bility of the tagged atom reacting with radicals which it has formed in losing its recoil energy.

Alternative Theory of Product Formation Following (n,γ) Activation.—Friedman and Libby and Fox and Libby[11] have interpreted their important data on the products of the (n,γ) reaction of bromine in liquid and solid propyl bromides to indicate that the parent molecule is the favored product when bonds are broken by high energy bromine atoms, and other products are favored when bonds are broken by recoiling atoms with energies only a few times greater than bond energies ("epithermal" energy range). We feel that there are a variety of theoretical reasons and types of experimental evidence which preclude the possibility that this subdivision of reaction probability which they have outlined is generally applicable. Some of these have been discussed earlier.[7] They include a consideration of: (1) the differences in collisions and in fragmentation probability in condensed phases as compared to the gas phase; (2) the low probability of "head-on" collisions in which a recoil atom can

(11) (a) L. Friedman and W. F. Libby, *J. Chem. Phys.*, **17**, 647 (1949); (b) Fox and W. F. Libby, *ibid.*, **20**, 487 (1952).

lose all of its energy to a target atom; (3) the fact that inorganic combination as well as organic combination has been shown to occur in the high energy region[6]; (4) the fact that a considerable fraction of both the organic and inorganic yield from the (n, γ) reaction on the alkyl bromides and alkyl iodides occurs after the recoil atoms have reached thermal equilibrium with the medium[6,7]; (5) the fact that the increase in organic yield in the solid phase as compared to the liquid which would be expected from the epithermal region theory does not occur in certain alkyl iodides[7]; (6) the fact that in the work of the present paper and in the case of methyl iodide it has been found that added elemental halogen reduces the yield of the simplest organic product molecules resulting from (n,γ) activation more rapidly than the yield of more complex products.

MADISON, WISCONSIN

Self-diffusion and Structure of Liquid Water. III. Measurement of the Self-diffusion of Liquid Water with H², H³ and O¹⁸ as Tracers[1]

BY JUI HSIN WANG, CHARLES V. ROBINSON AND I. S. EDELMAN[2]

Measurements of the diffusion of small amounts of deuterium hydroxide and tritium hydroxide in ordinary water were made at several temperatures. Previous data on the diffusion of $H_2^1O^{18}$ in ordinary water have been revised. The results confirm previous conclusions regarding the structure of water and the mechanism of self-diffusion, dipole orientation and viscous flow in water. The effect of the differences in the moments of inertia of various water molecules is discussed.

In previous work the self-diffusion coefficients of liquid water at different temperatures were determined with $H_2^2O^{16}$ and $H_2^1O^{18}$ as tracers, respectively.[1] But since in the former case when deuterium oxide (99.8%) was allowed to diffuse into ordinary water the measurements yielded only integral diffusion coefficients, direct comparison of these values with the tracer diffusion coefficients for other labeled water molecules (*e.g.*, $H_2^1O^{18}$ with average O^{18}-enrichment at or below 1 atom per cent.) is difficult. In the present work the diffusion coefficients of $H^1H^2O^{16}$ and $H^1H^3O^{16}$ in ordinary water are determined at several temperatures. The average enrichment of H^2 in the diffusion capillaries was about 1 atom per cent., that of H^3 about 0.0001 atom per cent. Consequently we may consider the measured diffusion processes as the diffusion of individual labeled water molecules in ordinary water and take the so obtained diffusion coefficients as the tracer diffusion coefficients for the corresponding molecules in ordinary water.[3]

(1) Paper I, THIS JOURNAL, **73**, 510 (1951); paper II, *ibid.*, **73**, 4181 (1951).

(2) Research Fellow of American Heart Association.

(3) For the definition of the term "tracer-diffusion," see J. H. Wang, THIS JOURNAL, **74**, 1182 (1952).

It is hoped that these tracer diffusion coefficients, taken together, will be as useful for theoretical studies on the structure of water as the true self-diffusion coefficient of liquid water which cannot be measured directly. Previous data on the diffusion of H_2O^{18} in ordinary water contained a systematic numerical error. This has been corrected and the revised values are included in the present article.

Experimental

Tracer Solutions.—The deuterium oxide used was supplied by Stuart Oxygen Company, San Francisco, Calif., and obtained on allocation from the Isotopes Division, U. S. Atomic Energy Commission. The deuterium oxide as shipped, 99.8% in deuterium oxide, was redistilled and diluted with ordinary conductivity water before use. The diluted heavy water contained about 2.5 atom per cent. excess of deuterium before diffusion. After diffusion the average concentration of deuterium left in the capillaries is about 0.5 atom per cent. excess.

The tritium was obtained in the form of hydrogen gas from the Isotopes Division, U. S. Atomic Energy Commission, Oak Ridge, Tennessee. The radioactive hydrogen gas was equilibrated with distilled water in the presence of platinum oxide as catalyst. The tritiated water so prepared had a specific activity of about 1 mc. per g. Thus the atom fraction of tritium in this radioactive water is less than 10^{-6}. This tritiated water was redistilled before use.

The O^{18}-enriched water contained, before diffusion, about

1.5 atom per cent. of O^{18} and was obtained from the same source as the deuterium oxide.

Diffusion Measurements.—The improved capillary method[4] was used in the present work. In each measurement a set of capillaries, which varied from 1.94 to 4.79 cm. in length and all had common cross-sectional area between 0.187 and 0.220 sq. mm., were filled with tagged water and held vertically in an auxiliary bath (with accurately adjustable water level) to reach thermal equilibrium with the bath at the desired temperature. After 20 min. or so these capillaries were lowered into steadily stirred bath filled with ordinary distilled water for diffusion measurements. The diffusion time was so adjusted that after diffusion only about $1/5$ of the original amount of tracer was still left in each of the capillaries. Under these conditions the solution of the one-dimensional tracer diffusion equation

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

can be represented with enough accuracy by

$$\frac{Dt_i}{(l_i - \Delta l)^2} = \frac{4}{\pi} \ln\left[\left(\frac{8}{\pi^2}\right)\frac{c_0}{A_i/(l_i - \Delta l)a}\right] \qquad (2)$$

where c_0 is the initial concentration of tracer, A_i is the total amount of tracer left in capillary i (with length l_i and cross-sectional area a) after diffusion has taken place for the length of time t_i, Δl is the common difference between lengths of diffusion paths and the geometric lengths of the corresponding capillaries with the same cross-sectional area a and held vertically at equivalent positions in the same circulating bath. The set of equations (2) can be solved for both Δl and D. Obviously for given a, Δl is a function of stirring rate, shape of vessel and viscosity of solution, etc. In all the present measurements the rate of stirring was so adjusted that $2\Delta l/l$ is negligible as compared to other experimental uncertainties in the present procedure of diffusion measurement. Thus under the present operating conditions, equation (2) can be written simply as

$$\frac{Dt_i}{l_i^2} = \frac{4}{\pi} \ln\left[\left(\frac{8}{\pi^2}\right)\frac{c_0}{(c_{av})_i}\right] \qquad (3)$$

where $(c_{av})_i = A_i/l_i a$. Equation (3) has been used in all computations of the present work. The temperature of each bath was kept constant within 0.01°.

Analysis of $H^1H^2O^{16}$ Samples.—After each diffusion period the water left in each capillary was well-mixed and sampled out by means of fine pipets. These samples were quantitatively diluted with ordinary water to a total volume of about 0.06 ml. by means of a semi-micro balance which is accurate to 0.00001 g. The diluted samples were sealed in clean, dry glass ampoules and kept for mass-spectrometric analysis. The details of the technique used in carrying out the mass-spectrometric analyses has been described previously.[5] Water samples were vaporized and converted into hydrogen gas by means of granular zinc at about 390°. Non-linearity errors of the mass-spectrometer were evaluated and corrected for by calibration against measured deuterium dilutions. The $(H_3)^+$ effect was corrected for by using the empirically determined (mass 3)/(mass 2) ratio vs. hydrogen pressure curves. In order to detect memory effects of the apparatus each diluted sample was divided to approximately four or more aliquot parts, and successively converted to obtain four or more samples of hydrogen gas. These gas samples were analyzed successively in the mass spectrometer. It was found that at deuterium concentrations encountered in the present work discarding the first one or two gas samples was sufficient to eliminate any noticeable error due to memory effect. A sample of these data is shown in Table I.

To avoid fractionation effect, the conversion of each aliquot part of each water sample was carried out to completion. In handling the water samples, care was taken to avoid contamination by moisture in air. To determine c_0, samples of the heavy water used to fill the capillaries were also taken before diffusion. These were diluted quantitatively to give approximately the same atom per cent. of deuterium as the diluted samples taken after diffusion and analyzed by the same procedure.

(4) J. H. Wang, *ibid.*, **74**, 1182 (1952).

(5) A. K. Solomon, I. S. Edelman and S. Soloway, *J. Clinical Investigation*, **29**, 1311 (1950).

TABLE I

DETECTION OF MEMORY-EFFECT IN DEUTERIUM ANALYSIS

Sample number	Ratio $(H^2H^1)/(H_2^1) \times 10^3$ determined from successive samples						Average ratio	Atom % of H^2
D-15	9.38	9.79	9.90	9.92	9.76	9.84	9.84	0.437
(discard)								
D-24	2.67	2.67	2.58	2.65	2.82		2.68	.118
D-26	2.68	2.55	2.50	2.54	2.45		2.51	.111
(discard)								

Since in obtaining equation (2) as the solution of equation (1) we imposed the boundary condition that the concentration of tracer in the circulating bath was kept at zero instead of at the natural abundance of deuterium in ordinary water, we should express all concentrations of tracer in atom per cent. excess of deuterium instead of the actual atom per cent. in the computation to obtain the diffusion coefficients. The abundance of deuterium in ordinary distilled water as determined in the present work is 0.015 atom per cent. This value has been used in all the computations for $H^1H^2O^{16}$ diffusion.

Analysis of $H^1H^3O^{16}$ Samples.—The tritiated water was quantitatively diluted in a similar manner as the deuterated water samples and then allowed to react with methylmagnesium iodide to form tritiated methane. The radioactive methane was then counted in a proportional counter described in another paper.[6] The reaction between tritiated water and Grignard reagent took place in a Pyrex bottle connected to the same vacuum line used to fill the proportional counters. The bottle was successively cleaned with hydrochloric acid, alcohol and ether, and heated in an oven every time before use. Under the operating conditions of the present work it was found that the memory effect was negligible. However, the reaction between water and Grignard reagent stopped before 100% completion, and thus it seemed possible that some fractionation error might have been introduced. Despite this it was found that by controlling the conditions of the reaction the specific activity of the tritiated methane so produced was reproducible and was directly proportional to the specific activity of the water samples. Since the natural abundance of tritium can be considered as zero, and since in diffusion computations only the ratio c_{av}/c_0 is involved, we assumed that no appreciable error was introduced in the final diffusion coefficients by the above mentioned fractionation effect.

Analysis of $H_2^1O^{18}$ Samples.—Previously reported data on the diffusion of H_2O^{18} in ordinary water[1] contained a systematic numerical error in the computation of analytical data. By correcting this error and by using the latest value of $K = 2.088$[7] as the equilibrium constant of the exchange reaction

$$CO_2^{16} \text{ (gas)} + H_2O^{18} \text{ (liq)} = CO^{16}O^{18} + \text{(gas)} + H_2O^{16} \text{ (liq)}$$
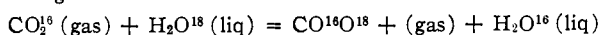
the earlier data on the analysis of O^{18}-enriched samples were recalculated. The method of computation is outlined below. Let

X_w, X_w' = atom fraction of O^{18} in water before and after equilibration, respectively

X_g, X_g' = atom fraction of O^{18} in CO_2(gas) before and after equilibration, respectively

At equilibrium we may write, with sufficient accuracy

$$\frac{(1 - X_w')(2X_g')}{X_w'(1 - 2X_g')} = 2.088 \qquad (4)$$

Material balance requires that

$$\frac{W}{M}X_w + \frac{PV}{RT}(2X_g) = \frac{W}{M}X_w' + \frac{PV}{RT}(2X_g') \qquad (5)$$

where W is the weight of O^{18}-enriched water equilibrated with carbon dioxide gas of volume V, pressure P at room temperature T, R is the gas constant and M is the average molecular weight of sample water. Since the O^{18}-content of water samples in this work is 1.5 atom per cent. or lower, we may simply use $M = 18.0$. The error introduced in the final results by assuming carbon dioxide to be a perfect gas

(6) C. V. Robinson, *Rev. Sci. Instruments*, **22**, 353 (1951).

(7) I. Kirshenbaum, "Physical Properties and Analysis of Heavy Water," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 66.

at room temperature $(n = PV/RT)$ is negligible. Solving (4) and (5) gives

$$X_w = \frac{X'_g}{1.044 - 1.088X'_g} + 2\left(\frac{PV}{RT}\right)\left(\frac{18.0}{W}\right)(X'_g - X_g) \quad (6)$$

The atom per cent. of O^{18} in water sample, X_w, can thus be calculated by means of (6) from the measured values of X'_g and X_g. In diffusion computations the normal abundance of O^{18} in ordinary water, which is equal to $1.04X_g$, was subtracted from all the X_w's thus obtained so that all the tracer concentrations were expressed in atom per cent. excess in conformity with the boundary conditions of equation (3).

The new calculations yielded considerably lower values of diffusion coefficients for $H_2^1O^{18}$ than those reported in Paper II of this series. The preliminary value of D for the diffusion of $H_2^1O^{18}$ into mixtures of $H_2^1O^{16}$ and $H_2^1O^{16}$ at 35° reported in that paper has to be discarded because the use of $K = 2.088$ for the equilibrium constant of the exchange reaction

$$H_2^1O^{18}(\text{liq}) + CO_2(\text{gas}) = H_2^1O^{16}(\text{liq}) + CO^{16}O^{18}(\text{gas})$$
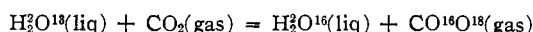
cannot be justified. Thus although we may not expect the true equilibrium constant for the above exchange reaction to be much different from 2.088, because of the low enrichment of the $H_2^1O^{18}$ used (0.1 to 0.3 atom per cent. excess in O^{18}) the values of c_{av} and c_0 which were expressed in atom per cent. excess of O^{18} might be in serious error.

Summary of Results

Results of the present work are summarized in Table II. Each diffusion coefficient listed in Table II is the average result of at least four measurements. The actual number of determinations made for each case varied considerably; e.g., for the diffusion of $H^1H^3O^{16}$ at 35°, the listed value $D \times 10^5 = 3.04 \pm 0.08$ cm.^{2}/sec. is the aver-

Fig. 1.—Values of log $(D \times 10^5)$ for liquid water plotted vs. $(1/T) \times 10^3$: ◐, tracer-diffusion coefficient of $H_2^1O^{18}$ in ordinary water; ●, tracer diffusion coefficient of $H^1H^3O^{16}$ in ordinary water; O, tracer diffusion coefficient of $H^1H^2O^{16}$ in ordinary water; □, tracer diffusion coefficient of $H^1H^2O^{16}$ in ordinary water determined by optical method (L. G. Longsworth); ◑, average diffusion coefficient of $H^1H^2O^{16}$ and $H_2^2O^{16}$ in mixtures of ordinary water and deuterium oxide.

age value of 14 determinations, but for the diffusion of $H^1H^2O^{18}$ at 55° only 4 measurements were made.

TABLE II

Diffusion of $H^1H^2O^{16}$, $H^1H^3O^{16}$ and $H_2^1O^{18}$ in Ordinary Water at Various Temperatures

Temp., °C.	$D \times 10^5$, cm.^{2}/sec.		
	$H^1H^2O^{16}$	$H^1H^3O^{16}$	$H_2^1O^{18}$
1.11			1.44 ± 0.097
4.9			$1.55 \pm .062$
5.0		1.39 ± 0.048	
10.0	1.57 ± 0.04		$1.90 \pm .04$
15.0		$1.83 \pm .055$	
18.0	$2.06 \pm .05$		$2.35 \pm .16$
25.0	$2.34 \pm .08$	$2.44 \pm .057$	$2.66 \pm .12$
35.0		$3.04 \pm .080$	$3.49 \pm .15$
45.0	$3.87 \pm .07$	$3.83 \pm .050$	$4.38 \pm .11$
55.0	$4.95 \pm .08$		$5.45 \pm .30$

Values of log D from Table II are plotted vs. $(1/T) \times 10^3$ in Fig. 1. Radii of circles in Fig. 1 represent the standard deviations listed in Table II. A single value of $D \times 10^5 = 1.128$ cm.^{2}/sec. for the tracer diffusion coefficient of $H^1H^2O^{16}$ in ordinary water at 1° obtained by Longsworth by the Rayleigh optical method[8] (represented by a small square point in Fig. 1) is also included in the plot for comparison. This last value was obtained by Longsworth by linear extrapolation of three measurements (at approximate deuterium concentration of 6, 12 and 25 atom per cent., respectively) to infinite dilution. It can be noticed from Fig. 1 that Longsworth's value agrees with the present values within the experimental uncertainties of the present data. Since the optical method has been developed to much greater precision than the present method, this agreement serves as an additional independent check on the reliability of results obtained by the capillary method in general.

Figure 1 indicates that the tracer diffusion coefficient of $H^1H^2O^{16}$ and $H^1H^3O^{16}$, respectively, in ordinary water cannot differ by an amount greater than the experimental uncertainties of the present data. However, comparison of the relative magnitudes of these two sets of diffusion coefficients, though interesting, has to be postponed until further refinements of the present experimental technique have made more accurate data available. On the other hand, Fig. 1 indicates that the diffusion coefficient of $H_2^1O^{18}$ is, on the average, about 14% higher than the values for $H^1H^2O^{16}$ and $H^1H^3O^{16}$ at the same temperature. Graupener and Winter[9] reported two values for the diffusion coefficient of $H_2^1O^{18}$ in water at 25 and 45°, respectively, which are equal to the corresponding values they obtained for $H^1H^2O^{16}$ within experimental uncertainties. This discrepancy seems to deserve further investigation.

The activation energy for diffusion at 25° calculated from the slopes of the log D vs. $(1/T) \times 10^3$ curves in Fig. 1 are 4.6 ± 0.1 kcal./mole for $H^1H^2O^{16}$ and $H^1H^3O^{16}$, and 4.4 ± 0.3 kcal./mole for $H_2^1O^{18}$ in water. These values should be approximately equal to the activation energy for true self-diffusion in liquid water at 25°.

(8) L. G. Longsworth, private communication.
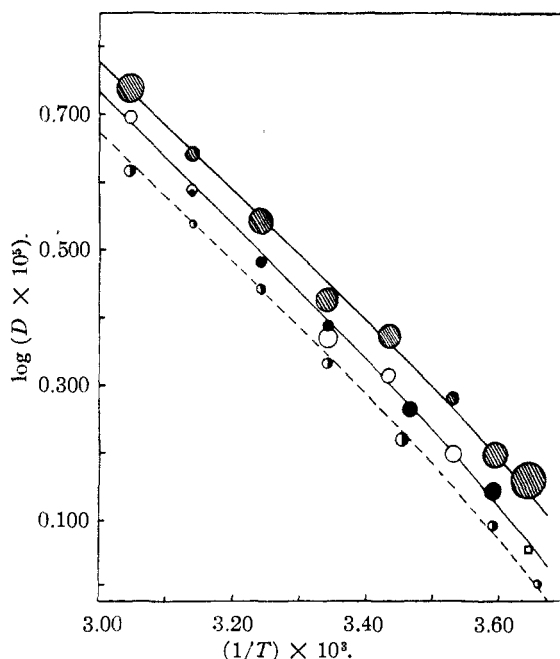(9) K. Graupener and E. R. S. Winter, J. Chem. Soc., 1145 (1952).

Discussions

Semi-crystalline Structure.—It was concluded in paper I of this series[1] that the constancy of $D\eta/T$ between 0 and 55° indicates that at room temperatures no definite species of associated water molecules (e.g., $(H_2O)_2$, $(H_2O)_4$, etc.) exist in liquid water, and that the latter has a semi-crystalline structure. The process of self-diffusion in water is then carried out essentially by the single H_2O molecules that are in thermal equilibrium with the large semi-crystalline water lattice. Our present result confirms this conclusion. An illustration for the case of $H^1H^3O^{16}$ is given in Table III.

TABLE III

Temp., °C.	$D \times 10^5$, cm.²/sec.	$\eta \times 10^2$, poise	$(D\eta/T) \times 10^{10}$
5	1.39	15.188	7.58
15	1.83	11.404	7.24
25	2.44	8.937	7.31
35	3.04	7.225	7.13
45	3.83	5.988	7.21
		Average	7.29 ± 0.15

The fact that $H_2^1O^{18}$ diffuses faster than $H^1H^2O^{16}$ or $H^1H^3O^{16}$ at corresponding temperatures shows that special mechanisms of fast hydrogen ion transfer, such as those similar to that which occurs in the electrolytic conduction by hydrogen ion, are negligible in the self-diffusion of liquid water.

Comparison with Dielectric and Viscosity Data.—According to the transition state theory of rate processes,[10,11] the relaxation time τ for dipole orientation of water molecules and viscosity η are given, respectively, by

$$D = \lambda^2 \left(\frac{kT}{h}\right) e^{\Delta S^{\ddagger}/R} e^{-\Delta H_*^{\ddagger}RT} \qquad (7)$$

$$\frac{1}{\tau} = 2\pi\nu = \frac{2\pi c}{\lambda_s} = \left(\frac{kT}{k}\right) e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}RT} \qquad (8)$$

and

$$\eta = A \left(\frac{h}{\lambda^2}\right) e^{-\Delta S^{\ddagger}/R} e^{\Delta H^{\ddagger}RT} \qquad (9)$$

where λ is the distance between two successive equilibrium positions of a diffusing water 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, $\Delta H^{\ddagger}$ the heat of activation, ν is the frequency and λ_s the wave length corresponding to the time of relaxation τ, and c the velocity of light. The constant A in equation (9) is a lattice factor and is, according to the original theory of Eyring, equal to $\lambda_1/(\lambda_2\lambda_3)$ where λ_3 is the mean distance between two neighboring water molecules in the direction of viscous flow, λ_2 the mean perpendicular distance between two adjacent rows of molecules having the same bulk velocity of motion, and λ_1 is the mean distance in the direction of velocity gradient between two adjacent layers of molecules. There is some doubt on the exact meaning of the constants λ_1, λ_2 and λ_3 in the case of semi-crystalline

structure. For the purpose of the present discussion we may replace them by the single noncommittal parameter A. Approximate calculations of the partition functions for the normal and activated states of the diffusing molecules have been made[10] to enable the estimation of the self-diffusion coefficients of several liquids. However, these approximate calculations are usually based on so many doubtful assumptions that at present it does not look encouraging for us to continue in this direction. If we assume, as in paper II of this series, that the activation processes in self-diffusion dipole orientation and viscous flow of water molecules are the same, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ should have the same values in equation (7) as in (8) or (9). Combining equations (7), (8) and (9), we have

$$D = \lambda^2/\tau = AkT/\eta \qquad (10)$$

Hence the corresponding activation energy

$$E = -R \frac{d \ln D}{d(1/T)} = R \frac{d(\ln \tau)}{d(1/T)} = R \frac{d(\ln (\eta/T))}{d(1/T)} \qquad (11)$$

should be the same whether calculated from self-diffusion, dielectric relaxation or viscosity data. The definition of experimental activation energy as $-R(d \ln D)/d \ln (1/T)$ instead of $-R(d \ln (D/T))/d \ln (1/T)$ has been discussed elsewhere.[12] The activation energy for true self-diffusion of ordinary liquid water should be approximately equal to that for the diffusion of $H^1H^2O^{16}$ or $H^1H^3-O^{16}$ or $H_2^1O^{18}$ determined in the present work. This is equal to 4.6 kcal./mole at 25°. The activation energy calculated according to (11) from the dielectric relaxation data on water[13] is 4.6 kcal./mole at 25°. The activation energy calculated by means of (11) from viscosity data is 4.59 kcal./mole at 25°. The close agreement of these three values confirm our earlier conclusion[1] that the self-diffusion, dipole orientation and viscous flow of liquid water involve essentially the same activation mechanism.

If we assume that the present diffusion coefficients for $H_2^1O^{18}$ may as first approximation be taken as the true self-diffusion coefficients of water, we may calculate λ^2 according to (11) from diffusional and dielectric data. The result is summarized in Table IV.

TABLE IV

Temp., °C.	$D \times 10^5$, cm.²/sec.	$\tau \times 10^{12}$, sec.	$D\tau \times 10^{16}$, cm.²
0	1.33	17.7	2.35
5	1.58	15.0	2.37
15	2.14	10.9	2.33
25	2.83	8.32	2.36
35	3.55	6.57	2.33
45	4.41	5.35	2.36
55	5.41	4.40	2.38
		Average	2.35 ± 0.02

From the average value of $D\tau = \lambda^2$, we get $\lambda = 1.5 \times 10^{-8}$ cm.

Vacancy Creation vs. Hydrogen Bond "Breaking."—Let us now investigate the significance of the activation energy of 4.6 kcal./mole computed

(10) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 524.

(11) R. E. Powell and H. Eyring, "Advances in Colloid Science," (Edited by Kreamer), Interscience Publishers, Inc., New York, N. Y., 1942, p. 213.

(12) J. H. Wang, THIS JOURNAL, **74**, 1612 (1952).

(13) C. H. Collie, J. B. Hasted and D. M. Ritson, Proc. Phys. Soc., **60**, 145 (1948).

above. According to the transition state theory the activation process for viscous flow or for self-diffusion of non-associating liquids involves essentially the creation of a vacancy in front of the diffusing molecule for the latter to move into. Consequently for a large number of "normal" liquids, this activation energy is equal to $1/4$ to $1/3$ the corresponding heat of vaporization. This picture is supported by the fact that the molal volumes of these liquids are larger than those for the corresponding solids and that with increasing pressure (i.e., decreasing the total volume occupied by the vacancies), the viscosity of these liquids increases. For structural liquids such as water, however, experimental evidences contradict this picture. Thus the molal volume of liquid water is smaller than that of ice, and at temperatures not far from $0°$ the viscosity of water decreases continually when the external pressure is increased from atmospheric pressure to about 1000 kg./cm.^{2}.[14] These facts indicate that in the self-diffusion of liquid water at room temperature and pressure the water molecules are so loose-packed in their normal state that enough vacancies exist to make the dissociation of water molecules from the semi-crystalline lattice the rate-determining step. Since the molecules in water are held together essentially by the so called hydrogen bonds, the activation energy should be related to the energy of each hydrogen bond and the average number of hydrogen bonds that are attached to each water molecule. If we assume that the energy of hydrogen bond in liquid water consists mainly of the energy due to dipole–dipole interaction along the O–H bonds,[15] it is clear that even in the activated state this energy cannot be zero, i.e., the hydrogen bonds between the diffusing molecule and its immediate neighbors cannot be completely "broken" by the process of activation in diffusion.[16] Consequently the activation energy for self-diffusion should be somewhat smaller than the hydrogen bond energy per water molecule. By using the activation energy of 4.6 kcal./mole obtained in the present work and the approximate energy of 4.5 kcal./mole given by Pauling for each hydrogen bond, we get the minimum number of hydrogen bonds per molecule in water as $4.6/4.5 = 1.02$. Since each hydrogen bond is shared by two water molecules, this shows that the average number of hydrogen bonds attached to each molecule in water should be somewhat greater than two. Furthermore since the slope of the log D vs. $(1/T) \times 10^3$ curve in Fig. 1 changes but slightly between 10 and 50°, this shows that only small changes in the structure of water take place in this temperature range. The slopes of both curves in Fig. 1 show the tendency to increase with decreasing temperature near 0°. If this apparent increase in activation energy which corresponds to an appreciable increase in the less close-packed "ice-structure" is real, it will be in agreement with the abnormal density change of liquid water near 0°.

(14) P. W. Bridgman, "The Physics of High Pressure," The Macmillan Co., New York, N. Y., 1931, p. 347.

(15) J. A. Pople, Proc. Roy. Soc. (London). A205, 163 (1951).

(16) This was first pointed out to one of us (J. H. W.) by Professor G. Scatchard.

Effect of Moments of Inertia.—Although at this moment we cannot yet decide on the relative magnitudes of the diffusion coefficients of $H^1H^2O^{16}$ and $H^1H^3O^{16}$ because of the relatively large experimental uncertainties, Fig. 1 shows that the tracer diffusion coefficients of $H^1_2O^{18}$ in ordinary water are apparently higher than those for $H^1H^2O^{16}$ and $H^1H^3O^{16}$. This difference in the values of D's, if confirmed by further work, is especially interesting for the case of $H^1H^3O^{16}$ and $H^1_2O^{18}$, since both of them have the same molecular weight of 20. A possible explanation is that although these two water molecules have practically the same molecular weight, the principal moments of inertia of $H^1H^3O^{16}$ are, on the average, almost twice as large as those of $H^1_2O^{18}$. Thus if we accept the general conclusion from molecular spectroscopy that molecules of the same chemical species but labeled with different isotopes have the same structure and electronic configuration, the $H^1H^3O^{16}$ molecule will have smaller residual energy (zero point energy) associated with the three highly hindered rotational degrees of freedom (i.e., intermolecular torsional oscillations). This smaller residual energy would cause the $H^1H^3O^{16}$ molecule to have a larger activation energy for diffusion and hence a smaller value of D if we assume that the isotope effect on the energy of the activated states of diffusing water molecules is comparatively small. The ratio of the observed diffusion coefficients of $H^1_2O^{18}$ and $H^1H^3O^{16}$ is about 1.14 at 25°. Actually a small difference of only 0.08 kcal./mole in activation energy would be sufficient to cause this 14% difference in diffusion coefficients. However, the present experimental accuracy is insufficient for us to detect such a small difference in activation energies. Furthermore the activation entropies should also be affected by the moments of inertia to compensate partly for the above mentioned effect on activation energies, although we would expect the latter still to be the dominating factor. Apparently the same qualitative explanation applies also to dielectric relaxation and viscosity data.

It is well-known that pure deuterium oxide has a higher degree of coördination than ordinary water at the same temperature and pressure. Our present result suggests that this may be due even more to the differences in moments of inertia than to the differences in molecular weights.

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