[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON UNIVERSITY]

Self-diffusion and Structure of Liquid Water. II. Measurement of Self-diffusion of Liquid Water with O^{18} as Tracer

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In order to correct for the possible errors involved in the measurement of self-diffusion of liquid water with deuterium as tracer reported earlier, the self-diffusion coefficients of liquid water have been redetermined with O^{18} as tracer between 1° and 55°. Results of the present measurements confirm the earlier conclusion that no definite species of associated water molecules exist in liquid water, and that liquid water actually possesses a semi-crystalline structure which changes only very little between 5° and 55°. Comparison with earlier measurements with deuterium as tracer shows that special mechanisms of hydrogen-atom transfer, such as those similar to that which occurs in the electrolytic conduction by hydrogen ion, are absent in the self-diffusion of liquid water. The activation energy for self-diffusion with $H_2^1O^{18}$ as tracer is slightly smaller than that with $H_2^2O^{16}$ as tracer, which is what one should expect because of the higher degree of coördination in H_2^2O than in H_2^1O. Comparison of the self-diffusion coefficients obtained in the present work with dielectric and viscosity data shows that Eyring's transition-state theory of rate processes is a fair description of the self-diffusion, viscous flow and dipole orientation for liquid water, and that these three processes involve essentially the same activation mechanism.

In an earlier work the self-diffusion coefficients of liquid water at various temperatures were determined and the non-existence of definite species of associated water molecules was shown.[2] From the measured activation energy for self-diffusion, the average number of hydrogen bonds attached to each water molecule in a large semi-crystalline lattice of liquid water was estimated to be about 2 at room temperatures. This rough estimation is meaningful only when the activation mechanism for self-diffusion is the direct dissociation of the diffusing water molecule as a whole from the surrounding semi-crystalline lattice. If some special hydrogen-atom transfer mechanisms, such as those similar to the successive exchange of hydrogen atoms between neighboring water molecules that occurs in the electrolytic conduction by hydrogen ion in its aqueous solutions, were present the earlier estimation would be entirely wrong. In order to justify the assumption that such mechanisms of hydrogen-atom transfer are absent or, in other words, negligibly slow in the self-diffusion of liquid water, the self-diffusion coefficients of liquid water have been redetermined with O^{18} as tracer. The use of O^{18} as tracer would also eliminate the errors introduced in the earlier measurements due to the difference between properties of H_2^2O and H_2^1O.

Experimental

Tracer Solution.—The tracer solution used, water enriched 1.3% in O^{18}, was supplied by Stuart Oxygen Company, San Francisco, Calif., and obtained on allocation from the Isotopes Division, U.S. Atomic Energy Commission. As before the "ordinary" water used had been doubly distilled from neutral potassium permanganate solution.

Diffusion Measurement.—Diffusion capillaries described in the previous work[2] were used exclusively in the present work. The manipulation techniques have already been described in the previous communication.

Analysis.—All the water samples were analyzed by means of a Consolidated-Nier type of mass-spectrometer. After each diffusion experiment, the water in each capillary was well-mixed, an aliquot part of it (about 0.005 g.) was equilibrated with known amount of pure ordinary carbon dioxide gas in a glass bulb for 24 hours. The equilibration bulb was then immersed in a Dry Ice–acetone-bath, and the CO_2 gas separated from the water and had its O^{18}-content analyzed. From the measured O^{18}-content of the CO_2 gas, the O^{18}-content of the original water sample can be calculated. The enrichment factor of 1.039 for the water–carbon dioxide exchange as given by Urey and Greiff[3] was used in the present calculations.

Results and Discussion

The results of the present measurements are listed in Table I. Each value of diffusion coefficient D listed in Table I is the average of at least 6 independent determinations. Because of the errors introduced in the weighing of small drops of water samples in the analytical procedure employed, the standard deviations are in general much larger than those reported in the earlier work[2] with deuterium as tracer. The accuracy of the diffusion technique itself, however, should be the same as in the earlier work.

TABLE I

Temp., °C.	D, cm.²/sec., × 10^5
1.11 ± 0.09	1.52 ± 0.07
4.9 ± .10	1.71 ± .027
10.0 ± .04	2.01 ± .09
18.0 ± .03	2.51 ± .20
25.0 ± .01	3.01 ± .22
35.0 ± .01	3.87 ± .052
45.0 ± .02	4.68 ± .12
55.0 ± .03	5.83 ± .30

Values of log ($D \times 10^5$) obtained in the present work are plotted in Fig. 1 *vs.* the reciprocal of absolute temperature. Previous values of D obtained with deuterium as tracer[2] are also plotted in Fig. 1 (lower curve) for comparison.

As can be clearly seen from Fig. 1, the self-diffusion coefficients of liquid water determined with O^{18} as tracer are in general from 35 to 45% higher than previous values obtained with deuterium as tracer. The activation energy for diffusion, as calculated from the slope of the log ($D \times 10^5$) *vs.* $1/T$ plot is 4.41 kcal./mole, which is smaller than the earlier value[2] of 4.58 kcal./mole. Because of the comparatively large experimental error involved in the present work, the numerical uncertainty in the activation energy of 4.41 kcal./mole is much larger than the earlier value of 4.58 kcal./mole. Thus quantitative comparison of these two activation energies is difficult. Careful examination of the present experimental data by the method of least squares does show, however, that it is more probable

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[2] J. H. Wang, *ibid.*, **73**, 510 (1951).

[3] H. C. Urey and L. J. Greiff, *ibid.*, **57**, 321 (1935).

for the present diffusion process to have an activation energy 3 or 4% lower rather than equal to that of the earlier work.

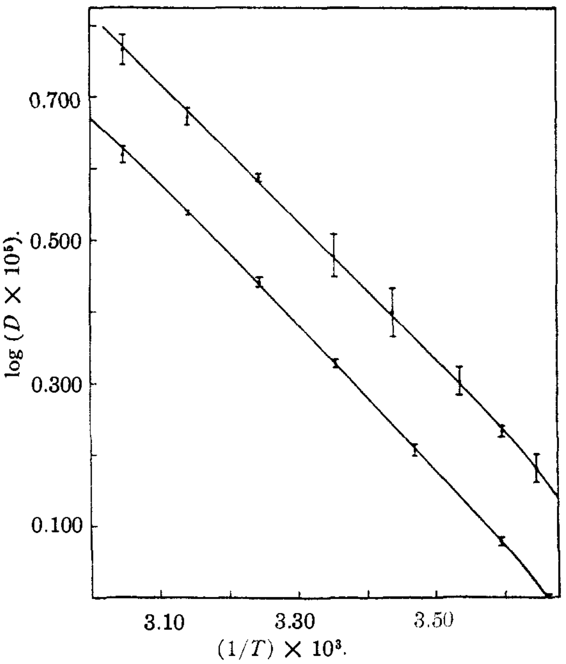

Fig. 1.—Values of log ($D \times 10^5$) for liquid water plotted *vs.* ($1/T$) $\times 10^3$: upper curve, present measurements with O^{18} as tracer; lower curve, previous measurements with H^2 as tracer.

The possibility of a special mechanism of hydrogen-atom transfer in self-diffusion, *e.g.*, like that which occurs in the electrolytic conduction by hydrogen ion, is dispelled because $H^1_2O^{18}$ used in the present work diffuses faster than $H^2_2O^{16}$ used in the earlier work at all the corresponding temperatures. That this difference between two diffusion coefficients is due to the difference in properties between H^1_2O and H^2_2O and not due to any unknown fast mechanism of transfer of oxygen atoms is demonstrated by diffusion measurements with $H^2_2O^{18}$ as tracer. In this last experiment the diffusion capillaries were filled with heavy water that contained 99.8% of H^2_2O enriched by 0.3% in O^{18}. After diffusion the average O^{18}-content in each capillary was determined by mass-spectrometric analysis. The average of six determinations gives a value of diffusion coefficient of (2.31 ± 0.24) $\times 10^{-5}$ cm.^{2}/sec. at 35.0 ± 0.02°. This value is much lower than the diffusion coefficient of $H^1_2O^{18}$, (3.87 ± 0.052) $\times 10^{-5}$ cm.^{2}/sec., at the same temperature. It is even lower than the diffusion coefficient determined with 99.8% $H^2_2O^{16}$ as tracer, which is (2.76 ± 0.037) $\times 10^{-5}$ cm.^{2}/sec. at 35.0°.[2] This last difference is probably due to the higher molecular weight of $H^2_2O^{18}$. However, because of the low enrichment in O^{18} of the $H^2_2O^{18}$ used, the uncertainty in the result of the last measurement is too large to show any quantitative dependence of diffusion coefficient upon the molecular weight. It does, however, eliminate any suspected fast mechanism of oxygen-atom transfer during diffusion.

The smaller activation energy for $H^1_2O^{18}$ diffusion as compared to that for $H^2_2O^{16}$ diffusion is in agreement with the fact that H^2_2O is more associated (contains a higher degree of "ice-structure") than H^1_2O at the same temperature. For example, the temperature of maximum density (where on heating the effect of thermal expansion begins to overcome contraction due to breaking down of the "ice-structure") is 11.22° for H^2_2O[4,5] but is 4.08° for H^1_2O. The dipole moment of H^2_2O in benzene[6] and dioxane[7] are all slightly larger (about 1%) than that of H^1_2O. Thus each hydrogen bond in H^2_2O is slightly stronger than that in H^1_2O, consequently each H^2_2O molecule in heavy water has statistically a slightly larger number of hydrogen bonds attached to it than each H^1_2O molecule in ordinary water. It follows then that the activation energy for diffusion of H^2_2O molecule in heavy water should be slightly higher than that for diffusion of H^1_2O molecule in ordinary water as has been formed experimentally. Quantitative comparison of the two sets of diffusion coefficients cannot easily be made because of the comparatively large experimental uncertainty in the activation energy obtained in the present work. Furthermore, in the present measurements with $H^1_2O^{18}$ as tracer (enrichment of O^{18} less than 1.5%) the diffusion coefficient is practically constant along the diffusion path and closely approximates the true self-diffusion coefficient of liquid water, but in the earlier work[2] with $H^2_2O^{16}$ (practically pure $H^2_2O^{16}$ diffusing into ordinary water) the diffusion coefficients vary with isotopic composition and the measured values are really a special kind of "integral" diffusion coefficients. Moreover, in the latter case the variation of activity coefficient of $H^2_2O^{16}$ along the diffusion path may have to be taken into consideration. In order to avoid this complication measurements of the self-diffusion of liquid water with $H^2H^1O^{16}$ as tracer (deuterium content of water in capillary before diffusion below 1.5 atom per cent.) are in progress. The results will be given in a third article of this series in the near future.

On the other hand, since the diffusion coefficients obtained with $H^1_2O^{18}$ as tracer closely approximate the true self-diffusion coefficients of liquid water, we may compute the values of $D\eta/T$, the reciprocal of which is a measure of the relative effective radius of the diffusion molecule at various temperatures, as in the earlier work.[2] The results are listed in Table II.

The constancy of ($D\eta/T$) in Table II indicates that no definite species of associated water molecules exists in liquid water between 0 and 55°. The approximate linear dependence of log D on $1/T$ between 5° and 55° for $H^1_2O^{18}$ diffusion as shown in Fig. 1 corresponds to the constancy of activation energy and shows that there is little change in structure of liquid water between 5° and 55°. Below 5° there is indication of a noticeable increase of activa-

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TABLE II

Temp., °C.	$D \times 10^5$, cm.²/sec.	$\eta \times 10^3$, poise	$(D\eta/T) \times 10^{10}$
0	1.45	17.921	9.51
5	1.74	15.188	9.49
15	2.31	11.404	9.15
25	3.00	8.937	8.99
35	3.82	7.225	8.95
45	4.81	5.988	9.05
55	5.90	5.064	9.11
		Average	9.18 ± 0.21

TABLE III

Temp., °C.	λ_s, cm.	$D_\tau = D\lambda_s/c = \lambda^2$ cm.²
0	3.34	16.1×10^{-18}
5	2.83	16.4×10^{-16}
15	2.06	15.9×10^{-16}
25	1.57	15.7×10^{-16}
35	1.24	15.8×10^{-16}
45	1.01	16.2×10^{-16}
55	0.83	16.3×10^{-16}
	Average	$(16.1 \pm 0.25) \times 10^{-16}$

tion energy due to considerable increase in the "ice-structure" in liquid water below 5°. All these facts are in agreement with previous results obtained with $H^2_2O^{16}$ as tracer and substantiate the conclusion advanced earlier.[2]

Comparison with Dielectric and Viscosity Data

According to the transition state theory of rate processes,[8] the self-diffusion coefficient D is given by

$$D = \lambda^2 \left(\frac{kT}{h}\right) e^{\Delta S^{\ddagger}/R}\, e^{-\Delta H^{\ddagger}/RT} \qquad (1)$$

where λ is the distance between two successive equilibrium positions of a diffusing molecule in the direction of diffusion, k is Boltzmann's constant, h Planck's constant, T the absolute temperature, $\Delta S^{\ddagger}$ the entropy of activation, and $\Delta H^{\ddagger}$ the heat of activation. The time of relaxation τ for dipole orientation is given by

$$\frac{1}{\tau} = \nu = \frac{c}{\lambda_s} = \left(\frac{kT}{h}\right) e^{\Delta S^{\ddagger}/R}\, e^{-\Delta H^{\ddagger}/RT} \qquad (2)$$

where ν is the frequency and λ_s the wave length corresponding to the time of relaxation τ, and c is the velocity of light. If we assume that the activation processes in self-diffusion and dipole orientation of water molecules are the same, the values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ in equation (1) should be equal to the corresponding values in equation (2). Dividing (1) by (2), we have

$$D_\tau = D\lambda_s/c = \lambda^2 \qquad (3)$$

thus values of λ can be computed from (3) by combining self-diffusion and dielectric data. Since there is little change in structure of liquid water between 5° and 55°, one may expect λ to be practically constant in this temperature range. Thus if our assumption that self-diffusion and dipole orientation of water molecules involve the same activation process is correct, the value of D_τ should remain constant between 5° and 55°. By using the relaxation times accurately determined by Collie, Hasted and Ritson[9] and the self-diffusion coefficients obtained with O^{18} as tracer in the present work, values of D_τ at different temperatures have been computed and listed in Table III. It is clearly shown in Table III that the value of D_τ remains constant within experimental error in this temperature range. From the average value of D_τ, one can compute λ to be 4.0×10^{-8} cm.

On the other hand, according to the transition state theory of rate processes, the viscosity η is given by[8]

$$\eta = \frac{\lambda_1}{\lambda_2\lambda_3}\left(\frac{h}{\lambda^2}\right) e^{-\Delta S^{\ddagger}/R}\, e^{\Delta H^{\ddagger}/RT} \qquad (4)$$

where λ_3 is the mean distance between two neighboring water molecules in the direction of motion of viscous flow, λ is, as before, the distance between two successive equilibrium positions in the direction of motion, λ_2 is the mean perpendicular distance between two adjacent rows of molecules having the same bulk velocity of motion, and λ_1 is the distance in the direction of velocity gradient between two adjacent layers of molecules. It is clear from the definition of these parameters that λ should be smaller than λ_3, because if we imagine a certain length l in the direction of flow that contains a large number, n, of water molecules and a large number, n', of vacancies, then λ is equal to $l/(n + n')$ and λ_3 is equal to l/n, hence $\lambda < \lambda_3$. It is also not difficult to see from pure geometric considerations that λ should be larger than λ_1. It is hard to guess the magnitude of λ_2 as compared to λ, but we know $\lambda_2 > \lambda_1$.

If we accept Eyring's idea of considering self-diffusion and viscous flow as involving the same activation process, then on multiplying equation (1) by (4), we obtain

$$\lambda_1/\lambda_2\lambda_3 = D\eta/kT \qquad (5)$$

The right-hand side of (5) has an average value of 6.65×10^6 cm.$^{-1}$ as calculated from the data listed in Table II. One may also consider $\lambda_1\lambda_2\lambda_3$ as the volume per water molecule, *i.e.*, $(0.997 \times 18.02)/(6.023 \times 10^{23})$ or 2.98×10^{-23} cm.³ Combining these two values we find

$$\lambda_1 = 1.4 \times 10^{-8} \text{ cm.}$$

and

$$(\lambda_2\lambda_3)^{1/2} = 4.6 \times 10^{-8} \text{ cm.}$$

These values are consistent with the value of $\lambda = 4.0 \times 10^{-8}$ cm. obtained from the data in Tables II and III. These results show that Eyring's transition-state theory of rate processes is a fair description of the self-diffusion, viscous flow, and dipole orientation of liquid water, and that these three processes involve essentially the same activation mechanism.

ST. LOUIS, MO.

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