It is interesting to note that Smith,[4] from his data at higher concentrations and without benefit of activity coefficient corrections, came to the conclusion that the reaction accounting for the solubility of bismuthyl nitrate in nitric acid is one where un-ionized $Bi(OH)(NO_3)_2$ is formed. He discarded this result as "coincidental" in favor of a conclusion from conductivity data that equation (4) represents the true reaction. This agrees with our conclusion.

The $BiO(OH)BiONO_3$–HNO_3 Equilibrium.—No easy explanation appears to exist for the data in Table I which show the solubility of BiO-(OH)-$BiONO_3$ in nitric acid. No single reaction could account for the data.

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Self-Diffusion and Structure of Liquid Water. I. Measurement of Self-Diffusion of Liquid Water with Deuterium as Tracer

BY J. H. WANG[1]

A method for measuring self-diffusion of liquids by means of capillaries is described*; the accuracy of the present method is within about 1%. The self-diffusion coefficients of liquid water in the temperature range 0 to 55° have been determined by both the capillary method and the usual diaphragm cell method with deuterium as tracer. Data of the present work support the quasi-crystalline structure of liquid water and are in contradiction with the assumed existence of definite species of associated water molecules in liquid water. The average apparent activation energy, 4.58 kcal./mole, for self-diffusion of liquid water in the temperature range 10 to 50° indicates that water in this temperature range is only very slightly more than two-coördinated. Below 5°, however, the apparent activation energy of self-diffusion increases appreciably as temperature drops, reaching the approximate value of 6.4 kcal./mole at 0°.

The self-diffusion coefficients of liquid water at various temperatures have been measured independently, by Orr and Butler,[2] Temkin[3] and by Rögener-Leipzig.[4] These measurements are interesting in the light they might throw on the structure of liquid water. However, Orr and Butler's data disagree with the values reported separately by Temkin and by Rögener-Leipzig far beyond the average experimental error reported by either worker. In the present work, the self-diffusion coefficients of liquid water at temperatures in the range 0 to 55° were measured with deuterium as tracer by two different methods. The result shows that Orr and Butler's values are too high.

Principle of Methods

In the first method fine uniform capillaries with lower end sealed were filled with heavy water and held in vertical position in a large circulating bath of pure ordinary water at constant temperature. The deuterium oxide and hydroxide are allowed to diffuse upward, the tracer concentration at the upper end of the capillaries were kept at zero by convection current in the large bath. Under these conditions, the solution of one dimensional linear diffusion equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (1)$$

where C is concentration of tracer at time t, x the coordinate along which diffusion takes place and D the diffusion coefficient becomes

$$\frac{C}{C_0} = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp[-(2n+1)^2\pi^2 Dt/4l^2]\cos\frac{(2n+1)\pi x}{2l} \qquad (2)$$

where C_0 is the initial concentration of tracer, and l is the length of capillary.

The average concentration of solution in the capillary at time t is given by

$$\frac{C_{av}}{C_0} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2\pi^2 Dt/4l^2] \qquad (3)$$

Values of $C_{av.}/C_0$ are plotted *vs.* Dt/l^2 in Fig. 1.[5]

Thus determination of average tracer concentration in the capillary after diffusion has taken place for a certain time interval t gives the value Dt/l^2, from which D can be readily calculated. The use of fine capillaries to determine self-diffusion coefficient has the special advantage that the measurement is relatively insensitive to slight vibrations or disturbances in the vicinity of the diffusion apparatus as compared to larger capillaries.[6]

In the second method, a slightly modified Northrop[7]–McBain[8] type of diaphragm cell was used. The formula originally developed by Northrop and Anson

$$D = \frac{1}{Kt}\ln\frac{\Delta C_0}{\Delta C} \qquad (4)$$

where K is the cell constant, ΔC_0 and ΔC are the differences in tracer concentrations at time zero and t, respectively, was used in the present calculations.

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* The measurement of self-diffusion by means of capillaries was first made by J. S. Anderson and K. Saddington (*J. Chem. Soc.*, 5381 (1949)).

(1) Monsanto Post-doctoral fellow, 1949-1950.

(2) W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 1273 (1935).

(3) M. Temkin, *Nature*, **136**, 552 (1935).

(4) H. Rögener-Leipzig, *Z. Elektrochem.*, **47**, 164 (1941).

(5) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947.

(6) J. H. Wang and J. W. Kennedy, THIS JOURNAL, **72**, 2080 (1950).

(7) J. N. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1928).

(8) J. W. McBain and T. H. Liu, THIS JOURNAL, **53**, 59 (1931).

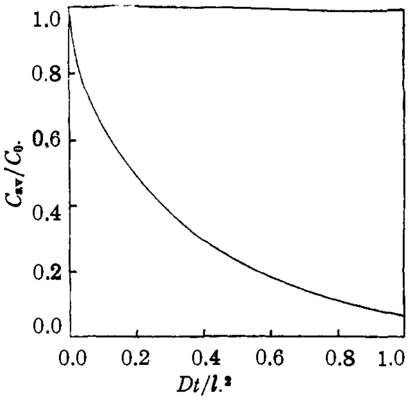

Fig. 1.—Values of C_{av}/C_0 plotted *vs.* Dt/l^2.

Experimental

Tracer Solution.—The tracer solution used, 99.8% in deuterium oxide, was supplied by Stuart Oxygen Company, San Francisco, Calif., and obtained on allocation from the Isotopes Division, U. S. Atomic Energy Commission. The exact ratio of H^2 to H^1 was determined by accurate density measurements after redistillation in an all-glass, moisture free distillation set. Since only relative concentrations of deuterium before and after diffusion are involved in the calculation, uncertainties in the exact densities of the H_2^2O–H_2^1O mixtures (*ca.* 0.01%) have no effect on the diffusion coefficients obtained in the present work, the "ordinary" water used had been doubly distilled from neutral potassium permanganate solution.

Apparatus and Manipulation.—The diffusion capillaries used have internal diameters about 0.5 mm. and are *ca.* 4 cm. long. They all have uniform cross-sectional area (calibrated by filling with pure mercury and weighing). The top end of each capillary was smoothly ground with fine carborundum, the other end was carefully sealed with a flat bottom.[9] Before diffusion the capillaries were filled with degassed tracer solution of known concentration at the desired temperature with fine pipets. They were then held vertically, with open end on top, in a large circulating bath of pure "ordinary" water at the same temperature (see Fig. 2).

After diffusion had taken place for a certain length of time, the capillaries were taken out of bath, excess water adsorbed on top of each capillary dried with absorbent paper, the solution in each capillary was well mixed and sampled out by means of a pipet. The deuterium content of the sample was then determined, from which D can be calculated. The time of diffusion was so adjusted that at the end of each experiment only about $^1/_6$ of the original tracer was still left in the capillary. This was convenient for the determination of deuterium concentration of solution in each capillary by the gradient-tube method to be described later. Four capillaries were used in each experiment.

The water in the circulating bath had a volume of about 1 liter so that the concentration of deuterium in bath at the end of each diffusion experiment is still practically zero, justifying the use of formula (3) in the calculation of D.

In the diaphragm cell method, a cell very similar to the McBain–Liu type was used. The sintered-glass disk of fine porosity was filled with silica gel, aged at 80–95° for several days, then again filled with silica gel and aged for several more times. Finally the disk was washed, dialyzed with distilled water and aged at room temperature for 6 months. The volume of the upper compartment of the diaphragm cell was 46.82 cc., that of the lower was 52.17 cc. Before diffusion, the upper compartment was filled with degassed tracer solution of known concentration at the desired temperature, the lower compartment filled with degassed ordinary water at the same temperature. The cell was then held in a constant temperature water-bath in such a position that the diaphragm was horizontal. Diffusion was allowed to take place for 4 or 5 hours to attain transient equilibrium in the diaphragm. Then the cell was taken out of bath, the two compartments were emptied and refilled with solutions of the same composition as before. This time diffusion was allowed to proceed for several days. Because of the density difference between heavy water and ordinary water, convection currents kept the liquid in both compartments at uniform concentration during the diffusion period. At the end of diffusion period, the solutions in the two compartments were sampled out separately and had their H^2 to H^1 ratio determined by density measurements. The diffusion coefficient was calculated by means of formula (4). The cell constant K was calculated by calibrating the cell with Rögener–Leipzig's value of 1.77×10^{-5} sq. cm./sec. as self-diffusion coefficient of liquid water at 14.7°. In this way the possible adsorption error that might occur when calibrating the cell with KCl solution was avoided. A material balance for either H^2 or H^1 was computed for each diffusion measurement as a cross-check.

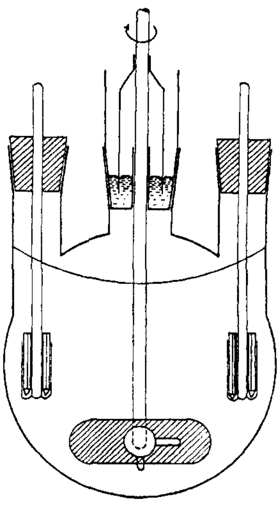

Fig. 2.—Capillary apparatus for measuring self-diffusion coefficients of liquids.

Analysis.—The H^2-content of samples in the diffusion capillaries was determined by density measurement by means of the gradient-tube method.[10] A graduated tube was filled with bromobenzene and kerosene mixtures so that the density of liquid mixture at 25° changes continuously from about 1.13 at the bottom to about 1.11 at the top of the tube. Eleven H_2^2O–H_2^1O mixtures of known composition with densities within the above range were used as standards. Instead of the usual method of interpolation by assuming linear relationship between density of liquid and height in the graduated column, a smooth curve was drawn by plotting the known densities of the standard drops *vs.* height of equilibrium positions in the gradient-tube. The densities of the unknown drops can thus be read from the density *vs.* height curve since their equilibrium height can be read directly from graduations of the gradient-tube. The density of each sample solution thus determined is accurate to within 0.01%.

In the diaphragm cell method, the densities of tracer solutions in both compartments were determined by means of a pycnometer with a long capillary plug; there was a ground-glass cap with a pin-hole for further prevention of evaporation during weighing. The weight of ordinary water filling the pycnometer at 25.00 ± 0.01° was 24.8242 g. The average error of density determinations for water by means of this pycnometer was about 0.001%.

Results

The self-diffusion coefficients of liquid water were determined at temperatures between 0 and 55° by the capillary method, and at temperatures between 5 and 55° by the diaphragm cell method with deuterium as tracer. The two sets of data agree fairly well with each other. In general, at temperatures much above or below room temperature the values obtained by the capillary method are more reliable. Data of the present work are summarized in Table I. The values of self-diffusion coefficients measured by the capillary method listed in Table I are the average value of at least four determinations for each temperature. Values previously reported in literature are also listed for comparison. Self-diffusion coefficients in Table I are plotted *vs.* $1/T$ in Fig. 3. It would appear from these comparisons that Orr and Butler's values are too high.

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[9] The author is indebted to Mr. A. Ottenberg for his coöperation in preparing these uniform capillaries.

[10] K. Linderstrøm-Lang, O. Jacobsen and G. Jacobsen, *Compt. rend. trav. lab. Carlsberg*, **23**, 17 (1938).

TABLE I

Temp., °C.	$D \times 10^5$ (cm.²/sec.) Capillary method (Present work)	Diaphragm cell method Present work	Diaphragm cell method Temkin	Diaphragm cell method Orr and Butler	Optical method (Rögener-Leipzig)
0.0 ± 0.1	1.00 ± 0.011	......	1.1	1.46	..
5.2 ± 0.1	1.23 ± 0.017	I, 1.28 II, 1.29 Av. 1.29	...	..	..
14.2	....	......	...	1.94	..
16.1 ± 0.05	1.65 ± 0.035	......	...	..	..
17.5	....	I, 1.78 II, 1.76 Av. 1.77	...	..	1.77
25.00 ± 0.01	2.14 ± 0.032	I, 2.12 II 2.12 Av. 2.12	...	2.64	..
28.0	....	......	2.5	..	..
35.00 ± 0.02	2.76 ± 0.037	I, 2.75 II, 2.74 Av. 2.75	...	3.88	..
45.0 ± 0.05	3.45 ± 0.024	I, 3.48 II, 3.55 Av. 3.52	...	4.75	..
55.0 ± 0.15	4.12 ± 0.074	I, 4.32 II, 4.45 Av. 4.39	...	..	..

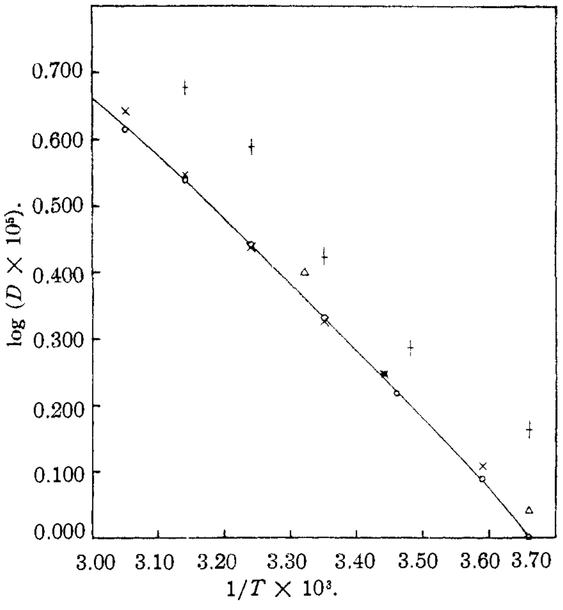

Fig. 3.—Values of log ($D \times 10^5$) determined by capillary method (○) and diaphragm cell method (×) in the present work, by Rögener-Leipzig (□), by Temkin (△) and by Orr and Butler (†) for liquid water plotted *vs.* $1/T \times 10^3$.

Average values of self-diffusion coefficients of water obtained in the present work, together with viscosities of water and corresponding values of the quantity $D\eta/T$ at various temperatures are listed in Table II.

TABLE II

Temp., °C.	$D_2 \times 10^5$ (cm.²/sec.)	$\eta \times 10^3$ (poise)	$D\eta/T \times 10^{10}$
0	1.00	17.921	6.56
5	1.20	15.188	6.45
15	1.61	11.404	6.37
25	2.13	8.937	6.38
35	2.76	7.225	6.46
45	3.45	5.988	6.49
55	4.16	5.064	6.43
		Av.	6.45 ± 0.06

Discussion

Liquid water has many properties that are characteristic of associated liquids. The anomalous temperature dependence of density and heat capacity of water have stimulated numerous suggestions[11] that liquid water at room temperatures is a mixture of various species of associated molecules, *e.g.*, hydrol H_2O, dihydrol $(H_2O)_2$, trihydrol $(H_2O)_3$, etc. Recently, Eucken[12] explained these anomalous properties of liquid water quantitatively by assuming that water is an ideal solution of molecules containing 1, 2, 4 and 8 H_2O each.

On the other hand, Raman spectra and X-ray data[11] showed that no definite associated molecules exist, that the structure of liquid water is best represented by a three-dimensional network of pliable branched chains of tetrahedra, and liquid water actually has a quasi-crystalline structure as first suggested by Bernal and Fowler.[13] This quasi-crystalline structure of liquid water seems to be the more favored picture recently. It is of interest to see whether we can decide from examination of self-diffusion data in the present work which of the above outlined two alternative structures of liquid water is the correct one. Table II shows that as temperature changes from 0 to 55° the self-diffusion coefficient of liquid water is increased about fourfold, but the quantity $D\eta/T$ remains constant within 1%. This means that although the usual generalized Einstein–Stokes formula for diffusion coefficient $D = K(T/\eta V^{1/3})$ where V is the volume of diffusing solute molecule, η viscosity of pure solvent and K a constant characteristic of the shape of molecule, is not expected to hold for molecules of size comparable to that of solvent molecules, for the special case of self-diffusion of liquid water, the fluidity, $1/\eta$, of solvent is approximately proportional to the mobility, D/RT, of diffusing water molecules, and that the effective volume as measured by $(D\eta/KT)^{-3}$, of diffusing water molecules remains practically constant from 0 to 55°. This means that only one type of water molecule can diffuse between 0 and 55°. The magnitudes of self-diffusion coefficients of liquid water obtained in the present work indicate that the type of molecule that controls diffusion between 0 and 55° is probably simply the unassociated molecule H_2O.

Thus the present result supports the quasi-crystalline structure of liquid water, but contradicts the assumption that liquid water, at room temperatures, is a mixture of various definite species of associated water molecules in thermal equilibrium with each other. *E.g.*, according to Eucken, if γ_1 γ_2, γ_3 and γ_4 represent, respectively, the mole-fractions of H_2O, $(H_2O)_2$, $(H_2O)_4$, $(H_2O)_8$, they have the following values

Temp., °C.	γ_1	γ_2	γ_3	γ_4
0	0.0500	0.3500	0.3000	0.3000
60	.1620	.5290	.2610	.0482

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(11) See N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Co., New York, N. Y., 1940, for earlier references.

(12) A. Eucken, *Z. Elektrochem.*, **52**, 255 (1948).

(13) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

Thus if Eucken's picture is correct, the effective volume of the diffusing water molecules, as approximately measured by $(D\eta/KT)^{-3}$, should decrease considerably as we raise the temperature from 0 to 55°; values of Table II show that this is not the case.

It can be noticed readily in Fig. 3 that the plot of log D *vs.* $1/T$ gives approximately a straight line, showing that the activation energy for self-diffusion of liquid water has approximately the constant value 4.58 kcal./mole between 10 and 50°. If we assume, as a first approximation, that the activation energy for self-diffusion in liquid water is equal to the energy required to break the hydrogen bonds that bind the diffusing molecule to its nearest neighbors, then, by taking 4.5 kcal./mole as the approximate energy of each hydrogen bond, we can calculate the average number of hydrogen bonds per water molecule to be $4.58/4.5 = 1.02$ for the temperature range 10 to 50°. This shows that water appears to be on the average only slightly more than two-coördinated and that relatively small changes in structure takes place in the temperature range 10 to 50°, agreeing with the conclusion drawn from studies of Raman spectra of liquid water.[14]

Below 5°, however, the log D *vs.* $1/T$ curve in Fig. 3 indicates that the activation energy of self-diffusion increases as temperature drops, reaching the value 6.4 kcal./mole at 0°. This increase in activation energy corresponds to an appreciable increase of the less closely-packed "ice-structure" in liquid water below 5°, and is in agreement with the "abnormal" density changes of liquid water below 5°.

The activation energy E for self-diffusion can also be calculated from the temperature dependence of viscosity as follows. Since

$$D = \left(\frac{KT}{\eta V^{1/3}}\right)$$

we have

$$\frac{\mathrm{d}\ln D}{\mathrm{d}(1/T)} = -T + \frac{\mathrm{d}\ln(1/\eta)}{\mathrm{d}(1/T)}$$

hence

$$E = -R\frac{\mathrm{d}\ln D}{\mathrm{d}(1/T)} = R\left[T - \frac{\mathrm{d}\ln(1/\eta)}{\mathrm{d}(1/T)}\right] \qquad (5)$$

At 25°, for example, $\mathrm{d}\ln(1/\eta)/\mathrm{d}(1/T)$ is equal to -2010. Equation (5) thus gives

$$E = \frac{1.987}{1000}\,[298 + 2010] = 4.59 \text{ kcal./mole}$$

agreeing with the value obtained directly from the slope of the log D *vs.* $1/T$ curve in Fig. 3, 4.58 kcal./mole, within experimental error.

This agreement should not, however, lead one to think that the diffusional mobility of solutes in general is proportional to the fluidity of solvent. The proportionality between the above two quantities is true only when the interaction between solute and solvent molecules is identical to that between solvent molecules themselves, a case that is realized only in the case of true self-diffusion. In general, the interaction between solute and solvent molecules is more or less different from that between solvent molecules themselves, and considerable amount of "distortion" in the structure of solvent exists in the vicinity of each solute molecule so that the mobility of solute is not proportional to the fluidity of pure solvent. For example, the product $\lambda_i^0\eta$ of ionic conductance, λ_i^0 of ion i in its aqueous solution at infinite dilution with the viscosity η of pure water, is found[15] to decrease with rising temperature, the decrease being greater the smaller the ion. Moreover, since hydration decreases as temperature increases, the actual deviation of $\lambda_i^0\eta$ from constancy should be still larger than the apparent deviation. But for larger ions such as $\mathrm{Li^+(aq)}$ or $\mathrm{N(C_2H_5)_4^+(aq)}$, the "distortion" in solvent surrounding the hydrated ion is smaller, and consequently the deviation of $\lambda_i^0\eta$ from constancy is less serious.

Since the measurement of self-diffusion coefficients of liquid water with deuterium as tracer might involve an appreciable error due to the tracer, *e.g.*, difference in mass of isotopes, difference in energy between the $\mathrm{H^1}$-bond and $\mathrm{H^2}$-bond, etc., further discussion is to be reserved for a later publication together with the result of self-diffusion measurements for water with $\mathrm{O^{18}}$ as tracer.

Summary

1. A method for measuring self-diffusion in liquids by means of capillaries is described, the accuracy of the present method is within about 1%.

2. The self-diffusion coefficients of liquid water in the temperature range 0 to 55° have been determined by both the capillary method and the usual diaphragm cell method with deuterium as tracer.

3. Data of the present work support the quasi-crystalline structure of liquid water. The average activation energy for self-diffusion of liquid water in the temperature range 10 to 50° indicates that water in this temperature range is slightly more than two-coördinated.

4. The temperature dependence of self-diffusion coefficient and that of viscosity of liquid water are compared and discussed.

ST. LOUIS, MISSOURI RECEIVED JULY 31, 1950

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[14] P. C. Cross, J. Burham and P. A. Leighton, THIS JOURNAL, **59**, 1134 (1937).

[15] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1943, p. 589.