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

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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.

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[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

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

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

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (2)$$

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

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

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

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

$$A = \frac{c_0 S}{2}\int_{-\infty}^{-2}\left[1 + \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]dx \qquad (4)$$

or

$$\frac{2A}{c_0 S} = \int_{-\infty}^{-2}\left[1 + \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]dx \qquad (5)$$

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

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

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

$$i.\,e.\ \frac{2A}{c_0 S} = \frac{2\sqrt{Dt}}{\sqrt{\pi}}\,e^{-\frac{1}{Dt}} + 2\,\mathrm{erf}\left(\frac{1}{\sqrt{Dt}}\right) - 2 \qquad (5a)$$

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

which is equivalent to equation (5) but in explicit form not requiring graphical integration.

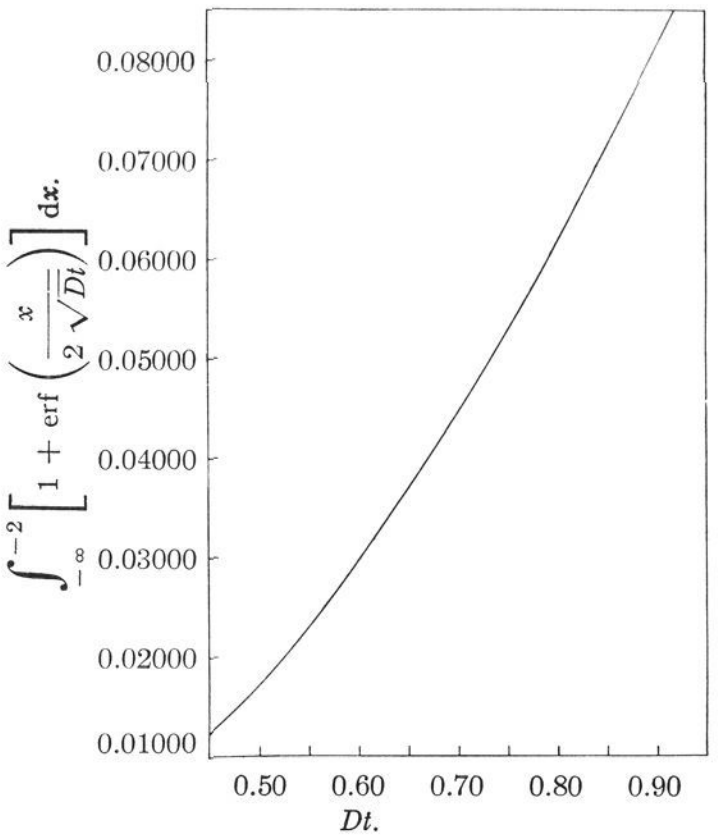

Fig. 1.—Values of $\int_{-\infty}^{-2}\left[1+\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]dx$ plotted *vs.* Dt.

In equation (5), A/c_0 is the experimentally determined radioactivity ratio, and S for each capillary is known, hence the value of the definite integral on the right-hand side of the equation is derived from the measurement. With a knowledge of this value, the value of Dt can be immediately read off from the curve in Fig. 1. Since t is known, D can be readily calculated.

It can be seen from the curve in Fig. 1 that the diffusion cell was so designed that a 1% change in the value of Dt results in a 3% change in the value of the integral and hence the measured radioactivity ratio. Thus the sensitivity of the measurement is enhanced. In this respect the type of diffusion cell employed in the present work is superior to that with a sintered glass disk.

Cell Design and Experimental Technique

The body of the diffusion cell was made by polymerizing liquid plastic "castolite" in a cylindrical glass mold with a one-fourth inch drill rod placed axially at the center and eight one-sixteenth drill rods evenly spaced around the former. After the polymerization process was completed, the drill rods were pulled out. The capillaries in the solid plastic made in this way were smooth and straight and uniform in cross-section. The dimensions and construction of the diffusion cell are shown in Fig. 2.

The various segments of the diffusion cell were mounted on a straight one-fourth inch stainless steel shaft. Between the various plastic segments

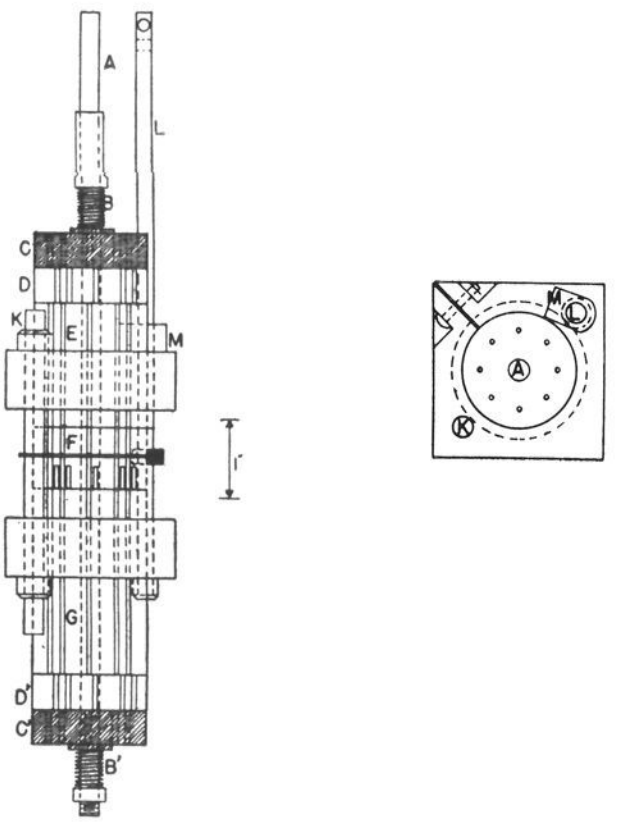

Fig. 2.—Diffusion cell.

a minimum amount of high-vacuum silicone grease, which has been previously extracted with redistilled water and dried, was used to lubricate the faces to insure smooth gliding of one segment against another and to make the cell water-tight. The average cross-sectional area of each of the eight capillaries was calibrated to be 0.0193 sq. cm. The centerpiece F was accurately machined to be 2.000 ± 0.003 cm. in length. The centerpiece has a gear on it so that it can be rotated slowly and smoothly by turning a long rod inserted into one of the holes on top of the gear shaft L. A key M was fastened to the gear shaft L at such an angle that when the key touches the outside surface of the cell proper, the capillaries in three main segments of the cell are most accurately lined up. The length of the cell was so designed that at the end of each diffusion period practically no tracer ions had diffused to the upper end of the cell.

The sodium iodide solutions were prepared by dissolving weighed amounts of dry sodium iodide in weighed amounts of doubly distilled water, were centrifuged to remove any fibers that might be present, and were degassed with an aspirator before use. The tracers used for Na^+ and I^- were Na^{22} (3.0 years half-life) and I^{131} (8.0 days half-life), respectively. The Na^{22} was produced through the bombardment of a magnesium target with deuterons. After the short-lived Na^{24} had practically all decayed the surface of the magnesium target was scraped off. The scrapings were dissolved in 2N nitric acid, evaporated to dryness on a platinum dish, and ignited to convert all magnesium nitrate into magnesium oxide. The residue on ignition was then extracted twice by boiling with doubly distilled water and centrifug-

ing out the magnesium oxide residue. Several drops of 6 N ammonia were added to the supernatant extract (about 40 ml. in volume) and, after the solution had been standing for several days, practically all the colloidal magnesium oxide particles settled to the bottom of the container. The clear supernatant solution of $(Na^{22})^+$ was pipetted off and used as tracer stock solution for Na^+. The solution contained less than 0.0001 g. of total solid per cc.

The I^{131} sample obtained from the Isotopes Branch of United States Atomic Energy Commission at Oak Ridge, Tennessee, was purified by the addition of twice its volume of 8 M sulfuric acid containing excess of ferric sulfate together with some ferrous sulfate, followed by distillation of the I^{131} as I_2, and its collection under water containing a small amount of sodium sulfite. This was used as tracer stock solution for I^-, and the approximate salt concentration in the most dilute solution was estimated from the weight of sodium sulfite used.

Sodium iodide solutions containing radioactive Na^+ or I^- were prepared by evaporation of calculated amount of the above tracer stock solutions to dryness under a heat lamp. The residue, barely visible, was dissolved in fiber-free sodium iodide solution and degassed before use.

Before the diffusion cell was filled, both the cell and the solutions to be used were kept in a thermostat at 25.00 ± 0.02° for several hours to ensure thermal equilibrium. The capillaries in the three main segments of the cell were first lined up, they were then filled with inactive sodium iodide solution of known concentration by means of a long, fine pipet which could be inserted through the top opening to reach to the bottom of each capillary. Care was taken to avoid any bubble being trapped in the capillaries during the filling process. After all the capillaries were filled, the top openings of the cell were closed by turning the end pieces D and C. Then the centerpiece F was gradually turned by means of a long rod (not shown in Fig. 2) attached to the gear shaft L until the capillaries in the lower main piece were lined up with the short single-ended capillaries in the centerpiece F. The cell was then held upside down, with its end pieces D' and C' just above water surface in the thermostat. The end of the cell was then opened, the inactive sodium iodide solutions in the capillaries in the segment G pipetted out, the capillaries dried with "fiberless" absorbent paper made in the form of fine, long sticks and then filled with radioactive sodium iodide solution (containing either radioactive Na^+ or radioactive I^-) of the same chemical concentration. Any bubble that might be formed in this last filling procedure would be trapped in the short single-ended capillaries and hence rendered harmless.

The cell was then held rigidly in upright position by clamping the end of center shaft A on a heavy vibrationless holder. When diffusion was being started or stopped, the centerpiece F was turned so slowly the operation took about four minutes. The amount of turbulent flow produced by this kind of turning is negligible, as could be demonstrated by filling the upper and lower halves of each capillary with solutions of different color.

After diffusion the cell was raised a little so that the top end piece C was a little above the water surface in the thermostat. The inactive sodium iodide solutions in the holes of the end piece D were removed and the holes in D dried with absorbent paper. Then the solutions in the capillaries of E were sampled out separately. Each capillary was washed five times with distilled water. Each sample solution together with washings was evaporated to dryness on a circular piece of microscope cover glass under an infrared lamp.

The tracer concentration in the lower half of each capillary before diffusion took place was also determined on an aliquot part of the radioactive sodium iodide solution shortly after the diffusion cell was filled. Since the original active solution was in general 200 times larger in tracer concentration than the diffusate sample taken, it was diluted with enough distilled water and inactive sodium iodide solution so that a 0.100-cc. sample of the diluted active solution has about the same radioactivity and contains the same amount of inert material as the diffusate sample taken. All the samples were kept in a desiccator before counting.

The measurement of radioactivity was made by means of a Geiger counter and associated scaling circuit. The counter used had a flat plateau, and also since each pair of radioactive samples (one sample of the diluted original active solution and one diffusate sample) were counted consecutively within ten or fifteen minutes, the error in the radioactivity ratio A/c_0 that might be caused by fluctuation in efficiency of the counter could be neglected. We estimated that any errors in the very thin and almost identical pairs of samples due to self-absorption effects were negligible.

Results

The results obtained in the measurement of self-diffusion coefficients of Na^+ and I^- in aqueous sodium iodide solutions of various concentrations at 25.00 ± 0.02° are tabulated in Table I. All concentrations m are expressed on the weight-molal scale.

In general, several independent determinations were made for each self-diffusion coefficient, and the root mean square deviation was taken as the error listed in Table I. The errors due to statistical fluctuations in the counting of radioactivity or to inaccurate estimation of the cross-sectional area of each capillary are quite negligible as compared to other possible errors; a 1% error in either of these introduces only a 0.3% error in D. The data in Table I are plotted in Fig. 3. The av-

TABLE I

SELF-DIFFUSION COEFFICIENTS OF Na^+ AND I^- IN AQUEOUS SODIUM IODIDE SOLUTIONS AT 25.0°

Concentration m of NaI solution, wt.-molal	$D_{Na^+} \times 10^5$, cm.²/sec.	$D_{I^-} \times 10^5$, cm.²/sec.
10^{-4} to 10^{-5}	1.445 ± 0.015	.....
5×10^{-4} to 10^{-3}	.....	2.035 ± 0.026
0.01	1.31 ± 0.02	1.962 ± .012
.02	1.284 ± .015	1.900 ± .020
.03	1.288 ± .030	
.05	1.283 ± .015	1.88 ± .03
.07	1.282 ± .015	1.87 ± .03
.10	1.274 ± .015	1.87 ± .03
.20	1.275 ± .020	1.851 ± .012
.30	1.275 ± .020	1.84 ± .03
.50		1.81 ± .03
.70	1.270 ± .015	
1.00	1.264 ± .015	1.735 ± .030
1.50	1.249 ± .015	1.67 ± .02
2.00	1.24 ± .03	1.630 ± .010
2.50		1.60 ± .03
3.50	1.239 ± .015	1.567 ± .025

erage tabulated error in the self-diffusion coefficients determined in the present work is about 1%.

Discussion

According to the Nernst limiting equation,[6] the self-diffusion coefficient D^0 and equivalent conductance λ_i^0 of an ionic species i at infinite dilution are related by

$$D_i^0 = \frac{RT}{ZF^2}\lambda_i^0 \qquad (6)$$

where Z is the charge of the ion in electronic units, F the faraday, R the perfect gas constant and T the absolute temperature. Using the values $\lambda^0_{Na^+} = \Lambda_0 t^0_{Na^+} = 50.1$ and $\lambda^0_{I^-} = \Lambda_0 t^0_{I^-} = 76.8$ where Λ_0 is the equivalent conductance of sodium iodide, $t^0_{Na^+}$ and $t^0_{I^-}$ the transference numbers of Na^+ and I^-, respectively, at infinite dilution, equation (6)

(6) Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

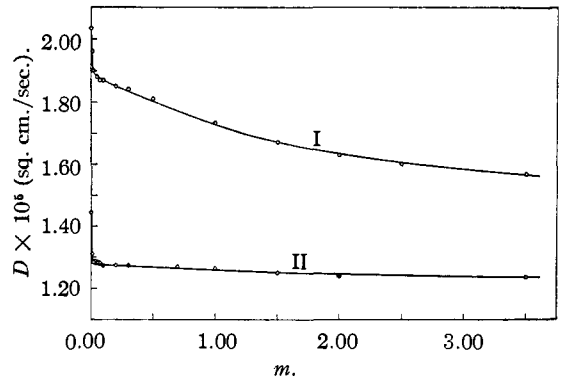

Fig. 3.—Self-diffusion coefficients of Na^+ (Curve II) and I^- (Curve I) in aqueous sodium iodide solutions at 25°.

gives $D^0_{Na^+} = 1.34 \times 10^{-5}$ cm.²/sec. and $D^0_{I^-} = 2.04 \times 10^{-5}$ cm.²/sec. This value of the self-diffusion coefficient of I^- at infinite dilution agrees with our experimental value $D^0_{I^-} = 2.035 \times 10^{-5}$ cm.²/sec., whereas that of Na^+ at infinite dilution is 7% lower than our experimental value $D^0_{Na^+} = 1.445 \times 10^{-5}$ cm.²/sec. It is also interesting to notice that the value of $D^0_{Na^+}$ as determined by Adamson[3] by the diaphragm cell method is 1.435×10^{-5} which agrees within 0.7% with our value.

Summary

1. A method for the determination of self-diffusion coefficients of ions in solution is described. The average error in this method is ±1%.

2. The self-diffusion coefficients of sodium ion and iodide ion in aqueous sodium iodide solutions at concentrations from 10^{-4} to 3.5 M at 25.0° have been determined.

3. The experimental values of the self-diffusion coefficients at infinite dilution are compared with the values predicted by the Nernst limiting equation.

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