam by opening stopcock 3. This was done to insure the absorption of oxygen from the bulbs.

After 11 days, the liquid amalgam was transferred to the clean bulb B, and stopcock 1 was opened. No change could be observed. Stopcock 4 was then closed and stopcock 3 was opened momentarily. Small lenses of water appeared almost instantly upon the surface of the amalgam, and a gas (hydrogen?) was liberated slowly until the water disappeared entirely, leaving small white flakes floating upon the surface. When more water vapor was admitted, the same cycle was repeated. The characteristic mirror formation was never in evidence, nor could any film be detected upon the surface.

Experiment 11

The apparatus shown in figure 1 was modified by providing it with two sets of amalgam bulbs, and by enlarging the drying chamber to 250-cc. capacity. Oxygen was dried in this for 49 days. The gas chamber was then connected momentarily to each of the amalgam chambers in turn. In both cases the amalgams remained bright, but the presence of a rigid film was disclosed when the apparatus was shaken. The oxygen reservoir was then connected permanently with the first amalgam chamber. After four months, there was no visible difference in the appearance of the two amalgams in contact with different amounts of oxygen.

Experiment 12

It is known that metallic sodium in air phosphoresces with a greenish light. Linneman (5) attributed this to oxidation; Reboul (7) attributed it to the reaction of sodium oxide with water vapor. More recently, Woodrow and Bowie (9) and Bowie (2) have concluded that the reaction is between metal and water vapor, and not a direct oxidation.

It was believed that if the film formation was due to a surface oxidation, and that if this oxidation gave rise to luminescence, it might be possible to detect a flash of light when the oxygen was first admitted. For this experiment, oxygen was dried for 10 days in the apparatus shown in figure 1. The oxygen was then admitted to the amalgam in a completely darkened room. There were two observers. One saw nothing, the other observed a faint flash of light in the tube leading from the stopcock to the amalgam. A small globule of amalgam had previously been transferred to this tube.

This experiment was repeated, drying the oxygen for 51 days. Two observers noticed the flash, a third did not.

This experiment was again repeated, drying the oxygen for 13 months. When the oxygen was admitted, one observer uttered an exclamation of surprise when he saw the light. He had no way of knowing the instant at which the oxygen was to be admitted.

In these experiments, no light was ever observed upon the surface of the amalgam in bulk. It was only seen in the tube where a small amount of amalgam was probably suspended in the rush of oxygen, and where the oxidation continued longer than it did on a stationary surface. It might be added that it is not possible to estimate the actual intensity of the light because the duration of the flash is exceedingly short, and because the greater part of the walls of the tube was instantly covered with an opaque mirror film.

Experiment 13

Previous experiments had indicated that sodium amalgams react to a limited extent with dry oxygen, but no indication had been obtained as to the actual amount of oxygen involved. In order to learn more regarding the quantities involved, the apparatus shown in figure 3 was constructed. After placing phosphorus pentoxide in bulb B, the system was evacuated. It was then filled with oxygen, a stream of oxygen being forced out through the manometer for about five minutes. After closing stopcock 2, the oxygen was allowed to dry for 167 days. The graduated tube T was then filled with amalgam. A small amount of gas was formed and this was removed by evacuating for 2 hours. Four hours later, 1.0 cc. of the amalgam was allowed to flow into the oxygen chamber (capacity 200 cc. ±). The amalgam was instantly covered by a rigid film. The absorption of oxygen caused less than 1 mm. change in pressure. After 24 hours, no change could be detected. An additional 2.0 cc. of amalgam was then added. After 2 days, the loss of oxygen was still too small to detect (less than 1 mm. of mercury). The apparatus was then rocked gently for 2 hours to break up the film and expose fresh surfaces to the oxygen. During that time the

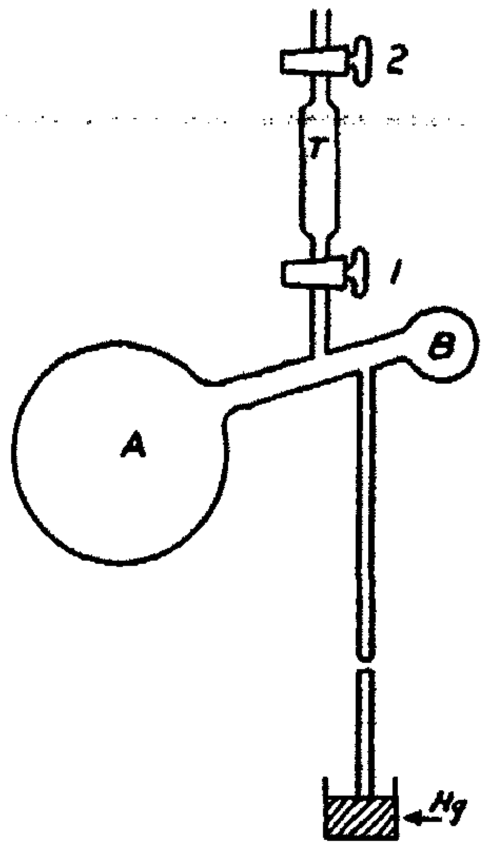

FIG. 3. APPARATUS USED TO DETERMINE THE AMOUNT OF OXYGEN INVOLVED

pressure fell 25.0 mm., and the surface of the amalgam became coated with a heavy scum.

DISCUSSION

As a result of the experiments which have been described, it is believed that sodium is attacked by dry oxygen, and that an impervious film is formed which prevents further oxidation.

From the nature of the problem, it is always possible to argue that the gases used were not dry enough for the results to be conclusive. It is necessary, therefore, to review the original evidence for the non-reaction of dry oxygen and sodium. Bonnsdorff (1) states: "In einer vollkommen trocknen und von Kohlensäure freien Atmosphäre oxydiert sich kein Metall. Auch Kalium und Natrium bleiben in derselben ohne Oxydation." However, he admits that there is a slight oxidation for he goes on to say, "Das Kalium läuft zwar gewöhnlich in kurzer Zeit unbedeutend an, aller Wahrscheinlichkeit nach eine Folge davon, dass die Versuch nicht mit solcher Genauigkeit gemacht werden kann, dass die Wirkung des Wassers völlig ausschlossen bleibe, aber das Metall erhält sich als dann unverändert." In his experiments, the air used was dried over sulfuric acid, and it doubtless contained much more moisture than the oxygen used in our experiments. On a later page he stages that the bright metal exposed to dry air "sich unverändert mit metallischen Glanz erhielten." Our experiments proved that the presence of metallic luster was not a safe indication of the absence of a surface film.

The paper of Holt and Sims (4) is frequently quoted on the subject of the oxidation of sodium by dry oxygen. In their conclusion they state, "Potassium and sodium (and probably lithium) are not attacked by dry oxygen and may be distilled in it without undergoing oxidation." However, a study of their paper reveals that they did not actually distill these metals. They merely fused them in an atmosphere of oxygen, and heated until fumes appeared. This is analogous to the experiments of Deville (3), who reported that aluminum was absolutely resistant to oxygen even when fused.

Furthermore, Holt and Sims make the enlightening statement: "In a few experiments made by passing a stream of dried oxygen direct into molten sodium at a temperature of 235°C., no oxidation took place except at the surface, ..."

In both of these papers it is admitted that some surface oxidation took place. In both cases the authors chose to ignore this as "unbedeutend," and assumed that since the reaction did not go to completion, it would not have occurred at all if water vapor had been entirely eliminated. According to their own writings, they did not actually reach this ideal condition. Hence it still remains to be proved that oxygen can be made so dry that it will not react with sodium.

It is not possible to prove that the oxygen used in these experiments was dry, but the evidence should be considered. All gases were dried over phosphorus pentoxide, which leaves no measurable amount of water vapor in the gas (6), and the drying periods were greatly prolonged. Other investigators have used calcium chloride or sulfuric acid, which are of doubtful value. In fact, Russel (8) has reported that the amount of water left in a gas by sulfuric acid is the optimum concentration for the rapid oxidation of phosphorus.

There is the possibility that all of the water was not removed from the glass surfaces by this treatment. Even if that were the case, the partial pressure exerted by the adsorbed water must have been infinitely small and can scarcely account for the extreme speed of the initial reaction,—an action which ceased immediately, but which began again the instant that a fresh surface was exposed.

Regarding the reaction responsible for the chemiluminescence of sodium, it is evident that no light could be detected by the eye unless the reaction continued for an appreciable interval of time. Therefore the evidence in the literature favoring the reaction with water is not valid, since it does not eliminate the possibility that water is not directly responsible for the luminescence, but merely makes it possible for the oxidation to proceed slowly by preventing the formation of protective films.

CONCLUSIONS

1. It remains to be proved that oxygen can be made so dry that it will not react with sodium.

2. When sodium amalgams were exposed to oxygen dried over phosphorous pentoxide for more than a year, the amalgams were instantly covered with a protecting film which prevented further action.

3. Sodium will react with dry oxygen at room temperature with the emission of light, but the reaction ceases instantly unless water vapor is present to prevent the formation of protective films.

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THE EFFICIENCY OF ARGON AS A RADIOCHEMICAL CATALYST

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When the catalytic or sensitizing effect of inert gases on gaseous reactions produced by alpha particles from radon was first discovered by Lind and Bardwell (6), they pointed out certain puzzling facts. It appeared strange that a radiochemically inert gas such as carbon dioxide should apparently not catalyze reactions in which it is formed. Furthermore, a peculiar "depletion" effect was observed; quite generally, after the partial pressure of reactants decreased beyond the point at which half of the total ionization fell upon the catalyst, the accelerating influence of the latter diminished rapidly.

It is now known that carbon dioxide actually does speed up the carbon monoxide oxidation (8), its effect being small compared to that of krypton, helium, and nitrogen. In the original study of radiochemical sensitization, it appeared that ions formed in the sensitizing gas were completely transferred to reactants. In the carbon monoxide oxidation it was found that the dioxide is extremely inefficient as a sensitizing agent, only 14.5 per cent of its ionization being effective in promoting reaction. Because its effect was so small, carbon dioxide was at first thought to be without any influence in the radiochemical carbon monoxide oxidation. Further work (10) has disclosed that the dioxide is characteristically inefficient as a catalyst in all reactions where its influence has been studied. In the combination of hydrogen and oxygen, again about 15 per cent of the ionization falling on the carbon dioxide is transferred to reactants, while in the acetylene polymerization as much as 30 per cent seems to be utilized.

It is of interest to note that from the very start of both last mentioned reactions, more than half of the total ionization falls upon the catalyst. Accordingly we are dealing with cases which are in the range of most marked "depletion." Actually if one assumes (6) that all the carbon dioxide ionization is utilized, then the resulting velocity constants, and of course $-M/N$ ratios (molecules reacting per ion pair formed), are far below those of the normal (unsensitized) reactions, and continue to decrease further as the reactions approach completion. Referring on the other hand to the recalculated velocity constants and $-M/N$ values based on the fractional efficiency of carbon dioxide, one obtains values comparable with those of the normal reactions, and which remain fairly constant throughout the catalyzed reaction. This is equivalent to a disappearance of the depletion effect. It thus appears possible to eliminate this puzzling feature of ionic catalysis by correcting for the proper efficiency of the ionic catalyst.

To test this possibility more fully, the existing data for reactions in which argon has been used as the inert gas have been considered more carefully from the point of view of fractional catalytic efficiency. For purposes of comparison with carbon dioxide, it is a happy coincidence that the three reactions in which the effect of the dioxide has been investigated have likewise been chosen by Lind and Bardwell (6) for a study of the argon effect.

Experimental determination of the fractional efficiency of an ionic catalyst has been fully described elsewhere (8, 10). It requires the graphical comparison of velocities of parallel reactions in spheres of the same size, containing equal quantities of radon and reactants, except that in one is found a known quantity of inert gas. Unfortunately the normal and argon catalyzed reactions were not studied under sufficiently similar conditions to permit a strict application of the method. The result is a decided downward trend in the calculated efficiency as the catalyzed reaction proceeds. However it was useful as an approximation, and in all reactions an intermediate value yielded a satisfactory fractional efficiency. Details of this preliminary work will of course be omitted. It is advisable, though, to summarize briefly the notation to be employed. Fuller descriptions are to be found in the papers already cited.

In general the velocity constant of a normal radiochemical reaction is given by

$$\left(\frac{k\mu}{\lambda}\right)' = \frac{2.303\,\Delta\log P_{\text{reactant}}}{E_0\cdot\Delta e^{-\lambda t}}$$

where $e^{-\lambda t}$ is the initial quantity of radon in curies, and P_{reactant} is the partial pressure of reactant. For a catalyzed reaction where no correction is made for the effect of the sensitizer, the constant is denoted by $\left(\frac{k\mu}{\lambda}\right)'_c$. If the catalytic effect is considered, the corrected constant becomes

$$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} = \frac{2.303\,\Delta\log\left[P_{\text{reactant}} + X\frac{i_{\text{catalyst}}}{i_{\text{reactant}}}P_{\text{catalyst}}\right]}{E_0\cdot\Delta e^{-\lambda t}}$$

where $\left[X\frac{i_{\text{catalyst}}}{i_{\text{reactant}}}P_{\text{catalyst}}\right]$ is termed the ionic equivalent of the catalyst. Here, X is the fractional efficiency,[1] P_{catalyst} is the partial pressure of the

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[1] The term "efficiency" as used in this paper should not be confused with the term "per cent efficiency" as used by Lind and Bardwell (6). These authors define

inert gas, and i_{catalyst} and i_{reactant} represent the molecular specific ionization (4) of the catalyst and reactant, respectively. The following values of specific ionization were used in this paper:

$$i_{\text{CO}} = 1.00;\ i_{\text{CO}_2} = 1.52;\ i_{\text{H}_2} = 0.24;\ i_{\text{O}_2} = 1.10;\ i_{\text{C}_2\text{H}_2} = 1.40;\ i_{\text{A}} = 1.245.$$

Consequently for mixtures of reacting gases we have:

$$i_{(2\text{CO}+1\text{O}_2)} = 1.03;\ i_{(2\text{H}_2+1\text{O}_2)} = 0.53$$

TABLE 1

The effect of argon on the water synthesis

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

D = 1.939 cm.; E_0 = 0.0463 curie of radon; P_A = 559.5 mm.

$e^{-\lambda t}$	$P_{(2H_2+1O_2)}$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$		$-M/N$ RATIO	
		I (assuming 100 per cent efficiency)	II (assuming 40 per cent efficiency)	I* (assuming 100 per cent efficiency)	II (assuming 40 per cent efficiency)
	mm. Hg				
1.000	557.5				
0.9705	517.5	15.3	27.2	3.60	5.82
0.9174	452.5	14.3	26.1	3.21	5.59
0.8447	374.0	13.3	24.8	3.12	5.29
0.8030	332.8	12.3	24.0	2.89	5.10
0.7663	297.4	12.6	24.7	2.95	5.25
0.7069	243.7	11.9	24.4	2.80	5.17
0.6400	185.9	11.8	25.1	2.78	5.31
0.5905	147.0	11.2	24.4	2.64	5.15
0.4786	66.6	10.5	24.4	2.48	5.13
0.4158	34.9	7.8	18.8	1.82	3.93
0.3271	1.2	6.1	15.0	1.42	3.11
Average					5.30†

* These $-M/N$ ratios are calculated with the use of older values of average intensity of ionization (5). Recalculation on the basis of F as given by Glockler and Heisig (1) would yield $-M/N$ ratios lower by approximately 7 per cent.

† Pressure drop average of values down to the broken line.

The $-M/N$ ratio (i.e., molecules reacting per ion pair formed in and contributed by catalyst to reactant) is calculated from the expression:—

$$-M/N = \frac{\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}}{F \cdot H} \, \frac{V}{D \cdot i_{\text{reactant}}} \, 1.668 \times 10^3$$

"percentage of catalytic efficiency" in a sensitized reaction as the ratio of the velocity constant obtained for a given interval (assuming complete utilization of ions formed in the catalyst, i.e., column I in tables 1, 2, and 3) over the normal velocity constant. The present author defines efficiency simply as the fraction (or per cent) of the ionization produced in the inert gas which appears to be effective in producing reaction.

where V and D are volume and diameter of the reaction sphere, H is the recoil atom correction (8), and F is the average intensity of ionization (1).

Tables 1, 2, and 3 show the influence of argon on the water synthesis, the carbon monoxide oxidation, and on the acetylene polymerization. Detailed accounts of the normal reactions as well as of the argon catalyzed water synthesis have already appeared in the literature. Only summaries of the argon catalysis of the two other reactions have been published (6). Fortunately, with Professor S. C. Lind's kind permission, the writer had access to the original experimental data collected by Lind and Bardwell, which are here presented.

From table 1 it is clear that less than 100 per cent efficiency is characteristic of argon. The $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$ and M/N values based on this efficiency (columns I) plainly show the so-called depletion effect. On the other hand a 40 per cent efficiency (columns II) yields a satisfactory velocity constant. and $-M/N$ ratio for the whole course of the reaction, this in spite of the fact that initially 71 per cent of the total ionization falls upon the catalyst. Furthermore the reaction proceeds uniformly to the point where as much as 96 per cent of the total ionization falls upon argon. Evidently the depletion effect has been eliminated; and the average $-M/N$ ratio of 5.30 for the catalyzed reaction is in harmony with the 5.13 value for the normal synthesis (3, 6).

TABLE 2

The effect of argon on the carbon monoxide oxidation

$2CO(g) + 1O_2(g) + A(g) = 2CO_2(g) + A(g)$

D = 1.930 cm.; E_0 = 0.0418 curie of radon; P_{A} = 563.4 mm.

$e^{-\lambda t}$	$P_{(2CO + 1O_2)}$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$		$-M/N$ RATIO	
		I (assuming 100 per cent efficiency)	II (assuming 40 per cent efficiency)	I (assuming 100 per cent efficiency)	II (assuming 40 per cent efficiency)
	mm. Hg				
1.0000	560.1				
0.9778	522.0	29.0	43.1	3.18	4.67
0.9254	444.0	26.2	40.0	2.88	4.33
0.8511	360.0	20.3	33.4	2.24	3.62
0.8076	321.0	17.5	28.6	1.94	3.10
0.7730	288.0	19.1	32.1	2.12	3.49
0.7109	243.0	15.1	25.7	1.67	2.79
0.6449	195.0	15.8	27.8	1.75	3.02
0.5983	165.6	14.2	25.6	1.58	2.77
0.4822	104.4	12.4	23.2	1.38	2.50
0.4190	74.4	11.6	22.8	1.29	2.46
0.2837	21.6	10.0	20.5	1.11	2.21

Table 2 contains a summary of the carbon monoxide oxidation. The efficiency of carbon dioxide is taken as 14.5 per cent.

Here again the assumption of a 40 per cent efficiency raises the $-M/N$ ratio. There still remains a decided downward trend which may be due to a still further diminishing efficiency of argon as reactants disappear and carbon dioxide appears. The appearance of the dioxide further complicates the system in that it contains two ionic catalysts, a type of system which is little understood. Nevertheless it is gratifying that the $-M/N$ ratio is approximately that of the normal reaction (8), which yields a value between 3 and 4.

TABLE 3

The effect of argon on the acetylene polymerization

$$xC_2H_2(g) + A(g) = (C_2H_2)_x + A(g)$$

D = 1.951 cm.; E_0 = 0.00845 curie of radon; P_A = 382 mm.

$e^{-\lambda t}$	$P_{C_2H_2}$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$			$-M/N$ RATIO		
		I (assuming 100 per cent efficiency)	II (assuming 50 per cent efficiency)	III (assuming 60 per cent efficiency)	I (assuming 100 per cent efficiency)	II (assuming 50 per cent efficiency)	III (assuming 60 per cent efficiency
	mm. Hg						
1.0000	762.6						
0.9851	733.3	212.2	256	247	17.0	20.3	19.5
0.9668	697.8	216.1	259	250	17.3	20.7	19.9
0.9489	666.2	206.0	246	236	16.6	19.7	18.9
0.9105	600.9	201.8	250	240	16.3	19.9	19.1
0.8384	489.8	203.3	256	244	16.5	20.6	19.7
0.8290	477.4	186.0	238	227	15.2	19.3	18.4
0.7945	430.9	177.4	256	242	14.5	20.8	19.6
0.6637	281.7	193.6	256	243	15.9	20.8	19.6
0.5850	211.6	178.2	254	234	14.7	20.6	19.1
0.5774	206.1	150.6	226	208	12.4	18.3	17.0
0.4886	142.9	163.4	245	223	13.5	19.8	18.1
0.4089	97.3	146.0	234	210	12.0	18.8	17.0
0.2805	45.0	119.1	201	196	9.8	16.1	14.2
0.2278	29.3	94.2	171	146	7.8	13.5	11.7
0.1371	12.3	61.0	116	99	5.0	9.1	7.9
0.0128	2.4	26.5	53	45.1	2.2	4.1	3.6
Average						20.2	18.8

A more decided example is the acetylene polymerization shown in table 3. Here it appears that argon is somewhat more efficient,[2] a value of 50 per cent or 60 per cent yielding a $-M/N$ ratio very close to the normal value. The original experiments of Lind, Bardwell, and Perry (7) sug-

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[2] Compare with reference 10. Just as for argon, the efficiency of carbon dioxide in the acetylene polymerization is also greater than in the other two reactions.

gested an average $-M/N$ ratio of 19.8. A reconsideration of ionization produced, based on the Mund calculation (9) as summarized by Glockler and Heisig (1), has led Heisig to give this figure as 18. Assumption of 50 per cent efficiency (columns II) yields a constant $-M/N$ value of 20.2, while 60 per cent efficiency (columns III) gives 18.8. It is not the purpose of this discussion to determine exactly the characteristic efficiency of argon. Undoubtedly it varies somewhat with the reaction studied. The fact which does remain certain is that recalculation results in a vanishing of the depletion phenomenon. In this reaction 69 per cent of the initial ionization falls upon the reactant; and a satisfactory constant $-M/N$ ratio is obtained to a point where 78 per cent of the ionization is being carried by the catalyst.

SUMMARY

1. Existing data on the radiochemical reactions in which argon is used as an ionic catalyst have been recalculated, assuming a fractional efficiency of the catalyst. It appears that approximately 40 per cent of the ionization produced in argon is utilized in promoting the hydrogen and carbon monoxide oxidations. In the acetylene polymerization it behaves as though it possessed an efficiency of 60 per cent.

2. Satisfactory velocity constants and $-M/N$ ratios are thus obtained in regions where by far most of the total ionization is being carried by the argon.

3. It appears possible by making such a correction to eliminate the puzzling depletion effect.

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THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN CEROUS CHLORIDE SOLUTIONS AT 25°C.

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INTRODUCTION

The activity coefficient of hydrochloric acid in the alkali and alkaline earth chlorides has been determined by a number of investigators (11). Work with trivalent chlorides has been reported by Harned and Mason (4) for aluminum chloride and by Randall and Breckenridge (9) for lanthanum chloride.

In this investigation the activity coefficient of hydrochloric acid has been determined in aqueous cerous chloride solutions. The cells

$$H_2 \mid HCl(m_1), CeCl_3\ (m_2) \mid AgCl \mid Ag$$

containing hydrochloric acid at 0.01 molal concentration and varying amounts of cerous chloride, and hydrochloric acid and cerous chloride mixtures at constant total ionic strength have been measured at 25°C.

EXPERIMENTAL

The measurements were obtained with the usual type of H cell without the employment of vacuum technique. At the concentration of acid employed, any hydrolysis of the cerous chloride was sufficiently suppressed as to have no noticeable effect.

The cerous chloride was prepared from spectroscopically pure cerium oxalate by the method of Hönigschmidt and Holch (1, 7). The cerous chloride solutions were prepared by weight from a stock solution. This was analyzed gravimetrically for chloride as silver chloride and for cerium as CeO_2. This latter determination was carried out according to the method of Moore and Bonardi (8), except that it was found necessary, as suggested by Hillebrand and Lundell (6), to heat the oxide at 1200°C. to obtain constant weight. The two methods checked to within 1 part in 700 for the concentration of the solution.

The hydrochloric acid used was obtained by distillation of a standard arsenic-free commercial acid, discarding the first and third portions.

The silver–silver chloride electrodes used were those described by Harned (3) as type 2.

The hydrogen electrodes were prepared in the usual manner from platinum foil. The cells measured were all corrected to one atmosphere partial pressure of hydrogen (2).

All the measurements were made in a standard water thermostat at 25°C. ±0.01°C.

TABLE 1

Electromotive forces of the cells H_2 | HCl (m_1), $CeCl_3$ (m_2) | AgCl | Ag *at 25°C.*

1. Constant acid; varying salt

MOLALITY OF HCl(m_1)	MOLALITY OF $CeCl_3$(m_2)	IONIC STRENGTH μ	E	ACTIVITY COEFFICIENT γ
0.010	0.000	0.010	0.46467†	0.904*
0.010	0.005	0.04	0.44509	0.839
0.010	0.010	0.07	0.43500	0.805
0.010	0.030	0.190	0.41546	0.745
0.010	0.050	0.31	0.40535	0.717
0.010	0.075	0.46	0.39678	0.699
0.010	0.100	0.61	0.39039	0.689
0.010	0.1650	1.000	0.37991	0.662
0.010	0.250	1.51	0.36998	0.655
0.010	0.3750	2.26	0.35898	0.664
0.010	0.500	3.01	0.34908	0.698
0.010	0.750	4.51	0.33389	0.767
0.010	1.00	6.01	0.32095	0.855

2. Constant total ionic strength of 1 μ

MOLALITY OF HCl(m_1)	MOLALITY OF $CeCl_3$(m_2)	E	ACTIVITY COEFFICIENT γ (observed)	ACTIVITY COEFFICIENT γ (calculated)‡
0.100	0.1500	0.31569	0.700	0.702
0.300	0.1167	0.28113	0.727	0.727
0.500	0.0833	0.26250	0.755	0.750
0.700	0.0500	0.24904	0.779	0.776
0.900	0.0167	0.23810	0.804	0.803
1.000	0.000	0.23342	0.814	0.815

* Randall and Young (10).

† Agrees within limits of experimental error with Harned and Schupp (5) for similar cells.

‡ Equation 3.

RESULTS

The electromotive forces of the cells

Ag | AgCl | HCl(m_1), $CeCl_3$(m_2) | H_2 | HCl (0.01) | AgCl | Ag

are related to the activity coefficients and concentrations involved by the equation

$$E = 0.1183 \log \frac{\gamma}{\gamma_r} + 0.05915 \log \frac{(m_1 + 3m_2)(m_1)}{(0.01)^2} \qquad (1)$$

where γ is the activity coefficient in the salt solution and γ_r that in the reference solution of pure hydrochloric acid. m is the concentration in grammoles per thousand grams of water. Using this equation the activity coefficients of hydrochloric acid have been calculated for the cells measured. γ_r was taken to be 0.904 for 0.01 molal hydrochloric acid (10).

Table 1 (section 1) gives results for the cells containing 0.01 molal acid and varying cerous chloride concentrations. Section 2 contains the measurements made at a constant total ionic strength of 1μ.

From the data in table 1 (section 2) we may test the equation

$$\log \gamma = \log \gamma_0 + \alpha\, m_1 \qquad (2)$$

which has been shown to be valid for solutions containing hydrochloric acid in uni-univalent chloride and aluminum chloride solutions at constant total ionic strength (4, 11). γ is the activity coefficient of the acid, m_1 its molality, and γ_0 its activity coefficient in the acid-free salt solution.

A plot of log γ against m_1 at constant total ionic strength of $1\ \mu$ gave a straight line expressed by the equation

$$\log \gamma = \bar{1}.8381 + 0.0740\, m_1 \qquad (3)$$

The last column of table 1 (section 2) gives the values of γ calculated from this equation. These agree, except for one concentration, to within three parts in the third decimal place of activity coefficient. This corresponds to an error of approximately 0.20 millivolt in the electromotive force of the cells.

SUMMARY

1. The activity coefficient of hydrochloric acid has been measured at 25°C. in aqueous cerous chloride solutions by means of the cell

$$H_2 \mid HCl\ (m_1),\ CeCl_3\ (m_2) \mid AgCl \mid Ag$$

2. The results at constant total ionic strength of 1μ verify the law of the linear variation of log γ and may be expressed by the equation

$$\log \gamma = \bar{1}.8381 + 0.0740\, m_1 \qquad (3)$$

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PHOTOVOLTAIC CELLS CONTAINING DYE SOLUTIONS

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It has long been known (7) that when two electrodes of platinum or any other noble metal are introduced into a solution of a fluorescent dye and one of them is illuminated, a difference of potential is set up between the two electrodes, the magnitude and sign of the P.D. depending among other things on the dye, the solvent, the concentration of the dye, and the nature and intensity of the incident light.

Various theories have been advanced from time to time to explain the mechanism of this interesting phenomenon, but with apparently little success. From the similarity of the current-potential curves, obtained when an auxiliary potential is impressed on the electrodes, to analogous curves for photoelectric emission, Goldmann (4) was led to the conclusion that photovoltaic effects owed their origin to photoelectric phenomena. Subsequently van Dijck (11) obtained with a copper oxide cell evidence which is singularly at variance with such conceptions. The extensive work of Grumbach (5) has fairly well established the fact that the seat of E.M.F. is in the illuminated electrolyte and that the electrode is practically inactive. Russell (9) pictured the process as a photochemical activation of the dye molecules and the building up of the E.M.F. by the impact of the activated molecules with the electrode surface. He traced the time lag of the photopotential curves to the formation of the active molecules at some distance from the electrode, which would take a measurable time to diffuse to the electrode. Ghosh (3) developed this concept further, assumed a mutual deactivation of the molecules by collision, and by applying the Nernst equation for concentration cells derived an expression for the time rate of the rise of potential on illumination, which was verified with the experimental data of Rule (8) on fluorescein. He also showed that the maximum photopotential developed would be proportional to the square root of the intensity of the incident radiation, a prediction also proved by the data of Rule.

The concept of a photochemical origin for the E.M.F. suggests at once a close relationship between photochemical absorption and photovoltaic potential. The complete lack of data of this type has excluded a crucial examination of the hypothesis of Ghosh. The following work was started to provide some of the required data. A point of further interest was the question of a possible parallelism between photovoltaic effects and the phenomenon of optical sensitization, so extensively employed in chromatic photography. Accordingly, erythrosin, a fluorescent dye very much used in the preparation of orthochromatic plates and a non-fluorescent dye, chrysoidine, were selected for investigation.

EXPERIMENTAL

The dyes employed were of the highest purity obtainable and were further purified by recrystallization from alcohol. A concentrated solution of the dye was first prepared by dissolving in water a weighed amount of the dye and making up the solution to a definite volume; a check on the concentration was obtained by weighing the residue on evaporating a measured volume of the solution to dryness over a water bath. The solution was preserved in the dark in stoppered bottles of resistance glass previously steamed. Under such conditions the stock solution showed no signs of deterioration and a solution of erythrosin aged in this way for four months gave results differing from a freshly made solution of the same concentration by less than 2 per cent. Solutions of desired strength were made by diluting the stock solution in the right proportion.

The dye solution was contained in a glass cell with plane parallel walls and about 4 cm. wide. A coating of non-reflecting black on the outer faces with a small rectangular patch 1.5 by 1.0 cm. on one face to admit the light served to shut off effectively stray light from the cell. The cell was mounted on a thick paraffin block.

The electrodes were rectangular pieces of platinum foil of the same size as the opening in the glass cell joined by a short length of platinum wire to sealed mercury cups. One face of the electrode and the platinum lead wire were coated with a thin film of paraffin wax, which greatly diminished local cell formation. The illuminated electrode was at a constant distance of 0.5 mm. from the glass wall and directly opposite the unpainted patch. The dark electrode almost touched the opposite wall of the cell. A light trap of a suitable shape immediately behind the illuminated electrode helped to screen efficiently the major portion of the electrolyte from the activating light.

The source of light was a transparent silica mercury burner (K.B.B. atmospheric—horizontal type) working at 85 volts and 2.0 amperes. The current in the burner was maintained constant by means of an adjustable rheostat in series. During the early experiments the entire radiation from the burner after passing through a glass cell containing cold water to filter the heat radiation was utilized for exciting the photopotentials, while, later, narrow spectral regions were isolated by interposing suitable Wratten filters of gelatin.

The cell showed a pronounced tendency to polarize; it was necessary to leave the cell a whole afternoon undisturbed when once it was polarized. The use of a potentiometer for measuring the photopotentials was thus excluded, for, during balancing, a small current is invariably drawn from the cell. A vacuum tube voltmeter was therefore considered to offer a distinct advantage; this instrument could further be made to give a continuous record of the growth of the photopotential. The principle of the valve-voltmeter is too well-known to need a full description here. It is however of interest to mention that a straight circuit utilizing a single valve operating well below its normal rated anode and filament potentials proved highly satisfactory. The arrangement was extremely stable, albeit a slight reduction in its sensitivity resulted thereby. A Philips B405 valve (normal rating,—anode 120 volts and filament 4.0 volts) was made use of with only 50 volts on the anode and 2.8 volts on the filament; the mutual conductance of the valve under these conditions was 1.0 milliampere per volt. This in conjunction with a Cambridge mirror galvanometer of sensitivity 0.33×10^{-8} ampere provided a means of measuring potentials of the order of 0.33×10^{-5} volt. The photopotentials were of the magnitude of a few millivolts. It was therefore necessary to shunt the galvanometer suitably in order to bring the potentials to be measured within the range of the instrument. Potentials of 10 millivolts and above were measured on a Cambridge microammeter with a central zero, while lower potentials could be easily measured on the mirror instrument shunted so as to give a deflection of one scale division for a grid swing of 3.3×10^{-5} volts.

It is necessary here to remark on the great stability of the arrangement. During an experiment which usually lasted some hours the creep of the zero of the instrument was ordinarily one scale division, but in inclement weather the creep at times amounted to even three divisions on the mirror galvanometer. Even this large creep meant only a change in the grid potential of a tenth of a millivolt.

The cell was connected directly between the grid and the negative end of the filament. The readings on the microammeter and the mirror galvanometer gave not only the magnitude of the photopotentials but also their sign directly.

RESULTS

The photopotentials were negative in sign in the case of erythrosin solutions, but positive with chrysoidine. It is yet early to attempt an explanation for this difference in behavior of the two dyes; possibly, the chemical constitution of the dye in addition to the solvent plays a part in determining the sign of the photo-E.M.F.

When freshly formed, the cell generally showed no P.D. between its electrodes; even in cases when the cell exhibited a minute P.D. initially, this was never more than a fraction of a millivolt and the change of P.D. on illumination was always the same. This minute dark E.M.F. has possibly its origin in the presence of traces of impurities on the electrode surfaces.

Figure 1 illustrates the time rate of the rise of the photopotential at various concentrations of the dye; curves a, b, c, and d refer to 0.035 mg., 0.00017 mg., 0.275 mg., and 0.825 mg., respectively, of erythrosin per cubic centimeter of solution, while curves e and f refer to 0.0364 mg. and 0.0018 mg., respectively, of chrysoidine per cubic centimeter of solution. It will be noticed that the rise of E.M.F. is rapid at first, then becomes comparatively slow, and finally reaches a saturation value. This saturation P.D. is determined by the concentration of the dye and the color and intensity of the exciting light. The gradual rise of E.M.F. on illumination is in accord with the concept of diffusion of activated molecules to the electrode, a process obeying a law similar to the curves of figure 1. Again, the disappearance of the photopotential on cutting off the illumination (cf. curve c) is a much slower process than the building up. Both erythrosin and chrysoidine exhibit this behavior in all concentrations. (Only one curve has been shown for convenience.) Another interesting feature of the curves of figure 1 is that the maximum potential is reached sooner in dilute solutions. Such a behavior is also explained easily on the diffusion theory, since with a decrease in the concentration of the dye more and more of the active radiation is transmitted to the molecules contiguous to the electrode, thus reducing the diffusion path. Secondly, decreased viscosity effects at smaller concentrations of the dye may also tend to accelerate the diffusion of the activated molecules. Further evidence in support of this hypothesis was obtained in this way. By slightly altering the position of the electrode the attainment of the maximum potential could be either retarded or accelerated.

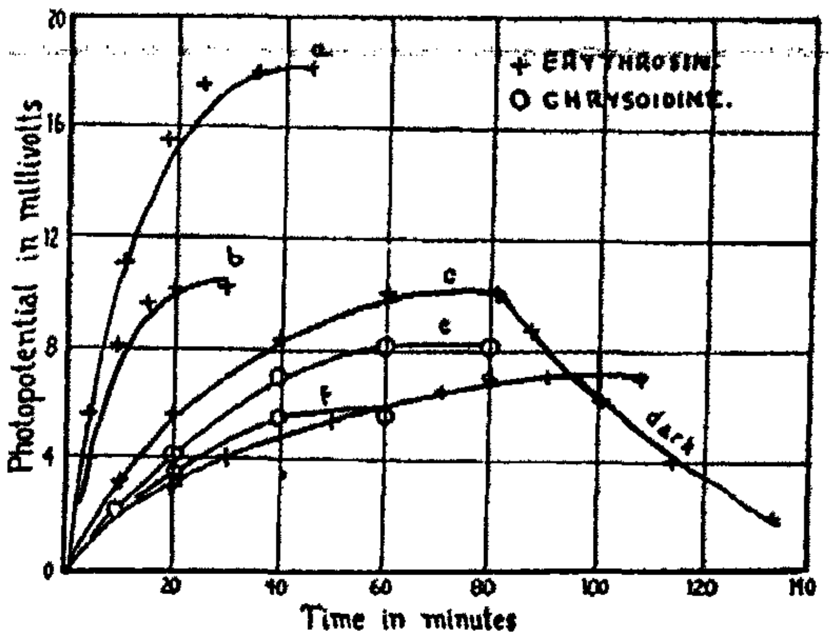

FIG. 1

PHOTOPOTENTIAL AND CONCENTRATION OF DYE

The variation of the maximum potential with the concentration of the dye in solution is shown in curves E_1 and C_R of figure 2 for erythrosin and chrysoidine, respectively, in the composite light of the mercury arc lamp. For convenience the concentration of the dye is plotted on a logarithmic scale. Curves E_2 and E_3, giving the maximum potential developed by erythrosin solutions in the light of the mercury arc after passing through a green and yellow filter, respectively, are of some interest. While in more concentrated solutions green light is more active, in dilute solutions yellow light develops higher potentials. This difference probably arises from a difference in the extinction coefficients of the dye for the two kinds of light.

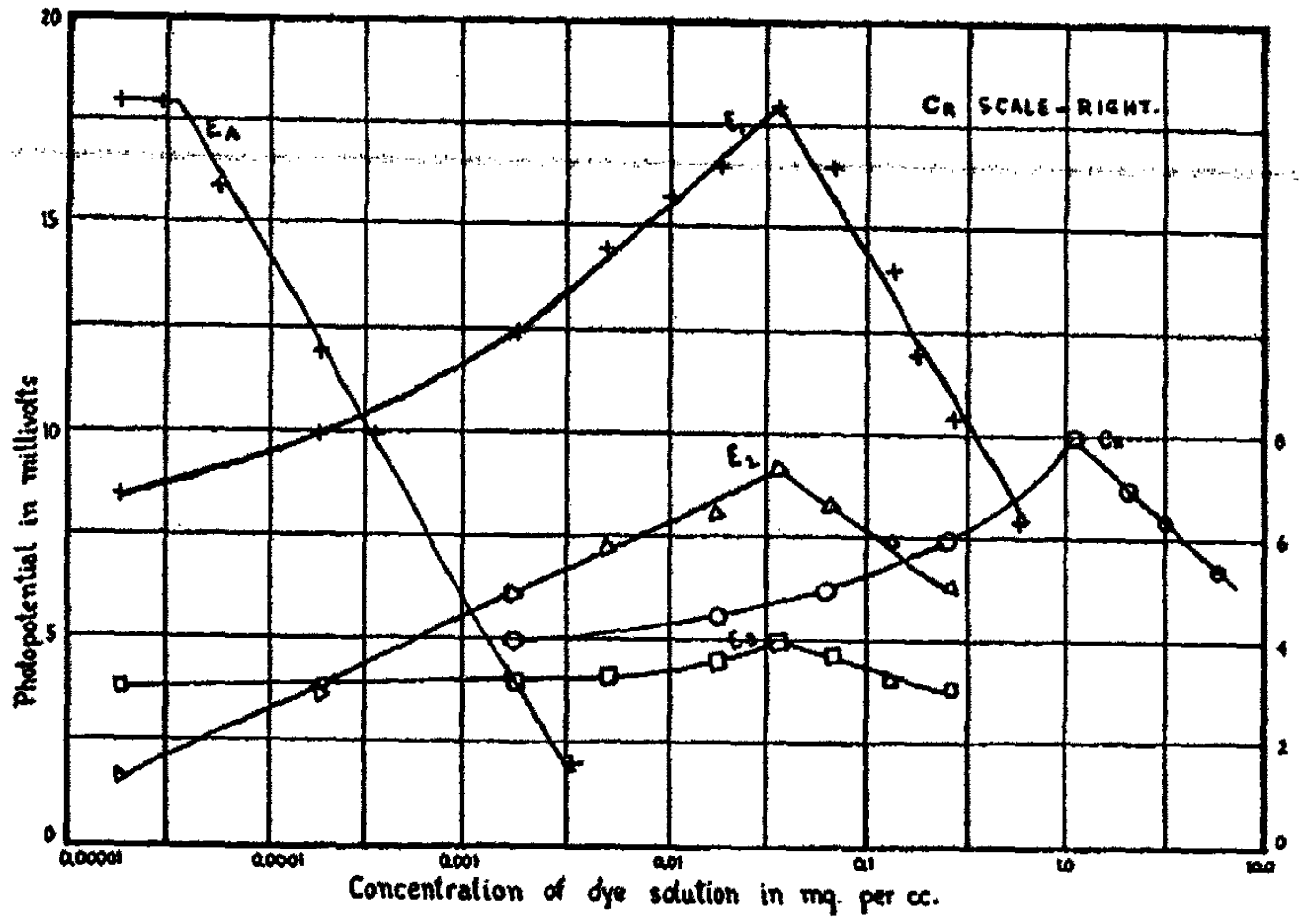

FIG. 2

Another feature of the curves E (1, 2, and 3) is that the maximum in the potential occurs at the same concentration of the dye solution irrespective of the nature of the exciting light. Still another characteristic of the curves of figure 2 (excepting E_A which will be discussed later) is that after the maximum potential has been reached, the fall of potential thereafter proceeds directly as the logarithm of the concentration of the dye solution. The same cannot be said however of the potential rise. The fall of E.M.F. with increasing concentration of the dye is most probably due to increasing absorption of the active radiation in layers immediately after the glass wall of the cell. Lowry (6) has shown by eliminating the presence of a thick absorption layer in front of the electrode that the potential-concentration curve exhibits no maximum, but that the potential merely tends to a saturation value. Of interest in this connection are the results of some experiments in which the exciting light traversed a column 4 cm. long of the dye solution of various concentrations in a separate absorption cell before being incident on the photo-cell. The photo-cell liquid contained 0.035 mg. of the dye erythrosin per cubic centimeter of solution corresponding to the optimum concentration. Curve E_A of figure 2 depicts these results, in which the maximum photopotential developed by the photo-cell is plotted against the concentration of the absorbing liquid. E_A and the descending part of E_1 are parallel to each other, pointing to a parallelism between the two mechanisms.

PHOTOPOTENTIAL AND INTENSITY OF LIGHT

The dependence of the maximum photopotential on the intensity of the incident light was next investigated in a cell containing the optimum concentration of the dye solution. Variations in intensity of the light were produced by interposing in its path neutral tint screens of known transmission. The results are shown in figure 3. Curve a refers to erythrosine and curve b to chrysoidine. It will be noticed that with both dyes the photopotential reaches a saturation value at higher light intensities. In curves a′ and b′ the photo-E.M.F.'s are plotted as functions of the square root of the intensity. The linear course of these curves is in agreement with the deductions of Ghosh (3).

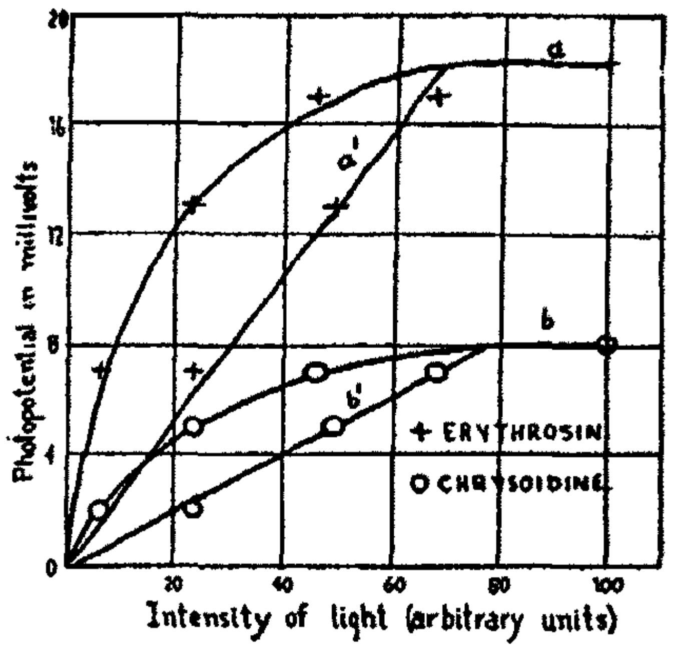

FIG. 3

PHOTOPOTENTIAL AND WAVELENGTH OF LIGHT

The next point of interest was the location of the spectral region most active in producing the P.D. The qualitative experiments in yellow and green light recorded previously are of no use, since the transmission powers of the filters are not known. Therefore the light from the arc was filtered through Wratten light filters; Nos. 26, 22, 12, and 35 appeared most suitable. Of these No. 26 cuts off sharply at 600μμ and transmits about 70 to 75 per cent of the very feeble orange lines of the mercury arc. No. 22 transmits 70 per cent of the yellow lines at 579 μμ, while No. 12 allows to pass through 73 per cent of the green line and 75 per cent of the yellow lines. No. 35 cuts off all the ultra-violet up to 340 μμ and the visible beyond 460 μμ. The transmission of this filter is about 27.5 per cent of the line at 365, 56 per cent of that at 405, and again only 27.5 per cent at 436 μμ. This is indeed a very wide band, but sufficiently narrow to show the comparative activity of the shorter wavelengths. The results are shown in table 1.

Since the distribution of energy in the mercury arc is very different for the different wavelengths, in order to compare the activities of the various spectral bands it is necessary to know this energy distribution. Bensley (2) has measured this in an arc of the same type and working under similar conditions of current and voltage. He gives the following values for the energy of the different lines in the mercury arc spectrum. In addition there is present the luminous background of the arc; since this is very feeble, appreciable errors will not be introduced by neglecting it.

TABLE 1

Activity of different regions of the spectrum in producing photopotentials

FILTER	PHOTOPOTENTIAL	
	Erythrosin	Chrysoidine
	mv.	*mv.*
No. 26	1.5	0
No. 22	9.0	1.4
No. 12	11.4	5.0
No. 35	6.0	2.0
Composite light	18.3	7.8

Energy distribution in the K.B.B. mercury arc—horizontal type, current 2 amperes, voltage 85.

Wave-length	*Energy in arbitrary units*
577–9	13
546	19
404–8	2.5
366	9

By taking into account this unequal distribution and variation of photopotential with intensity illustrated in figure 3, the transmission factors of the Wratten filters employed, the values given in table 2 are calculated for the activity of the different regions of the spectrum in producing the photopotentials. Before discussing these values further it is advantageous to consider the absorption of the dyes. Erythrosin in water shows very slight absorption at 360μμ followed by strong absorption between 455 and 562μμ with a maximum at 518μμ and is transparent from 562 to 630μμ, while chrysoidine is transparent from 330 to 360μμ and from 540 to 630μμ with a pair of unseparated bands in the region 360 to 540μμ (10). It is clear from a comparison of the data for photovoltaic activity with the absorption of the dye, that the maximum potential is induced by regions of the spectrum immediately following the long wavelength limit of the absorption band, both in the case of erythrosin and chrysoidine. Further, erythrosin is known to sensitize the photographic plate to wavelengths up to 600μμ with a pronounced maximum in the neighborhood of 580μμ (1). The conclusion therefore seems to be reasonable that the same factors come into play both in exciting photopotentials and in optical sensitization.

TABLE 2

Calculated activity of different regions of the spectrum in producing photopotentials

WAVELENGTH	CALCULATED PHOTOPOTENTIAL	
	Erythrosin	Chrysoidine
	mv.	*mv.*
615μμ	3.2	0
577–9μμ	20.0	2.7
546μμ	15.2	12.0
<436μμ	10.0	4.2
Composite light	18.3	7.8

SUMMARY

From a study of the photovoltaic effects in aqueous solutions of erythrosin and chrysoidine, it is shown that:

1. The usually observed maximum in the potential-concentration curve is to be attributed to the absorption of the active radiation in the column of the electrolyte in front of the electrode.
2. The photopotential varies directly as the square root of the intensity of light.
3. Wavelengths immediately following the long wave limit of the absorption band of the dye are most active in producing these potentials.

My best thanks are due to Professor H. E. Watson for continued help and guidance. The greater part of this work was carried out in the General Chemistry Department of the Indian Institute of Science, Bangalore.

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THE COMPLEXES OF MANNITOL AND SORBITOL WITH SODIUM ARSENITE AND BORAX

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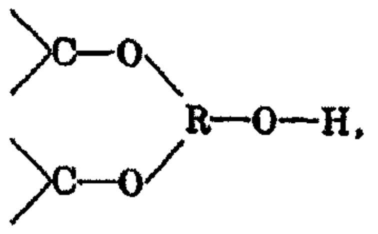
It is known that boric acid, on addition to polyhydric alcohols, enhances their optical rotation and suffers an increase in acidity (5, 8, 14, 20). These properties have been utilized for the estimation of mannitol (17), and for the titrimetric determination of boric acid (13).

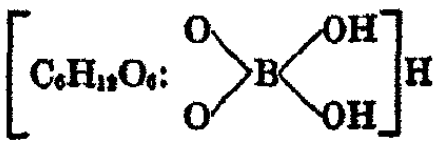
~~van't Hoff (19) assumes in this reaction the formation of a complex~~ having the cyclic grouping



where R represents the inorganic constituent. Magnanini (15) by conductivity measurements supports the formation of a compound from one molecule of mannitol and three of boric acid, while, according to Ageno and Elena Valla (1) the ratio of mannitol to boric acid is 1:1. Fox and Gauge (9) claim to have isolated mannito-boric acid as a definite compound.

The work of Böeseken and his coworkers at Delft for the past twenty years has revealed that this property is more generally shared by a large number of polyhydroxy compounds. The ease with which these boric acid–diol complexes are formed is dependent on the positions of the hydroxyl groups, the most favored configuration being the situation of the two hydroxyl groups in the same plane and on the same side of the carbon atoms to which they are bound (4). Irvine and Steele (12) support the findings of Böeseken by a study of electrical conductivity and specific rotation of the methylated mannitols. Dubrisay (6) indicates compound formation between boric acid and mannitol, by measuring the optical rotation and surface tension of the system, as also the critical solution temperature of phenol and water in presence of the complex.

The possibility of boric acid and its salts forming more than one complex with mannitol is shown by the work of Grün and Nossowitsch (11) and by Gilmour (10) from optical rotation data. The last-mentioned author obtains a maximum rotation of 37.6° by treating sodium mannitoborate and sodium metaborate in molecular proportions. Thus is explained the exaltation of rotation on mannitol from 22.5° (Vignon) to 28.3° (Fischer) under the influence of an excess of borax. The theory of ring structures of the boric acid complexes first suggested by van't Hoff and later adopted by Böeseken, is extended in the work of Meülenhoff (16) who ascribes to the boric acid complex of mannitol the formula



Bancroft and Davis (3), however, in a paper on "The Boric Acid Problem" doubt the compound formation between boric acid and organic hydroxy bodies, and attribute the enhanced acidity of boric acid to its increased dissociation in presence of the organic compounds dissolved therein, while the change in optical rotation is explained by "the abnormal effect of boric acid solutions."

Besides borax, sodium arsenite also induces dextrorotation (Vignon (20)), providing a method for the estimation of mannitol (2). In a solution in which the ratio of arsenious acid to mannitol is not less than 17.5, the specific rotation of the hexitol is 46.53°. From a study of the increase in solubility and neutralization values of arsenious acid in presence of mannitol, sorbitol, and other polyhydroxy compounds, Englund (7) has postulated that this acid forms with hydroxy bodies compounds similar to those formed by boric acid.

In spite of the large number of physicochemical measurements like optical rotation, electrical conductivity, hydrogen-ion concentration, solubility, and phase study, that have been applied to reveal the nature of combination of boric acid and arsenious acids with mannitol and other polyhydroxy compounds, the question remains yet unsettled. The measurement of volume changes, should they accompany the formation of these "complexes," would throw new light on the problem. The present communication relates to a dilatometric investigation of the complexes of mannitol and sorbitol with sodium arsenite and borax.

MATERIALS AND METHODS

The dilatometer devised by Sreenivasaya and Sreerangachar (18) was used in these investigations, as being best suited for the study of reactions in which the equilibrium is attained almost immediately when the reacting components are mixed. All dilatometric measurements were made at 30°C. in a thermostat. A triple shade polarimeter illuminated by a mercury arc was employed for determining the optical rotations in a 200-mm. tube at room temperature (27°C. ±1.0°C.).

d-Mannitol and *d*-sorbitol (B.D.H. products) were recrystallized from water, samples dried at 100°C., and kept in a vacuum desiccator over phosphorus pentoxide. Solutions of these were prepared by dissolving weighed amounts of the substance in distilled water and made to volume. Arsenite solutions were prepared by boiling 198 g. of arsenious oxide with 132.5 g. of sodium carbonate, and the solution was made up to a liter (2). The strength of arsenite solution was determined iodometrically. Borax solutions saturated at 30°C. were used, the amount of dissolved borax ($Na_2B_4O_7 \cdot 10H_2O$) being estimated by acidimetric and alkalimetric titrations.

TABLE 1

Dilatometers and reaction mixtures

DILATOMETER	REACTION MIXTURE	
	Small bulb	Big bulb
Control	5 cc. of water	50 cc. of arsenite or borax solution
Experimental	5 cc. of mannitol or sorbitol solution	50 cc. of arsenite or borax solution

TABLE 2

Mannitol–arsenite

EXPERIMENT	MOLES OF ARSENITE PER GRAM-MOLE OF MANNITOL	DILATOMETRIC RISE	VOLUME INCREASE PER GRAM-MOLE OF MANNITOL	OBSERVED ROTATION $[\alpha]^{27^\circ}_{5461}$	[M]
		cm.	*cc.*		
1	0.0	—	—	—	—
2	2.4	9.1	8.05	0.26	45.88
3	4.8	12.9	10.52	0.36	63.53
4	7.2	13.8	12.14	0.39	68.84
5	9.6	14.3	12.53	0.41	72.36
6	19.2	17.3	15.22	0.49	86.48
7	24.0	17.3	15.22	0.49	86.48

The dilatometers and the reaction mixtures used were as given in table 1. As large quantities of arsenite or borax are necessary to react with a definite amount of sugar alcohol, the big bulb always received the inorganic salt solution, while the hexitol occupied the small one. The details of the experimental procedure were those followed in a previous communication (18). On mixing the solutions, one observes a depression in the control dilatometric column due to dilution of the salt solution, the order of depression depending on the strength of arsenite or borax solution used. But the experimental dilatometer treated as above records a definite rise. The equilibrium is attained within fifteen minutes, when the final readings of the dilatometers are taken. The difference between the readings of the two dilatometers is a measure of the volume change accompanying the formation of the complex. The solutions are finally polarized. The whole operation takes one and a half hours.

TABLE 3

Mannitol-borax ($Na_2B_4O_7 \cdot 10\ H_2O$)

EXPERIMENT	MOLES OF BORAX PER GRAM-MOLE OF MANNITOL	DILATOMETRIC RISE	VOLUME INCREASE PER GRAM-MOLE OF MANNITOL	OBSERVED ROTATION $[\alpha]^{27°}_{5461}$	[M]
		cm.	*cc.*		
1	0.0	—	—	—	—
2	0.5	16.6	16.47	0.20	39.73
3	1.0	17.5	17.34	0.22	43.7
4	1.5	18.2	18.03	0.23	45.68
5	2.0	19.1	18.92	0.25	47.67
6	2.5	19.5	19.32	0.25	49.66
7	3.3	19.7	19.52	0.28	49.66
8	5.0	20.2	20.02	0.25	49.66
9	7.5	21.0	20.81	0.26	51.65
10	10.0	21.0	20.81	0.26	51.65

TABLE 4

Mannitol-arsenite

EXPERIMENT	MANNITOL	DILATOMETRIC RISE	DILATATION CONSTANT (*V*)	OBSERVED ROTATION $[\alpha]^{27°}_{5461}$	$[\alpha]^{27}_{D}$
	mg.	*cm.*	*cc.*		
1	72.7	4.95	15.24	0.14	47.15
2	87.8	5.95	15.17	0.17	47.71
3	122.1	8.30	15.21	0.23	46.41
4	162.5	11.05	15.22	0.31	47.02
5	254.2	17.30	15.22	0.49	47.51
Mean.			15.21		47.22

RESULTS

"*Complexes*" *of mannitol*

Preliminary experiments were conducted to study the effect of adding increasing quantities of arsenite and borax to a given quantity of mannitol. Five cc. of 5 per cent mannitol and 50 cc. of arsenite or borax solutions of varying concentrations (prepared from the standard stock solutions by dilution) were used. The results are given in tables 2 and 3 and represented graphically in figure 1.

The above results show that the dilatometric change and optical rotation reach a steady maximum, beyond which further additions of arsenite or borax are no more accompanied by increases either in volume or in optical activity. To bring about this maximum change, about 19.2 moles of arsenite (see reference 2) or 7.5 moles of borax (decahydrate) per gram-mole of mannitol is found necessary. Further, this maximum corresponds to a volume increase of 15.22 cc. with arsenite and 20.81 cc. with borax per gram-mole of mannitol.

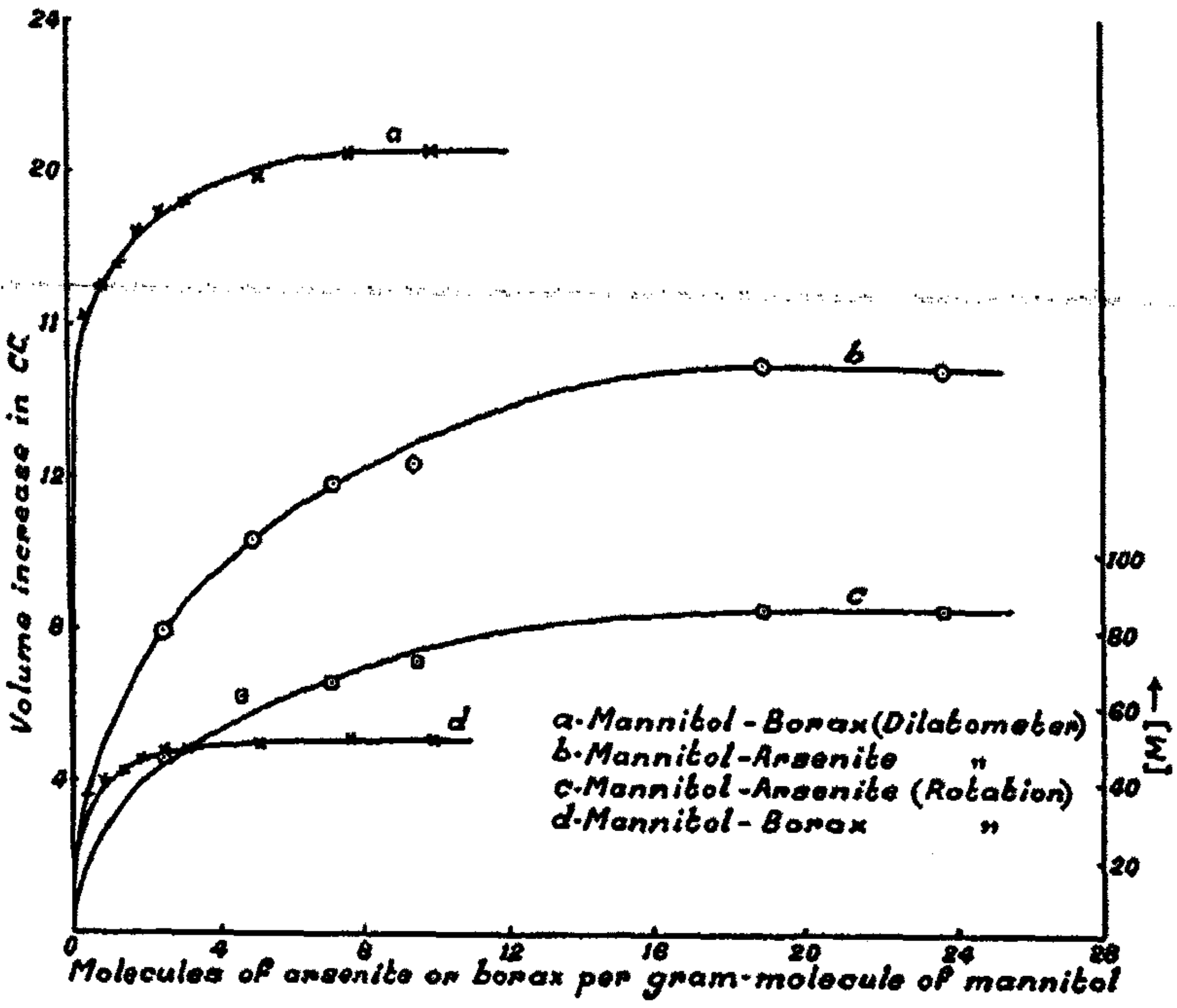


FIG. 1

The experiments were repeated with varying concentrations of the sugar alcohol and calculated amounts of arsenite and borax to induce maximum changes, and the results, incorporated in tables 4 and 5 and figure 2, confirm the above findings.

"*Complexes*" *of sorbitol*

A dilatometric study of the sorbitol–arsenite and sorbitol–borax systems has given the results embodied in table 6 and figure 2. It will be seen that the dilatation constants per gram-mole of sorbitol are 16.93 cc. and 22.38 cc. with arsenite and borax, respectively.

ACCURACY OF THE METHODS

Table 7 gives the dilatometric and polarimetric readings (taken from the previous tables) and their errors corresponding to maximum and minimum amounts of mannitol.

DISCUSSION

On mixing solutions of mannitol and sorbitol with a solution of either arsenite or borax, there occurs an appreciable increase in volume corresponding to the exaltation in optical activity (tables 2 and 3 and figure 1). This volume change observed in the case of the two hexitols is a new property found to accompany the formation of the "complexes."

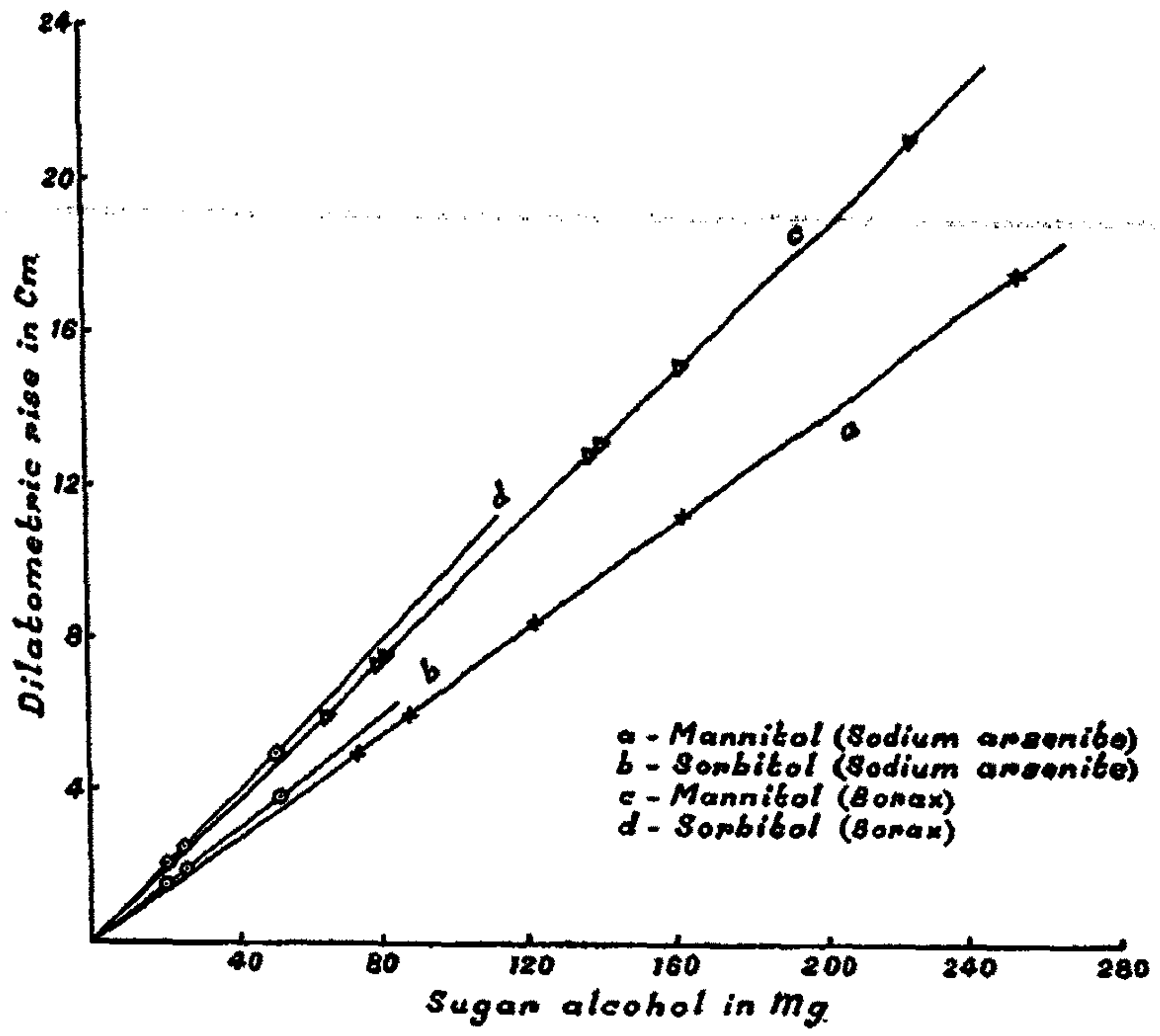


FIG. 2

A strict proportionality exists between volume change and the amounts of mannitol and sorbitol forming the complex (tables 4, 5, and 6 and figure 2).

As compared with the polarimetric estimation of mannitol or sorbitol now adopted, the dilatometric method offers a more convenient mode of determination, ensuring greater accuracy. Table 7 gives the errors in estimating mannitol in two concentrations by the two methods. It will be seen that the error in the dilatometric estimation is about 0.2 to 1 per

TABLE 5

Mannitol-borax

EXPERIMENT	MANNITOL	DILATOMETRIC RISE	DILATATION CONSTANT (*V*)	OBSERVED ROTATION $[\alpha]^{27°}_{5461}$	$[\alpha]^{27°}_{D}$
	mg.	*cm.*	*cc.*		
1	65.00	6.05	20.83	0.08	30.33
2	79.20	7.39	20.87	0.09	27.80
3	81.25	7.55	20.80	0.10	30.33
4	138.00	12.86	20.77	0.16	28.57
5	140.00	13.10	20.81	0.16	28.16
6	162.50	15.15	20.85	0.19	28.82
7	225.80	21.00	20.81	0.26	28.38
Mean.			20.82		28.91

TABLE 6

Sorbitol-arsenite and sorbitol-borax

EXPERIMENT	SORBITOL	ARSENITE		BORAX	
		Dilatometric rise	Dilatation constant (*V*)	Dilatometric rise	Dilatation constant (*V*)
	mg.	*cm.*	*cc.*	*cm.*	*cc.*
1	20	1.5	16.78	2.0	22.38
2	25	1.9	17.00	2.5	22.38
3	50	3.8	17.00	5.0	22.38
Mean.			16.93		22.38

TABLE 7

Accuracy of the methods

	MANNITOL	DILATOMETRIC			POLARIMETRIC		
		Reading	Error in reading	Error	Reading	Error in reading	Error
	mg.	*mm.*	*mm.*	*per cent*	*degrees*	*degrees*	*per cent*
Arsenite.	72.7	49.5	±0.5	±1.0	0.14	±0.01	±7.0
	254.2	173.0	±0.5	0.3	0.49	±0.01	2.0
Borax.	65.0	60.5	±0.5	0.8	0.08	±0.01	12.5
	225.8	210.0	±0.5	0.2	0.27	±0.01	3.7

cent, while the polarimetric method involves an error of about 2 to 12.5 per cent, which gets considerably multiplied if the test solutions happen to be colored. This limitation does not affect dilatometric estimations.

Since the volume change per gram-mole of mannitol or sorbitol is greater with borax than with arsenite, borax complexes are to be preferred for the dilatometric estimation of these sugar alcohols.

The dilatometric data obtained in this investigation strongly point to the existence of a definite compound in the systems studied. Solutions of arsenite or borax which suffer a decrease in volume on dilution with water (shown by controls) should undergo further decrease on mixing with mannitol or sorbitol solutions, if it is only a question of enhanced electrical conductivity, according to Bancroft and Davis (3). On the other hand, a definite increase in volume on mixing the two solutions has been recorded in all the experiments. Further, mannitol and sorbitol (at the concentrations used) do not register any volume change on mixing with water. Hence the dilatometric changes are more the characteristics of the formation of a new entity than the additive behavior of the preëxisting constituents. These, along with the strict proportionality found to hold between the volume increase and the amounts of hexitol reacting, point to the formation of a compound as shown by Böeseken in the course of his extensive researches.

SUMMARY

1. The formation of the "complexes" of mannitol and sorbitol with sodium arsenite and borax has been investigated in the dilatometer and also followed by polarimetric estimations in the case of mannitol.

2. The reaction is accompanied by appreciable increases of volume, which correspond to 15.21 cc. and 20.82 cc. at 30°C. per gram-mole of mannitol with arsenite and borax, respectively. The corresponding dilatation constants for sorbitol are 16.93 cc. and 22.38 cc.

3. The dilatation constants of the hexitols being higher with borax than with arsenite, borax complexes have to be preferred for the dilatometric estimation of these hexitols. It is shown that this method is more convenient and accurate than the polarimetric one now in vogue.

4. The volume expansions attending the "complex" formation and their definite relationship to the concentration of mannitol and sorbitol, suggest the formation of compounds as shown by Böeseken.

In conclusion, one of us wishes to thank the Government of Madras for the award of a scholarship that has enabled him to pursue this investigation.

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NEW BOOKS

Mass-spectra and Isotopes. By F. W. Aston. 248 pp. New York: Longmans, Green and Co., 1933. Price: $4.80.

The present volume replaces the earlier well-known monograph of the author published by the same company under the title "Isotopes" (second edition, 1924). In expanding the title the author has sought to restrict the scope of the book somewhat, though its length has necessarily increased with the expansion of the experimental material and of its theoretical significance.

A very welcome part of the new book gives a detailed account of the construction of the new focusing mass-spectrograph and of the theory and practice of its use. The more accurate values of the relative mass of individual atoms have shown definitely the departure from the whole number rule and have established the highly important "packing fractions" for most elements and the general shape of the curve as a function of atomic mass.

As sixty-six of the possible eighty-four elements have now been subjected to isotopic analysis, the statistics have a broad significance. Only twenty simple elements have been found, and no element of odd atomic number has been found to have more than two isotopes. Two very interesting chapters on the isotopic effect in molecular and atomic spectra have been added.

As we have just entered on new and highly interesting phases of nuclear transmutation, Aston's packing fractions are an indispensable guide in the calculation of the interchange of mass and energy.

S. C. Lind.

Modern Thermodynamics by the Methods of Willard Gibbs. By E. A. Guggenheim. xvi + 206 pp.; 10 figures. London: Methuen and Co., Ltd., 1933. Price: $3.50.

This book can be heartily commended to the attention of teachers and advanced students of thermodynamics. That it is not written for the beginner is evident from the fact that the author pays scant attention to the experimental basis and physical significance of the first and second laws, contenting himself with advising the reader to make himself familiar with the treatment in Planck's "Thermodynamics."

The theorems of thermodynamics are developed in a logical way, the mathematical method employed being the straightforward, analytic one. The author quite rightly criticizes the "method of cycles" on the ground that when it is simple it is usually inexact and when it is exact, it is usually complicated. The author must also be commended for employing, as Gibbs did, the illuminating term, "chemical potential," in place of the verbose expression, "the partial molal free energy." A very valuable feature of the book is the author's treatment of activities and activity coefficients. The serious student will find especially helpful the chapters on electrochemical systems, gravitational field and surface phases.

F. H. MacDougall.

Fundamentals of Biochemistry in Relation to Human Physiology (Fourth Edition). By T. R. Parsons. 12 x 18.5 cm.; 435 pp.; 26 figures. Cambridge: W. Heffer and Sons, Ltd., 1933. Baltimore: William Wood & Company, 1933. Price: $3.00.

The emphasis of this book is on *fundamentals.* In automobile parlance it is the stripped and cut-away chassis delineating the biochemical reactions characteristic of the vital processes of the human organism.

The book is written in an extremely "human," almost conversational, style and reads as though the author were sitting across the table from you and confidentially telling you (a novice) of the wonderful chemical mechanisms operating within your body. In fulfilling this purpose the author is admirably successful. The reader needs only a minimum amount of chemical background to profit by the reading of this book. Even a good course in high school chemistry should be sufficient.

The book is thoroughly up to date and should prove of great value to the individual who wishes to acquaint himself with the essentials of animal biochemistry. It is also recommended for use in introductory courses in medical schools, for nurses, or similar groups of students.

Certain physicochemical phases of physiology are considered in chapters XVIII and XIX (pp. 327-403). Here again extremely graphic illustrations are used. For example, in speaking of hydrogen-ion concentration and bodily reactions we read "Human life as a whole is like this. Let the blood become ever so slightly acid—not even as acid as distilled water that has absorbed a trace of CO_2 from the atmosphere—and the patient dies in coma; let it become even so faintly alkaline as tap water is, and the subject goes into tetany. Between these two limits we have all our lives to try to steer a middle course." . . . . "these two extremes do not differ from each other by as much as a millionth of a gram of hydrogen ions per litre of blood!"

Each chapter has appended a list of literature citations so that the interested reader can follow up in detail such items as he wishes to pursue past the rather elementary treatment of the text.

Ross Aiken Gortner.

Hydrides of Boron and Silicon. By Alfred Stock. 250 pp.; 36 figures. Ithaca, N. Y.: Cornell University Press, 1933. Price: $2.00.

This volume contains a portion of the subject matter of the George Fisher Baker Non-resident Lectures in Chemistry, given by Professor Stock at Cornell University in the spring of 1932. The work for the last thirty years on hydrides by Professor Stock and his coworkers is so well known that it hardly needs comment. In the present volume these excellent researches are summarized and presented in masterly fashion. Every chemist should read this volume. The ingenuity and patience shown in the execution of the experiments move one to admiration. The importance of the boron hydride problem for valency theory cannot be overestimated. This problem has special significance in the development of our ideas of chemical bonds. Main Smith has said: "These compounds of boron must be regarded as a decisive test of any theory of valency." Any theory of valency which cannot explain the structure of the hydrides of boron in a logical and self-consistent manner is doomed to failure. It is obvious then that the volume before us is one of the very important additions to the literature of chemistry.

The material is divided into thirty-two chapters. The individual hydrides are described carefully and methodically in separate sections. For cross-reference one finds complete chapters on the important reactions of these compounds. The investigator and reader desirous of looking up any certain point can find the information with the greatest ease. The apparatus used and especially developed for these researches is described fully in a special appendix. Here a warning regarding mercury poisoning is included. It is well known that Professor Stock has taken a leading position in advising research workers to use greater care in the handling of exposed mercury. The theoretical problem of the structure of these hydrides is treated fully in four of the chapters. Literature references are given in great detail. The physical make-up of the book is excellent.

It has been a great pleasure and a privilege to the writer to have had the opportunity of reviewing this splendid treatise.

GEO. BLOCKLER.

Abridged Scientific Publications from the Kodak Research Laboratories (Volume XV, 1931–1932). Rochester, N. Y.: Eastman Kodak Company, 1933.

This volume contains complete and readily understandable summaries of sixty-one papers which have been published in a variety of journals. The subject matter of the articles varies from the description of technical procedures of interest to commercial photographers to the presentation and discussion of experimental results of importance to theoretical photochemists and physical chemists. The typography and the reproduction of illustrations are excellent.

ROBERT LIVINGSTON.

Introduction to Physical Chemistry. By ALEXANDER FINDLAY. 21 x 14 cm.; vi + 492 pp. London: Longmans, Green and Co., 1933. Price 7s. 6d. 4

Any book from the pen of such an experienced and competent writer as Professor Findlay is certain to have a number of outstanding qualities, and the present work is no exception. The author is of the opinion that the historical method of treatment is the one which is most sound educationally and this has been adopted successfully in the book under review; the student will read that Cailletet was an ironmaster and Joule a brewer, and these human touches should lend interest to his studies! All the subjects normally included in an introductory course of physical chemistry are discussed in an up-to-date manner: the activity concept finds frequent reference and the Lewis and Randall symbols are used in connection with the first and second laws of thermodynamics; in the brief treatment of the Nernst heat theorem, however, the German symbols have been used. A few minor errors have been noted, but the only one likely to be misleading is the statement (p. 231) that "In the ammonia equilibrium . . . . the equilibrium *constant varies* inversely as the square of the pressure." (The italics are the reviewer's.) The book, which concludes with an appendix containing some one hundred and fifty numerical problems, is worthy of consideration by all teachers of physical chemistry.

S. GLASSTONE.

Laboratory Experiments in Organic Chemistry. By ADAMS AND JOHNSON. Revised edition. xiii + 363 pp. New York: The MacMillan Company, 1933. Price: $1.90. 3

This is a new edition of the authors' laboratory manual, first printed in 1928. The new edition retains all of the distinctive features of the old one, and, in addition there has been considerable expansion—sixteen new experiments being included. The expansion considerably improves the book and places it in the first rank as a laboratory manual, for either the short or long courses. The list of supplementary experiments, somewhat more difficult than the average of those in the body of the text, is well selected. The printing and binding are excellent.

LEE IRVIN SMITH.

The Chemistry of Organic Compounds. By JAMES B. CONANT. x + 623 pp. New York: The MacMillan Company, 1933. Price: $4.00. 3

This new book by Professor Conant combines a wealth of information regarding the carbon compounds with an adequate, modern theoretical treatment. In simplicity and clarity of style the book is outstanding, and this, with the excellent choice of material and orderly arrangement, makes the book very readable. The section on natural products is well done, and the reviewer is glad to see at last a text book of organic chemistry in which stereochemistry is treated so well. The printing and binding are splendidly done, and there are very few typographical errors. Altogether a fine piece of writing and book making.

Lee Irvin Smith.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. 25 x 17 cm. (a) System Nummer 8: Jod, Lieferung 2. xxiii + 245–660 pp. Price: 68.50 M (subscription price: 60 M); (b) System Nummer 59: Eisen, Teil A, Lieferung 5. xiv + 847–1166 pp. Price: 50 M (subscription price: 43.50 M). Berlin: Verlag Chemie G.m.b.H., 1933.

(a) The volume on iodine deals with hydriodic acid, the iodides of nonmetals and metals, polyhalogenides, the oxides and oxyacids of iodine, iodine fluorides, chlorides, and bromides, nitrogen iodides, and an appendix to the first part of the volume on iodine which has already appeared. In all cases the treatment is exhaustive, accurate, and critical, full numerical data, curves, and discussions of physicochemical topics being included. The literature has been very completely covered and very modern work finds its place in the treatment.

(b) The volume on iron deals with the physicochemical foundations of the technical production of malleable iron. The systems Fe–O–C, Fe–Si–O, Fe–Mn–O, Fe–P–O, Fe–S–Mn, etc., are considered. Deoxidation with manganese, carbon, silicon, aluminum, titanium and combinations of these is next dealt with. The casting of iron and steel is considered in relation to melting in crucibles, cupolas, reverberatory furnaces, Siemens-Martin furnaces, converters, and electric furnaces. The treatment of ferrous alloys includes those with manganese, chromium, molybdenum, tungsten, nickel, titanium, and vanadium. The treatment throughout is linked with technical processes and abundant references to literature are given.

The two volumes considered fully maintain the high standard of Gmelin and are unexcelled in completeness and accuracy in their field. They are very valuable contributions to the literature of chemistry.

J. R. Partington.