lecular shape among the straight-chain bromides has very little effect upon the calculated moment. The values of $g^{1/2}\mu_0$ for the more dilute solutions of chlorobenzene and *o*-dichlorobenzene are remarkably close to the gas values, but the solution values for ethyl bromide differ in no consistent manner from that for the pure liquid.

Summary

The dielectric constants at 520 kilocycles, the viscosities, and the densities not available in the literature have been measured at temperatures from 1 to 55° for twenty-seven liquid organic halides. The refractive indices for the sodium D line of the liquids have been measured at 25°.

The dielectric constants of the straight-chain alkyl bromides are a linear function of the number of dipoles per cc. of liquid.

The Onsager and Kirkwood equations have been used with some success to calculate dipole moment values from these dielectric constants and others taken from the literature The discrepancies between observed and calculated values seem to be not closely related to molecular structure.

PRINCETON, NEW JERSEY RECEIVED JULY 2, 1949

[CONTRIBUTION FROM METCALF CHEMICAL LABORATORIES, BROWN UNIVERSITY]

The Dielectric Constants of Water, Hydrogen Peroxide and Hydrogen Peroxide-Water Mixtures[1,2]

BY PAUL M. GROSS, JR.,[3] AND ROBERT C. TAYLOR[4]

I. Introduction

The dielectric constants of most polar liquids at room temperature lie below 20 but in the case of certain compounds such as water, some alcohols, hydrogen peroxide, hydrogen fluoride and a few others, much higher values are found. These high values of the dielectric constant are greatly in excess of those to be expected even for large values of the molecular dipole moments and are characteristic of liquids in which molecular orientation and short range structure exist as a result of hydrogen bonding. Inasmuch as many properties, and in particular the electrical properties, are markedly affected by such factors, an accurate knowledge of the dielectric constants is of general interest in connection with the study of associated liquids. Of this group of liquids, water has received the greatest attention, both experimentally and theoretically. Hydrogen peroxide being the liquid most closely related to water would seem to merit a corresponding amount of consideration in the study of how specific factors modify the general behavior. Unfortunately, however, the rather appreciable experimental difficulties involved in dealing with the compound have discouraged any extensive amount of work.

Only two sources of information are available in the literature concerning the dielectric constant of hydrogen peroxide. Calvert[5] in 1900 reported the dielectric constant of an aqueous (40%) hydrogen peroxide solution, while a number of years later Cuthbertson[6a] and Maass[6b] published a more extensive series of measurements at 0° for a range of concentrations varying from pure water up to 99.45% hydrogen peroxide. These latter data until now have provided the only information on the pure compound.

The dielectric constants presented in this paper cover the concentration range from 0 to 99.2% hydrogen peroxide and the temperature range from approximately −65 to 30°; data for pure hydrogen peroxide were obtained by a short extrapolation. The measurements are of moderate precision and were made mostly at a frequency of 200 Kc. using a bridge circuit of a new design. As a preliminary to the measurements on hydrogen peroxide, the dielectric constant of pure water was measured as a function of temperature with excellent agreement with the results given by Wyman.[7] The important problem of decomposition, which is always present when working with hydrogen peroxide, was overcome by selection of suitable materials and proper pretreatment.

II. Apparatus and Procedure

Apparatus.—The design, construction and residual errors of the bridge and associated equipment with which the measurements were made have been described recently by Cole and Gross[8] and will not be discussed in detail in this paper. Certain features, however, are pertinent to the experimental procedure and will be discussed briefly. The bridge design is such that admittances due to guard ring circuits have a negligible effect on the bridge balance. This important feature eliminates the second balance usually necessary when guard rings are incorporated into a cell design and greatly simplifies the measurements. One of the chief advantages resulting was that a

---

[1] This paper is based on a portion of a thesis presented by Paul M. Gross, Jr., in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, October, 1948.

[2] This work was supported in part by the Office of Naval Research under Contract N6ori-88, Task Order No. 1.

[3] Present address: Cobb Chemical Laboratory, University of Virginia, Charlottesville, Virginia.

[4] Present address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

[5] H. L. Calvert, *Ann. phys.*, [4] **1**, 483 (1900).

[6] (a) A. C. Cuthbertson and O. Maass, THIS JOURNAL, **52**, 489 (1930): (b) E. P. Linton and O. Maass, *ibid.*, **53**, 957 (1931).

[7] J. Wyman, *Phys. Rev.*, **35**, 623 (1930).

[8] R. H. Cole and P. M. Gross, Jr., *Rev. Sci. Instruments*, **20**, 252 (1949).

fixed capacitance cell holding a relatively small amount of liquid could be designed in which the measured capacitance was independent of the exact volume of liquid contained, and the dielectric constant is simply the ratio of capacitances of the cell when filled and empty. In the measurements, the capacitance of the cell appears in the conventional way as the change in capacitance of a parallel bridge condenser as the cell is switched in and out of the circuit. Conductance measurements could be made simultaneously although these data were of secondary interest in the present investigation.

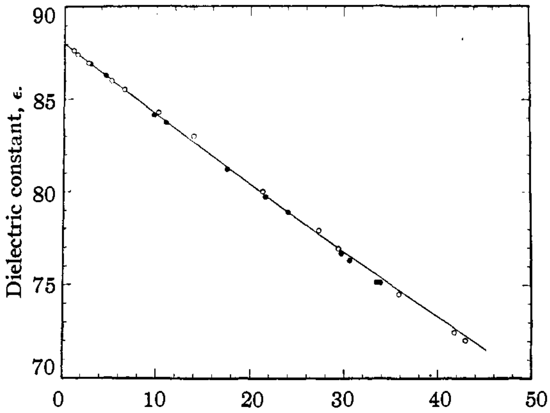


Fig. 1.—Dielectric constants of water: —, Wyman; ○, run 1; ◎, run 2.

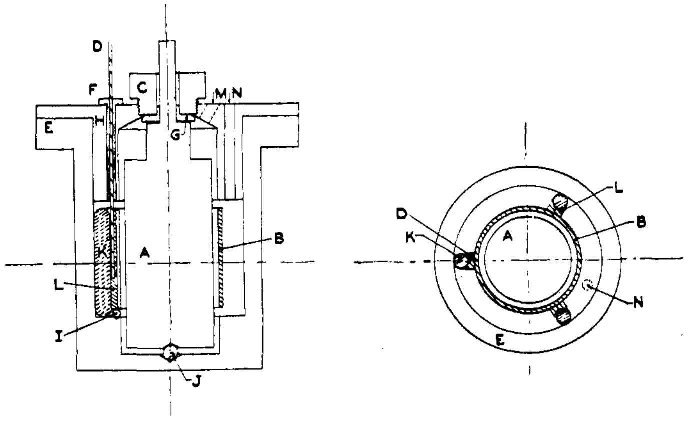
Since the equipment had been constructed immediately prior to the start of this work, it was desirable to test its performance on a system for which accurate data are available. Water was the logical choice since its properties are very similar to the solutions contemplated for study. Inasmuch as the cell could not be closed tightly to the air, equilibrium conductivity water was used. The values of the dielectric constant obtained as a function of temperature are shown graphically in Fig. 1 and are compared with the empirical curve given by Wyman[7]; for the most part, the deviation of the points from the curve is less than 0.2%. The excellent agreement indicates that sources of error frequently encountered in bridge measurements had a negligible effect in the present design. Other tests made during the course of the measurements illustrated the effect of frequency and cell conductivity on the measured dielectric constant. For example, variation of the frequency from 100 kilocycles to 1.5 megacycles produced no detectable change in the bridge balance with 97% peroxide in the cell.[9]

The effect of cell conductivity *per se* on capacitance data is illustrated by a second example in which shunting the cell by a conductance of 2.5×10^{-4} reciprocal ohm changed the measured dielectric constant of the liquid in the cell from 94.3 to 94.4 or about 0.1%. This change in value was very close to the precision of the measurements. No solution conductance this high was encountered in the actual measurements.

The cell was thermostated in a large silvered Dewar flask containing isopropyl alcohol. After equilibrium had been established following each temperature change, the bridge was balanced and the temperature of the sample determined immediately afterwards by a calibrated copper–constantan thermocouple and a Leeds and Northrup type K potentiometer.

Cell Construction and Pretreatment.—Since many of the customary construction materials such as brass, platinum, gold, etc., act as decomposition catalysts for hydrogen peroxide, a series of preliminary tests were necessary to enable a suitable selection to be made. Of the various metals and alloys tested, a type 304 stainless steel with the composition 0.08% C, 18% Cr, 8% Ni and 74% Fe was finally selected as representing the best compromise between factors of low catalytic activity, availability, strength, good machining characteristics and ease of polishing. For insulation, du Pont "Teflon," which also exhibited low catalytic activity, was used.

A diagram of the cell is given in Fig. 2. The high potential electrode, A, is a small cylinder 0.75 inch in diameter and whose main body is 1.875 inches long. It is centered and insulated at the bottom by means of the fused quartz ball, J. The low potential electrode, B, has an inside diameter of one inch and a length of one inch. As an aid in centering, B was milled out of a piece of solid rod in such a way that three grooved lugs, L, were left symmetrically spaced on the outer circumference of the electrode. The electrode is held in position by compression using clear quartz rods, K, between the lugs and the outside container, E. To prevent vertical slippage, three small quartz balls, I, are placed in recesses on the ledge of the outer shell, E, directly below each of the lugs. The body of the cell, E, is kept at ground potential and is constructed so as to perform the function of a guard ring. The part, H, which serves as the upper guard ring is machined so that it fits tightly down into E as shown and is bolted to E. The gaps between the low potential electrode, B, and the guard rings, E and H, are about 0.1 of an inch. The high potential electrode is held at the top by the nut, C, and the "Teflon" insulator, G. The low potential lead, D, is also insulated by a "Teflon" tube, F. To fill the cell, the hole, M, is used, while a thermocouple in a thin glass sheath is inserted through N so as to be in direct contact with the liquid in the cell. In practice, the cell is placed inside a close fitting capped brass container about twice the length of the cell to prevent condensation on the external leads while cold.



Vertical section Cross section

Fig. 2.—Dielectric constant cell.

Mechanical polishing of the stainless steel used in the cell proved unsatisfactory as very small particles of the polishing agent were always left embedded in the metal surface. A variety of electrolytic polishing solutions were therefore tried and a modification of the procedure described by Uhlig[10] was found to give the most satisfactory result. The solution was made up by weight of 47% glycerol, 42% H_3PO_4 (reagent 85%) and 11% distilled

---

[9] This measurement was made at −9°; however, order of magnitude calculations using the simple Debye relation and an extrapolated value for the viscosity indicate that even at −70° the dispersion frequency differs from 200 kilocycles roughly by a factor of 1000. Errors from dispersion effects, consequently, are not to be expected in the range of the measurements.

[10] H. H. Uhlig, *Trans. Electrochem. Soc.*, **78**, 265 (1940).

water. The part to be polished was connected as the anode with a piece of stainless scrap as the cathode. The current density was 0.1 ampere per square inch and the polishing was carried out for twenty to thirty minutes with the temperature of the solution at about 150°. After polishing, the metal parts of the cell were treated with phosphoric acid for a few minutes and then suspended in near boiling water for several hours to remove residual traces of the polishing solution. The quartz rods and balls prior to assembling the cell were treated with hot fuming sulfuric acid, rinsed, flamed strongly, retreated with hot fuming sulfuric acid and finally rinsed thoroughly with distilled water. The "Teflon" gaskets were treated similarly with hot fuming acid followed by a thorough rinsing. After assembly, the whole cell was flushed out with steam for several hours and then filled with 30% hydrogen peroxide and allowed to stand for two or three days. When not in use, the cell was kept filled with conductivity water. Before making a series of measurements it was rinsed thoroughly with fresh conductivity water and dried by evacuation in a vacuum desiccator.

The effectiveness of the guard ring feature was checked by measuring the capacitance of the cell as a function of the volume of liquid contained. In Fig. 3 the capacitance determined after each successive addition of a small amount of benzene is plotted *versus* the total amount of liquid added. The constancy of the measured cell capacitance below about 4 ml. of added liquid and above about 27 ml. indicates that the fringing field between the high and low potential electrodes is satisfactorily limited and that the data obtained are independent of the total volume of liquid in the cell provided the total volume is greater than 27 ml.

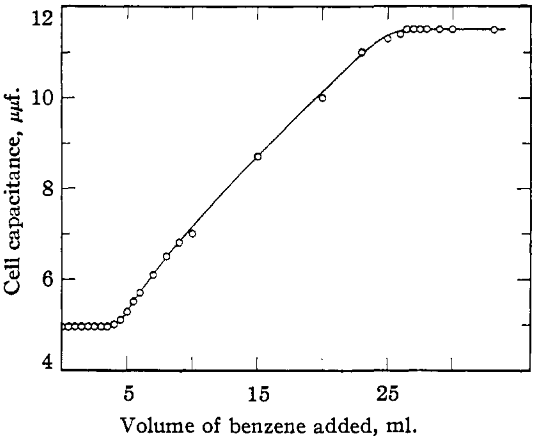


Fig. 3.—Volume calibration of dielectric constant cell.

The air capacitance of the cell was determined by a standard iterative method in which the cell was placed in parallel with one arm of the bridge and the bridge balanced successively with the cell connected and disconnected in such a way that the total capacitance increase in the corresponding arm of the bridge represented the product of the cell capacitance by the number of times the operation was repeated. The capacitance of the small switch used to connect and disconnect the cell was determined in the same manner and a small correction applied. In practice, the process was repeated forty times, the value so obtained for the air capacitance being 4.95 $\mu\mu f$. This value was checked regularly between runs. Prior to the last run, the cell was disassembled for inspection and, upon reassembly, the air capacitance was found to be 4.91 $\mu\mu f$. The conventional cell constant, $K(\text{cm.}^{-1})$, necessary in calculating the specific conductance from the measured conductance of the liquid was calculated from the air capacitance, $C(\mu\mu f)$, by the relation $K = 0.8988/4\pi C$, in which the numerical factors account for the difference in basis of definition and systems of units.

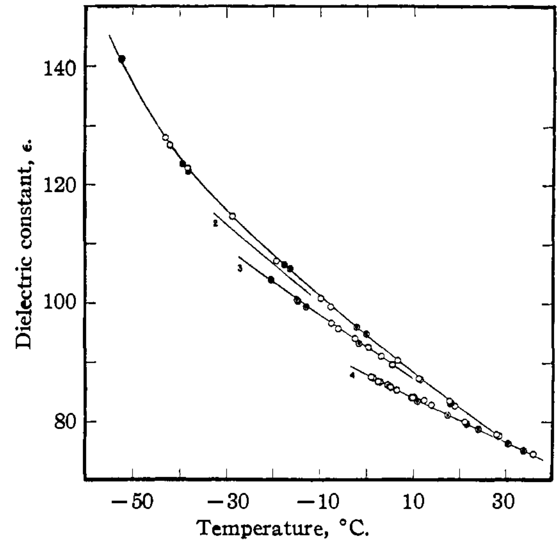


Fig. 4.—Temperature variation of dielectric constant for aqueous hydrogen peroxide solutions: curve 1, 46.5 weight % H_2O_2; curve 2, 35.3 weight % H_2O_2; curve 3, 26.2 weight % H_2O_2; curve 4, water; ○, increasing temperatures; ◎, decreasing temperatures.

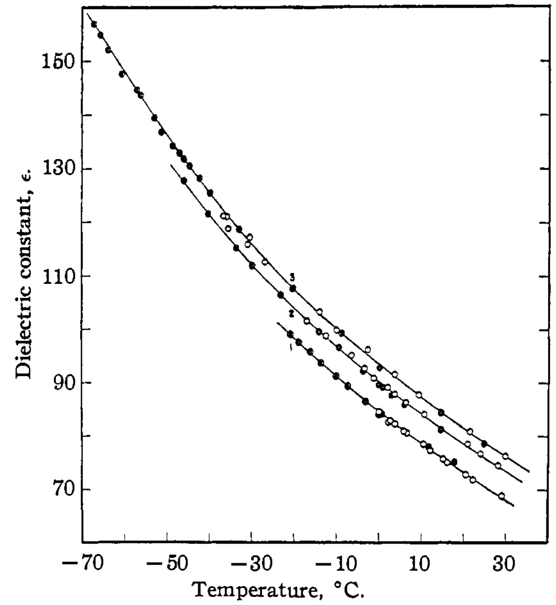


Fig. 5.—Temperature variation of dielectric constant for concentrated aqueous hydrogen peroxide solutions: curve 1, 99.0 weight % H_2O_2; curve 2, 85.2 weight % H_2O_2; curve 3, 75.4 weight % H_2O_2; ○, increasing temperatures, ◎, decreasing temperatures.

Purification of Materials.—The source of hydrogen peroxide was a 90% solution donated by the Buffalo Electrochemical Company. This material was stated to contain no stabilizer and only of the order of 15 parts per million of impurity, chiefly nitric and sulfuric acids. The same Company also supplied a specially prepared sample of 98% material stated to contain virtually no impurity and five parts per million of phosphoric acid as stabilizer. In both cases further purification was carried out by distillation. The procedure was to make the liquid approxi-

TABLE I

DIELECTRIC CONSTANT–COMPOSITION ISOTHERMS FOR HYDROGEN PEROXIDE–WATER SOLUTIONS

H_2O_2, N	Wt. % H_2O_2	30°	20°	10°	0°	−10°	−20°	−30°	−40°
0.0	0.0	76.7	80.4	84.1	88.0	....	...	...	...
.0406	7.4	76.3	80.7	85.0	89.4	(93.7)	...	...	...
.0638	11.4	(76.9)[a]	81.3	85.7	90.4	(95.3)	...	...	...
.1582	26.2	(77.6)	81.9	87.3	92.8	98.2	103.7	...	...
.1602	26.5	..	(82.4)	87.7	93.1	98.4	...	...	...
.2241	35.3	(77.5)	83.1	88.8	94.6	100.6	106.7	113.3	...
.3151	46.5	(76.8)	82.6	88.6	94.7	101.2	108.0	115.4	124.7
.3626	51.8	(77.7)	83.3	88.9	95.3	102.3	109.9	117.0	125.0
.3785	53.5	(78.6)	83.9	89.8	95.9	102.6	109.6	116.9	(125.0)
.4947	64.9	..	..	(89.5)	(95.0)	101.7	109.0	117.1	126.5
.6187	75.4	(75.9)	81.3	87.3	93.5	100.1	107.7	115.9	125.3
.7529	85.2	(73.6)	78.8	84.3	90.4	104.5	112.0	122.0	...
.9377	96.6	(69.9)	74.7	80.1	85.9	92.4	...	...	...
.9813	99.0	(69.5)	73.2	78.7	84.7	91.3	98.7	106.3	...
.9850	99.2	(68.6)	73.6	79.0	84.9	(91.4)	...	...	...

[a] Parentheses indicate extrapolated values.

mately 0.001 N in sodium hydroxide and then distil it under its own vapor pressure into a receiver cooled with Dry Ice–isopropyl alcohol mush. During the process, the system was pumped continuously with a Hyvac pump. If the temperature was kept below 40°, the liquid evaporated quietly with no ebullition providing the distilling flask had been pretreated properly. By using two receivers in series and cooling the one farther from the boiler first, the liquid could be fractionated and nearly 100% material obtained without the possibility of contamination by dust. Dilutions, when necessary, were made with special conductivity water. In general, measurements were begun as soon as possible after the completion of the distillation so as to reduce the opportunity for chance contamination.

All solutions were analyzed by titrating a small weighed sample with standard permanganate solution by a procedure very similar to that described by Huckaba and Keyes.[11] Unless stated otherwise, all concentrations are expressed in weight per cent.

Procedure.—At the start of a series of measurements on any given solution, the dried cell with leads attached and thermocouple in position was placed in its brass outer jacket and cooled to a temperature slightly above the freezing point of the solution.[12] The hydrogen peroxide, also cold, was then pipetted into the cell and the latter replaced in the cold bath. Starting at this temperature, measurements were made stepwise at successively higher temperatures until the solution showed signs of slight decomposition. This usually occurred at about 30 to 35° and was indicated by difficulty in balancing the bridge accurately. At this point, the procedure was reversed and the measurements were made at intervals for decreasing temperatures. The series was terminated when the liquid froze. Due to the unusual supercooling properties of the solutions, freezing ordinarily did not occur until the temperature was 20 to 40° below the freezing point given by Giguere and Maass.[12]

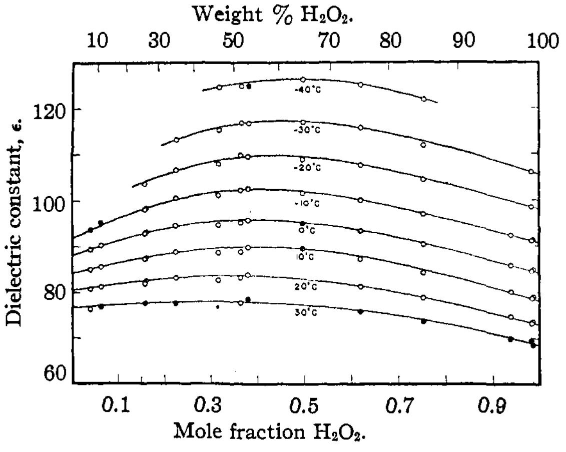


Fig. 6.—Dielectric constant–composition isotherms for the water–hydrogen peroxide system: ○, interpolated data; ◎, extrapolated data.

III. Experimental Results

Since the primary data are rather extensive for presentation in tabular form, we have chosen to present in Figs. 4 and 5 typical curves showing the temperature variation of the dielectric constant for constant composition. Each curve shows the data obtained from one series of measurements on one sample and indicates the agreement obtained. In practice, these data were plotted to large scale on millimeter cross section paper and a smooth curve was drawn through the points representing successively increasing temperatures. The data presented in Table I, together with the dielectric constant–composition isotherms shown in Fig. 6, were taken from these smoothed curves.

Inasmuch as the primary interest of this investigation lay in the values of the dielectric constant, no effort was made to obtain consistent values for the conductivity. The chief factor which rendered this difficult apparently was a slight solubility of the glass container in the concentrated peroxide. This was indicated by the dependence of the conductivity of a given sample on the length of time it had been stored in glass without free access to the air. However, a sufficiently accurate idea of the over-all conductivity behavior was obtained to confirm in a qualitative way Schumb's

---

[11] C. E. Huckaba and F. G. Keyes, THIS JOURNAL, **70**, 1640 (1948).

[12] The phase diagram for the H_2O-H_2O_2 system has been determined by P. A. Giguere and O. Maass, *Can. J. Research*, **18B**, 66 (1940).

results at 25°.[13] He reports that the specific conductivity-concentration curve for water-peroxide mixtures exhibits a maximum at approximately 50% by weight of hydrogen peroxide with the specific conductivity differing roughly by a factor of ten from that of the pure materials. The lowest value found in this work for the specific conductivity of nearly pure (99.2%) hydrogen peroxide was 4×10^{-7} ohm.$^{-1}$. This value is in agreement with, although slightly lower than, the extrapolated value reported by Schumb.[13]

Values of the dielectric constant for pure (100%) hydrogen peroxide were not measured but were obtained by a short extrapolation of the isothermal curves shown in Fig. 6. The data are expressed by the following empirical equation where t is in degrees Centigrade.

$$\epsilon = 84.2 - 0.62t + 0.0032t^2$$

This equation represents the data with a standard deviation of 0.13 and a maximum deviation for any one point of 0.2.

IV. Discussion of Results

In any experimental work on hydrogen peroxide, bubble formation resulting from trace decomposition is perhaps the prime potential source of error. This is particularly true in the measurement of a bulk property of the liquid such as the dielectric constant. In the present work, considerable attention was devoted to this problem and it is felt that errors from this source have been reduced to a minimum.

The careful polishing and pretreating of the cell before use have been described in the experimental section. Identically treated test strips of the same metal as the cell placed in contact with hydrogen peroxide solutions at room temperature exhibited no visible bubble formation over periods of several hours. Quartz, the other material in contact with the liquid in the cell, also has low catalytic activity. Proper precautions were taken during transfer and handling of the liquid to avoid contamination by dust particles which might serve as foci for decomposition. The cell was filled while both it and the solution were maintained just above the freezing temperature in order to take advantage of the marked temperature dependence of the decomposition. The initial measurements of a series were thus begun at low temperatures and proceeded to high. As a check, after the highest temperature reading, the procedure was reversed and measurements were made for descending temperatures. If bubbles had formed on the electrodes during the course of the measurements, the two sets should not agree. The data shown in Figs. 4 and 5 are satisfactory in this respect.

The values reported for the dielectric constant in this paper are appreciably lower than those reported by Cuthbertson and Maass[6a] at 0°. The order of agreement is indicated by the brief comparison in Table II.

TABLE II

DIELECTRIC CONSTANTS OF AQUEOUS HYDROGEN PEROXIDE AT 0°

Wt. % H_2O_2	This work	Ref. 6
0.0	88.0	84.4
32.0	93.7	120
55.0	96.0	113
100.0	84.2	89.2[a]

[a] The value 89.2 was revised to 93.5 in a subsequent paper.[6b]

Their failure to reproduce the accepted value of Wyman[7] for the dielectric constant of pure water is indicative of a rather low order of accuracy in their measurements. In the present work, the data are estimated to be accurate to within 0.5%. Cuthbertson and Maass further reported that the dielectric constant reached a maximum in a 32% solution. A maximum was also observed in the present work; however, at 0° it is only 8-9% greater than the value for pure water and, moreover, appears at a concentration of about 55%. This maximum becomes increasingly pronounced and shifts to higher peroxide concentrations as the temperature is lowered. At −67.1°, the high value of 157 was found for the dielectric constant of a 75.4% solution.

The dielectric constant of pure hydrogen peroxide is less than that of water at all temperatures for which they can be compared despite the higher dipole moment of the peroxide molecule. The effect of this larger dipole moment in increasing the dielectric constant is, to a certain extent, compensated for by the decreased number of dipoles per unit volume. However, the correlation factor, g, introduced by Kirkwood into the Debye expression for the molar polarization is appreciably less for hydrogen peroxide than for water at 0°. This fact would seem to indicate that the extent of short range order in liquid hydrogen peroxide is less than in liquid water, a suggestion that is not unreasonable in view of the greater complexity of the molecule and the fact that two isomeric forms are possible if the bent non-planar configuration is correct. Moreover, the internal potential barrier opposing the twist of the two hydroxyl groups around the O–O axis is probably sufficiently low so that much of the specific directional nature of the OH groups in liquid water is lost in the case of hydrogen peroxide. Unfortunately, the X-ray data available on liquid hydrogen peroxide do not appear capable of furnishing a satisfactory model which could be used as a basis of comparison.

The maximum observed for the aqueous solutions is somewhat unusual and suggests that the short range structure and coördination in water is enhanced by the addition of hydrogen peroxide. It is of interest to note that the phase diagram for the water–hydrogen peroxide system[14] shows a

---

(13) W. C. Schumb, *Ind. Eng. Chem.*, **41**, 992 (1949).

(14) P. A. Giguere and O. Maass, *Can. J. Research*, **18B**, **66** (1940).

congruent melting point corresponding to $H_2O_2 \cdot 2H_2O$, or at approximately the composition for which the dielectric constant maximum is found.

Acknowledgment.—The authors are deeply indebted to Dr. Robert H. Cole for his generous advice and assistance during the course of the work, and to Dr. Paul M. Gross, Sr., for his advice on the construction of the cell.

V. Summary

1. The dielectric constants of aqueous hydrogen peroxide solutions have been measured in the concentration range from zero to 99.2% hydrogen peroxide and for temperatures ranging from 30° to approximately $-65°$. The dielectric constant of pure hydrogen peroxide is found to be less than that of water at all temperatures for which they are compared.

2. The measurements, which are of moderate precision, deviate rather markedly from those previously reported at 0°.

3. The dielectric constant–composition isotherms of aqueous hydrogen peroxide solutions all exhibit a broad maximum at intermediate concentrations. This maximum becomes more pronounced and appears progressively at higher peroxide concentrations as the temperature is lowered.

PROVIDENCE, R. I. RECEIVED SEPTEMBER 15, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Self-diffusion Coefficients of Sodium Ion and Iodide Ion in Aqueous Sodium Iodide Solutions[1]

BY J. H. WANG AND J. W. KENNEDY

The measurement of self-diffusion coefficients of various ions or molecules in their aqueous solutions by means of isotopic tracers is an interesting problem. Hitherto, only the self-diffusion coefficients of H_2O in liquid water at various temperatures,[2] of Na^+ in aqueous sodium chloride solution at 25°,[3] of Na^+ in aqueous sodium iodide solutions at 25°,[4] and of Na^+ and Cl^- in aqueous sodium chloride solutions at 35°[5] have been determined. In all of these measurements except the last a diaphragm cell was employed; in the last measurement a diffusion tube was used. We present here another type of convenient and accurate apparatus and technique for measuring self-diffusion coefficients by means of isotopic tracers.

Theory of the Method

The general differential equation for diffusion in one dimension is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{1}$$

where c is the volume concentration of the diffusing species, t the time, x the coördinate along which diffusion takes place, and D is the diffusion coefficient. Since for self-diffusion the diffusion medium at different points along the diffusion path is chemically identical, the value of D, self-diffusion coefficient, is a constant and is independent of the concentration of the diffusing tracer ions or molecules. Consequently, equation (1) can be written as

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{2}$$

If the diffusion takes place, as in the present work in a capillary practically infinite in length and if before diffusion the concentration c of tracer ions or molecules is constant in one-half of the capillary but zero in the other half, *i. e.*, at $t = 0$, $c = 0$, for $x < 0$, $c = c_0$ for $x > 0$, then

$$\frac{c}{c_0} = \frac{1}{2}\left[1 + \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{3}$$

where $\operatorname{erf}(y)$ is the error function of y defined by $\operatorname{erf}(y) = \frac{2}{\sqrt{\pi}}\int_0^y e^{-\xi^2}d\xi$.

In the present work the diffusion time t was so adjusted that the value of Dt was about 0.7. After diffusion the total amount A of tracer in the diffusate between $x = -2.000$ cm. and $x = -\infty$ cm. was determined. This should be

$$A = \frac{c_0S}{2}\int_{-\infty}^{-2}\left[1 + \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]dx \tag{4}$$

or

$$\frac{2A}{c_0S} = \int_{-\infty}^{-2}\left[1 + \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]dx \tag{5}$$

where S is the cross-sectional area of the capillary. Equation (5) was solved graphically for Dt and the resulting curve is shown in Fig. 1. Alternatively, equation (4) may be written as

$$A = SD\int_0^t\left(\frac{\partial c}{\partial x}\right)_{x\,=\,-2}dt = SD\int_0^t\left(\frac{c_0}{2\sqrt{\pi Dt}}\right)e^{-\frac{1}{Dt}}dt$$

$$A = Sc_0\left[\sqrt{\frac{Dt}{\pi}}\,e^{-\frac{1}{Dt}} + \operatorname{erf}\left(\frac{1}{\sqrt{Dt}}\right) - 1\right]$$

$$i.\ e.\ \frac{2A}{c_0S} = \frac{2\sqrt{Dt}}{\sqrt{\pi}}\,e^{-\frac{1}{Dt}} + 2\operatorname{erf}\left(\frac{1}{\sqrt{Dt}}\right) - 2 \tag{5a}$$

---

(1) From the doctoral dissertation of J. H. Wang, University Fellow 1948–1949, Washington University, St. Louis.

(2) Orr and Butler, *J. Chem. Soc.*, 1273 (1935).

(3) Brady and Salley, THIS JOURNAL, **70**, 914 (1948).

(4) Adamson, *J. Chem. Phys.*, **15**, 762 (1947).

(5) Jehle, Ph.D. Thesis, University of California, Berkeley, 1938.