A Simplified Model for the Structure of Water

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Water is very special in its physical properties as well as very familiar to us in its occurrence on the earth. Its peculiarity has been considered to be caused mainly by the hydrogen bonds formed between water molecules. Bernal and Fowler[1] studied for the first time the quasi-crystalline structure of water by X-rays and found it to be composed of the intermediate of trydimite, crystobalite and the closest packing. Eucken[2] described the peculiar properties of water, especially from the points of view of the density and the compressibility, assuming that water is an equilibrating mixture of four species: H_2O, $(H_2O)_2$, $(H_2O)_4$ and $(H_2O)_8$. Recently, the structure of water was discussed variously on the bases of bending in the hydrogen bonds by Pople[3], of the covalency in the hydrogen bonds by Frank[4] and of the radial distribution function of water by X-rays by van Panthaleon van Eck et al.[5,6] and by Brady et al.[7-9] These works seem to be too complicated and rigorous to explain the simple observed facts, and often involve too many assumptive parameters. Hall[10] tried to simplify Eucken's model and regarded water as existing in two different energy states to account for the excess ultrasonic absorption of water. Using this model, the pressure effects of the ultrasonic absorption[11,12] and of the thermal conductivity[13] of water were also treated. In the present paper, various properties of water will be explained by a simple two-state model that water is equilibrated between the so-called "iceberg" having locally the ice structure and the structure more closely packed than the iceberg.

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

[2] A. Eucken, *Nachricht. Akad. Wiss. Göttingen, Math.-Phys. Klasse*, 38 (1946).

[3] J. A. Pople, *Proc. Roy. Soc.*, **A205**, 163 (1951).

[4] H. S. Frank, ibid., **A247**, 481 (1958).

[5] C. L. van Panthaleon van Eck, H. Mendel and W. Boog, *Discussions Faraday Soc.*, **24**, 200 (1957).

[6] C. L. van Panthaleon van Eck, H. Mendel and J. Fahrenfort, *Proc. Roy. Soc.*, **A247**, 471 (1958).

[7] G. W. Brady and J. T. Krause, *J. Chem. Phys.*, **27**, 304 (1957).

[8] G. W. Brady, ibid., **28**, 464 (1958).

[9] G. W. Brady, ibid., **29**, 1371 (1958).

[10] L. Hall, *Phys. Rev.*, **73**, 775 (1948).

[11] A. H. Smith and A. W. Lawson, *J. Chem. Phys.*, **22**, 351 (1954).

[12] T. A. Litovitz and E. H. Carnevale, *J. Appl. Phys.*, **26**, 816 (1955).

[13] A. W. Lawson, R. Lowell and A. L. Jain, *J. Chem. Phys.*, **30**, 643 (1959).

Equilibrium between Icy State and Packed State

Ice melts at 0°C, accompanied by an abrupt decrease in volume, and water yet continues a gradual contraction as the temperature is raised after melting, until it arrives at a minimum volume at 3.98°C, over which it begins to expand, under an atmospheric pressure. This fact would be recognized by a new model relating to the structure of water, proposed by the author that liquid water consists of two states of aggregation, namely icy state $(H_2O)_{icy}$, with lower density and packed state $(H_2O)_{packed}$, with higher density and that these two states hold a chemical equilibrium

$$(H_2O)_{icy} \rightleftarrows (H_2O)_{packed} \qquad (1)$$

The volume of liquid water is the sum of those of the two states, and the equilibrium trends to the right-hand side of the equation when the temperature is raised, each of the states showing the respective thermal expansions. Water molecules of the icy state correspond to the molecular associates with local and temporary quasi-crystalline ice structure, which have hitherto been called "iceberg", "cluster" or "icelikeness" drifting in liquid water, by several workers[14].

Then, the equilibrium constant K of Eq. 1 is expressed by the following equation, x being the mole fraction of $(H_2O)_{icy}$ at t°C, and ΔG the free energy.

$$K=\frac{1-x}{x}=\exp(-\Delta G/RT) \qquad (2)$$

When the volumes of the icy and the packed states at 0°C and at t°C are represented by $v_i{}^0$ and $v_p{}^0$, and v_i and v_p in cc. g^{-1} respectively, and the coefficients of thermal expansion α_i and α_p respectively, the volume of liquid water v is given by

$$\begin{aligned} v &= xv_i+(1-x)v_p \\ &= xv_i{}^0(1+\alpha_i t)+(1-x)v_p{}^0(1+\alpha_p t) \qquad (3) \end{aligned}$$

where, for the values of $v_i{}^0$ and α_i, can be used those for the pure ice. From the observed values of v at various temperatures[15], x's can be known at the respective temperatures, only assuming that x is just equal to 0.2 at 100°C. This assumption is introduced by the method of trial and error, so as to be consistent with other properties of water most satisfactorily, as will be mentioned in the next chapter.

Although, in Eucken's model[2], the total mole fraction of associating molecules at 100°C was also 0.2, there were introduced some other numerical assumptions which were ambiguous in physical meanings, while the present model involves no other assumptions than that of $x=0.2$ at 100°C. Thus, x's at various temperatures are computed as shown in Table I, α_p being determined from this assumption.

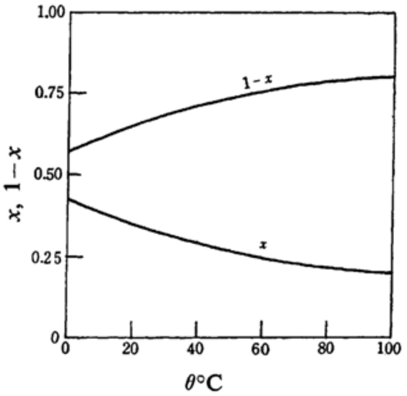

Fig. 1. Temperature dependence of x and $1-x$.

Table I. Mole fractions of the icy state x and of the packed state $1-x$ at various temperatures

t°C	v, cc.g^{-1}	v_i, cc.g^{-1}	v_p, cc.g^{-1}	x	$1-x$	K
0	1.0001	1.0905	0.9334	0.4246	0.5754	1.355
1	1.0001	1.0907	0.9343	0.4207	0.5793	1.377
2	1.0000	1.0908	0.9353	0.4161	0.5839	1.403
3	1.0000	1.0910	0.9362	0.4121	0.5879	1.427
4	1.0000	1.0911	0.9372	0.4081	0.5919	1.450
5	1.0000	1.0913	0.9381	0.4040	0.5960	1.475
6	1.0000	1.0914	0.9391	0.3999	0.6001	1.501
7	1.0001	1.0916	0.9400	0.3964	0.6036	1.523
8	1.0001	1.0917	0.9410	0.3922	0.6078	1.550
9	1.0002	1.0919	0.9419	0.3887	0.6113	1.573
10	1.0003	1.0920	0.9429	0.3850	0.6150	1.597
15	1.0009	1.0930	0.9476	0.3665	0.6335	1.729
20	1.0018	1.0938	0.9523	0.3495	0.6505	1.861

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[14] H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, 24, 133 (1957).

[15] "Chemical Handbook", Ed. by Chem. Soc. Japan, Maruzen, Tokyo (1952), p. 287.

The basic values for calculations are as follows.

$$v_i^0 = 1.0905 \qquad v_p^0 = 0.9334 \text{ cc. g}^{-1} \tag{4}$$

$$\alpha_i = 1.52 \times 10^{-4} \qquad \alpha_p = 1.013 \times 10^{-3} \text{ deg}^{-1} \tag{5}$$

The variation of the mole fraction of the icy state, x, and that of the packed state, $1-x$, over the temperature range 0∼100°C are depicted in Fig. 1. The icy state is found to remain unmelted as much as 40% of the whole liquid water at 0°C.

Properties of Water Explained by the Model

Heat of Fusion of Ice.—As is shown in Fig. 2, one obtains a fine straight line by plotting $\log K$ against $1/T$, from which the intrinsic heat of fusion of ice, ΔH_f, i. e. the enthalpy of the transition $(H_2O)_{\text{icy}} \rightarrow (H_2O)_{\text{packed}}$ at 0°C is calculated.

$$\Delta H_f = 2.51 \text{ kcal. mol}^{-1} \text{ at } 0°\text{C} \tag{6}$$

The commonly known value as the heat of fusion of ice, 1.43 kcal. mol^{-1}, is not per mole in reality but per $1-x=0.5754$ mol. at 0°C. The true corrected value per mol. is $1.43 \div 0.5754 = 2.49$ kcal. mol^{-1}, which agrees very well with Eq. 6.

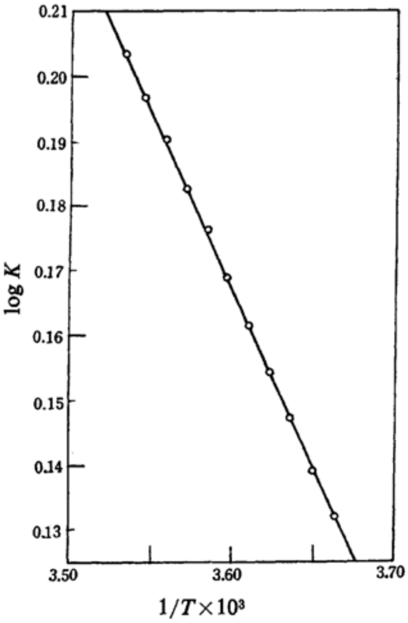

Fig. 2. The intrinsic heat of fusion of ice.

Free Energy and Entropy of Fusion of Ice.—Free energy and entropy of fusion of ice at 0°C, ΔG and ΔS_f, are easily calculated from K's in Table I and ΔH_f in Eq. 6, as follows.

$$\Delta G = -165.1 \text{ cal. mol}^{-1} \text{ at } 0°\text{C} \tag{7}$$

$$\Delta S_f = 9.79 \text{ cal. deg}^{-1} \text{ mol}^{-1} \text{ at } 0°\text{C} \tag{8}$$

Entropy of fusion of ice obtained from the observed heat of fusion is $1.43 \div (0.5754 \times 273.1) = 9.10$ cal. deg^{-1}mol^{-1}, which does not greatly differ from Eq. 8. In general, entropies of fusion for normal triatomic molecules should have nearly equal values: those for carbon disulfide and nitrous oxide are, for instance, 8.4 and 8.6 cal. deg^{-1} mol^{-1}, respectively[16], to which the value of Eq. 8 is fairly approximate*.

Specific Heat.—Using the observed results of specific heats of ice[17], one obtains the following empirical formula for ice at the temperature range of −60∼0°C.

$$c_i = 0.48986 + 1.357 \times 10^{-3} t - 2.625 \times 10^{-7} t^2 + 3.708 \times 10^{-7} t^3 \text{ cal. deg}^{-1}\text{g}^{-1} \tag{9}$$

If Eq. 9 is applicable to an imaginary piece of ice above 0°C, namely the icy state in liquid water, an equation for the specific heat of water can be given, the partial fusion of the icy state with rise of temperature being taken into account.

$$C = xC_i + (1-x)C_p - \Delta H_f \frac{dx}{dT} \tag{10}$$

where C, C_i and C_p are the molecular heats of the liquid water, the icy state and the packed state, respectively. Then, from Eqs. 2 and 10, the molecular heat of the packed state is given by

$$C_p = \frac{C - xC_i}{1-x} - \frac{x(\Delta H_f)^2}{RT^2} \tag{11}$$

In Table II, the values of C_p at various temperatures are listed. The molecular heat

TABLE II. MOLECULAR HEAT OF THE PACKED STATE OF WATER

t °C	c[13] cal.deg^{-1}g^{-1}	c_i cal.deg^{-1}g^{-1}	c_p cal.deg^{-1}g^{-1}	C_p cal.deg^{-1}mol^{-1}
0	1.0092	0.48986	0.3928	7.071
5	1.0051	0.49669	0.4325	7.784
10	1.0021	0.50377	0.4705	8.469
15	1.0001	0.51141	0.5076	9.136
20	0.9988	0.51986	0.5418	9.752

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16) J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids", John-Wiley, New York (1954), p. 285.

17) "International Critical Tables", Vol. V (1929), p. 95.

* For comparison, the calculated thermodynamic values at 0°C together with those of the previous investigators are shown as follows.

	ΔG cal.·mol^{-1}	ΔS_f cal. deg^{-1}·mol^{-1}	ΔH_f cal.·mol^{-1}	x
Present author	−165.1	9.79	2510	0.4246
Lawson et al.[13]	−150	11.5	3000	0.42
Litovitz et al.[12]	−500	5	870	0.32
Smith et al.[11]	0	9.5	2600	0.50
Hall[10]	+500	—	—	0.70

Hall assumed a possibility of a two-state representation, one state of larger volume and lower energy and the other state of smaller volume and higher energy, which is quite different from the models of the present author and other investigators except Hall.

of liquid water is ordinarily known to be 18 cal. deg^{-1}mol^{-1}, but C_p's of the packed state over the temperature range of 0∼20°C lie between 7 and 10 cal. deg^{-1} mol^{-1}, which seems to be appropriate compared with the values of the molecular heat for methyl alcohol (18.7 cal. deg^{-1}mol^{-1} at 12°C) or for ethyl alcohol (26.6 cal. deg^{-1}mol^{-1} at 20°C).

Vapor-pressure and Heat of Vaporization. — The ratios of the vapor-pressure of liquid water, p, to that of ice, p_i, are expressed empirically as a function of temperature as follows[18].

$$\log\frac{p}{p_i}=\frac{-1.1489\,t}{273.1+t}-1.330\times10^{-5}t^2+9.084\times10^{-8}t^3 \qquad (12)$$

Admitting that water is an ideal mixture of the icy and the packed states, the vapor-pressure of the liquid water can be shown, according to Raoult's rule.

$$p=xp_i+(1-x)p_p \qquad (13)$$

Then, the partial pressures of the packed state, p_p's, are calculated at various temperatures by the following equation derived from Eqs. 12 and 13 and are listed in Table III, where p's are known empirically[19].

$$p_p=\frac{1-x\dfrac{p_i}{p}}{1-x}p \qquad (14)$$

Table III. Vapor-pressure of water

t, °C	p/p_i	p[19], mmHg	p_p, mmHg
0	1.00000	4.579	4.579
1	0.99048	4.926	4.892
2	0.98093	5.294	5.221
3	0.97140	5.685	5.542
4	0.96207	6.101	5.935
5	0.95284	6.543	6.323
6	0.94372	7.013	6.735
7	0.93469	7.513	7.168
8	0.92576	8.045	7.628
9	0.91693	8.609	8.113
10	0.90819	9.209	8.627

As is pictured in Fig. 3, the plot of $\log p_p$ against $1/T$ gives a straight line, from the slope of which is obtained the heat of vaporization of the packed state $\varDelta H_{v(p)}$.

$$\varDelta H_{v(p)}=9.70 \text{ kcal. mol}^{-1} \text{ at } 0°\text{C} \qquad (15)$$

Since the heat of vaporization of water, $\varDelta H_v$, is represented by

$$\varDelta H_v=x\varDelta H_s+(1-x)\varDelta H_{v(p)} \qquad (16)$$

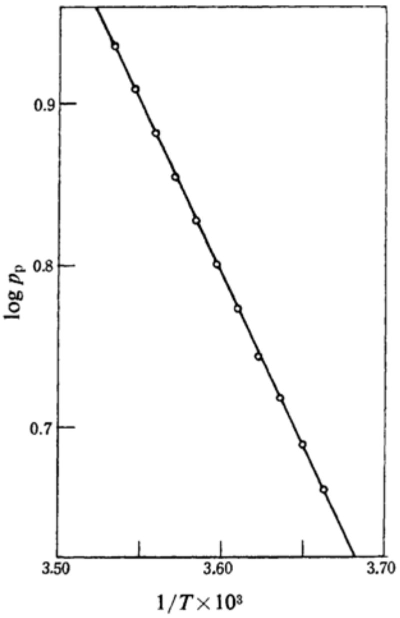

Fig. 3. Heat of vaporization of water.

and since the heat of sublimation of ice, $\varDelta H_s$, is expressed by an equation $\varDelta H_s=\varDelta H_f+\varDelta H_{v(p)}$, $\varDelta H_v$ is expected to be composed of the heat of fusion of the icy state and of vaporization of the packed state by the following relation:

$$\varDelta H_v=x\varDelta H_f+\varDelta H_{v(p)} \qquad (17)$$

Therefore,

$$\varDelta H_v=10.77 \text{ kcal. mol}^{-1} \text{ at } 0°\text{C} \qquad (18)$$

$$\varDelta H_s=12.21 \text{ kcal. mol}^{-1} \text{ at } 0°\text{C} \qquad (19)$$

The heat of vaporization of liquid water and the heat of sublimation of ice directly observed by experiments at 0°C are 10.73 kcal. mol^{-1} and 12.16 kcal. mol^{-1} respectively, both of which agree with Eqs. 18 and 19 quite satisfactorily.

Molar Volume and Molecular Distance.— According to the additivity rule that molar volume of a normal liquid is predicted by the algebraic sum of the individual atomic volumes of composing atoms of the molecules, the calculated molar volume of the packed state may be 14.8 cc. mol^{-1}, which approximates 16.8 cc. mol^{-1} computed from Eq. 4.

From the works of van Panthaleon van Eck et al.[5,6], the radial distribution curve of water measured by X-rays is reproduced in Fig. 4, which reveals two peaks in the curve at the molecular distances 3.1 and 4.5Å. Van Panthaleon van Eck et al. concluded that the nearest molecular distance 3.1Å coincides with the theoretical value of the molecular distance between the first neighbors, calculated from the density of liquid water, when liquid water

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[18] J. H. Perry, "Chemical Engineers' Handbook" McGraw-Hill, New York (1950).

[19] "Chemical Handbook", Ed. by Chem. Soc. Japan, Maruzen, Tokyo (1952), p. 382.

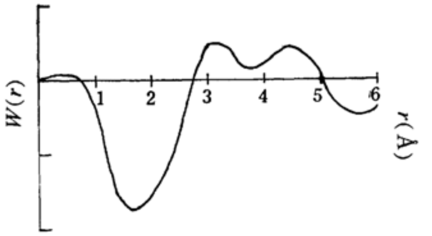

Fig. 4. Radial distribution curve of water at 2.6°C (quoted from C. L. van Panthaleon van Eck et al.[5,6]).

is assumed to be octahedrally coordinated, and that, therefore, water has a uniform structure of octahedron in liquid state, instead of that of the tetrahedron which is popularly believed to exist in ordinary ice.

But, on the contrary, the present new model concerning liquid water can describe more naturally the results of Fig. 4 as follows. Since the icy state has, of course, the ice-structure, water molecules in the icy state takes a tetrahedral arrangement, and the O–O distance of hydrogen bond must be 2.76 Å as usual. And it is reasonable to consider that the packed state of water has lost the icelike structure with hydrogen bondings between O–O atoms and is rather more densely packed in closest packing, as is often seen in case of general ideal liquids, such as argon or molten metals. From the molar volumes of the icy and the packed states (Eq. 4), the molecular distances at 0°C are calculated, and listed in Table IV.

TABLE IV. MOLECULAR DISTANCE AND COORDINATION NUMBER OF THE TWO STATES

	Icy state (Tetrahedral)		Packed state (Closest packing)	
	Distance Å	Coordination number	Distance Å	Coordination number
First neighbor	2.76	4	3.46	12
Second neighbor	4.51	12	4.89	6

According to this model, the peak at 3.1 Å can be explained as the result of the overlapping of two curves, each corresponding to the icy and the packed states, with the weights of the mole fraction and the coordination number, respectively. If the two curves, which exhibit peaks at 2.76 and 3.46 Å by the first neighbors, respectively, are gently sloping near the maximum points, the resultant curve of the two may have a single peak between the two individual peaks, at 3.1 Å.

In addition, the observed fact that the number of the first neighbors increases gradually as the temperature is raised[20] seems to be caused by the successive transition of the icy state with smaller coordination number to the packed state with larger coordination number. If liquid water were uniformly octahedral, the number of the first neighbors would rather decrease, since the number of holes caused by thermal agitation should increase with temperature. The fact that both the peak at 4.5 Å and the bottom at 5.6 Å of the radial distribution curve at 2.6°C shown in Fig. 4 almost diminish at 60°C[5] may be due to the results of only existence of the short range order of liquid.

Surface Tension.—Regarding water of the packed state as a normal liquid, the molecular parachor is found to be $P=50.8$ from the summation of the individual atomic parachor[21],*. Thence, the surface tension of the packed state γ_p can be derived by use of the relation between the parachor and the surface tension,

$$P=M\gamma_\mathrm{p}^{1/4}/(\rho-\rho_0) \tag{20}$$

where M is the molecular weight of water, and ρ and ρ_0 are the density of water of the packed state and of vapor upon the packed state, respectively, which are known from Eq. 4 and Table III.

$$\gamma_\mathrm{p}=83.58\ \mathrm{dyn.\,cm^{-1}}\ \text{at}\ 0^\circ\mathrm{C} \tag{21}$$

This value of γ_p is slightly larger than that observed for liquid water at 0°C, 75.64 dyn. cm^{-1}.

The surface tension of a mixed liquid is expressed as follows, the heat of mixing being taken as zero[22].

$$\gamma=\gamma_\mathrm{i}+\frac{\boldsymbol{RT}}{A_\mathrm{i}}\ln\frac{x'}{x}=\gamma_\mathrm{p}+\frac{\boldsymbol{RT}}{A_\mathrm{p}}\ln\frac{1-x'}{1-x} \tag{22}$$

where A_i and A_p are the molar area of water in the icy and the packed states respectively, and x' is the mole fraction of the icy state on the surface of liquid water. As $A_\mathrm{p}=6.043\times10^8\ \mathrm{cm}^2$, x' is calculated from the following equation.

$$\frac{1-x'}{1-x}=\exp\left[(\gamma-\gamma_\mathrm{p})A_\mathrm{p}/\boldsymbol{RT}\right] \tag{23}$$

$$x'=0.819\ \text{at}\ 0^\circ\mathrm{C} \tag{24}$$

From the value of Eq. 24, it is found that the icy state is positively adsorbed on the surface of liquid water; in other words, it behaves like a so-called "surface active substance".

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[20] J. Morgan and B. E. Warren, *J. Chem. Phys.*, **6**, 666 (1938).

[21] R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids", McGraw-Hill, New York (1958), p. 21.

* Since the hydrogen atom in the packed state does not form any hydrogen bond, the atomic parachor of hydrogen must be not 10.0 but 15.5, the former being the value for hydrogen in OH and the latter for ordinary hydrogen as in hydrocarbons[21].

[22] J. A. V. Butler, *Proc. Roy. Soc.*, **A135**, 348 (1932); J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes", Reinhold (1950), p. 406; T. P. Hoar and D. A. Melford, *Trans. Faraday Soc.*, **53**, 315 (1957).

Energy State of Water.—The various energy relations of water mentioned above are illustrated all together in Fig. 5. An assumed state of energy of water that only the hydrogen bondings in ice are broken but that the geometrical molecular configuration is still maintained to be tetrahedral, is drawn as T-state in the figure, and it is 6.5 kcal. mol^{-1} higher in energy than the packed state, the latter state being realized by the cohesion force between the dipoles of water molecules from the former state, since the energy of a hydrogen bond O-H···O in ice is 4.50 kcal. bond^{-1}. The phenomenon of premelting of ice would be demonstrated as the local occurrence of the T-state in ice structure.

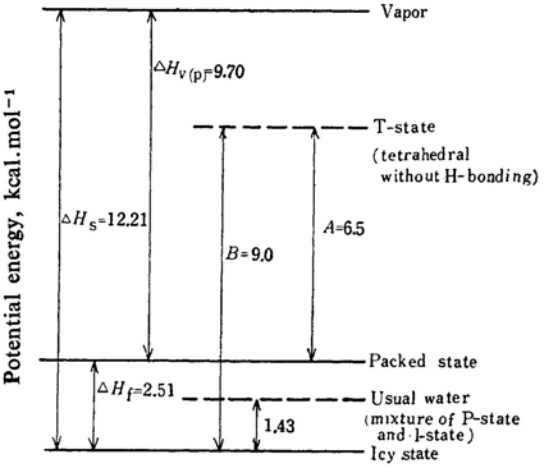
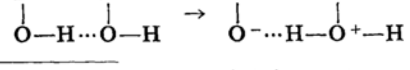


Fig. 5. Energy state of water at 0°C.

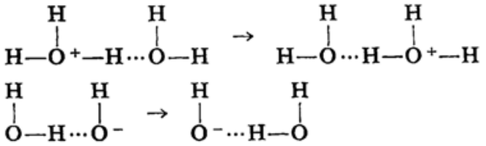
Activation Energy of Self-diffusion. — The observed value of the activation energy of self-diffusion of liquid water is 5.3 kcal. mol^{-1} [23]. Since water molecules of the icy state may be compared to "macromolecules" although unstable, it might be rather single molecules of the packed state that take a greater part in self-diffusion in liquid water. And, since the intermediate state in the process of self-diffusion must necessarily be of an open structure with many holes, similar to the T-state shown in Fig. 5, the activation energy of self-diffusion must be approximately equal to A (=6.5 kcal. mol^{-1}), which agrees with the observed value without serious error.

Heat of Ionization.—In order to dissociate a water molecule into a hydrogen ion and a hydroxyl ion, three steps must take place: (a) a proton jump between adjacent two water molecules through a hydrogen bonding,



$$\mathrm{\overset{H}{\underset{}{O}}{-}H\cdots\overset{H}{O}{-}H \;\rightarrow\; \overset{H}{O}{}^{-}\cdots H{-}\overset{H}{O}{}^{+}{-}H}$$

(b) successive proton transfers along the chains combined by hydrogen bondings,



$$\mathrm{H{-}\overset{H}{O}{}^{+}{-}H\cdots\overset{H}{O}{-}H \;\rightarrow\; H{-}\overset{H}{O}\cdots H{-}\overset{H}{O}{}^{+}{-}H}$$

$$\mathrm{\overset{H}{O}{-}H\cdots\overset{H}{O}{}^{-} \;\rightarrow\; \overset{H}{O}{}^{-}\cdots H{-}\overset{H}{O}}$$

and (c) rotation of either of H_3O^+ ion, OH^- ion and H_2O. Steps a and b means separation of the charge or ionization in a narrow sense, but the separated ions have yet a large probability of recombination or association via the reverse paths of steps b and a. Step b is a proton jump between two symmetrical structures, and therefore proceeds athermally, while step a is an asymmetrical charge separation, thus being endothermic, and the activation energy of step a might be about 4 kcal. mol^{-1}, somewhat larger than that of step b, according to Conway et al.[24],* For the completion of ionization of a water molecule, it is needed that the chain of hydrogen bonds through which proton transfers occur must be broken down in order to interfere with an easy recombination of the two ions once separated. This breakdown of the chain can be carried out through step c by an insertion of chain imperfection, such as a doubly occupied hydrogen bond O-H···H-O or a vacant bond O···O. Since the rotation of H_3O^+, OH^- or H_2O can take place only when the rotating particle overcomes the attractive force between the dipoles and destroys the hydrogen bond, it requires energies near to the heat of sublimation of ice 12.2 kcal. mol^{-1}. After all, it is concluded that the apparent activation energy for protonic dissociation of water may be $12.2+4\approx16$ kcal. mol^{-1} and the heat of dissociation a certain value between 16 and 12.2 kcal. mol^{-1}. The observed values of the activation energy and the heat for dissociation of water are 15.5~16.5 kcal. mol^{-1} and 13.5 kcal. mol^{-1} respectively[25], both of which agree with the above considered expectation very well.

Activation Energy of Electric Conduction.—The measured values of d. c. electric conductance of the sufficiently carefully prepared ice[26],* and liquid water[28] at near 0°C, κ_i and κ, are

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[23] N. Morita and T. Titani, This Bulletin, 13, 543 (1938).

[24] B. E. Conway, J. O'M. Bockris and H. Linton, *J. Chem. Phys.*, **24**, 834 (1956).

* The activation energy of symmetric proton jump is 3.85 kcal. mol^{-1} [24].

[25] M. Eigen and L. de Maeyer, *Proc. Roy. Soc.*, **A247**, 505 (1958).

[26] R. S. Bradley, *Trans. Faraday Soc.*, **53**, 687 (1957).

* According to the results of Gränicher et al.[27], the apparent activation energy of electric conduction of ice is 13.8 kcal. mol^{-1}, being slightly larger than Eq. 25.

[27] H. Gränicher, C. Jaccard, P. Sherrer and A. Steinemann, *Discussions Faraday Soc.*, **23**, 50 (1957).

[28] "Chemical Handbook", Ed. by Chem. Soc. Japan, Maruzen, Tokyo (1952), p. 601.

represented by the following empirical formulas.

$$\kappa_{\mathrm{i}}=23.4\exp(-12300/\boldsymbol{RT})\ \Omega^{-1}\mathrm{cm}^{-1} \quad (25)$$

$$\kappa=0.119\exp(-8570/\boldsymbol{RT})\ \Omega^{-1}\mathrm{cm}^{-1} \quad (26)$$

Since ice and liquid water were nearly equally electroconductive at near 0°C, it was thought that the mechanisms of the electric conduction in both media must also resemble each other. But recently, it was found that the mobility of a proton in ice is twice faster than that in liquid water, while the concentration of dissociated ions in ice is half as much as that in water[25]. These facts are convinced by a statement that, since the chains connected by hydrogen bondings in ice are longer and in better order than those in water, the proton jump is easier, the lattice imperfection arises with less probability, and, therefore, the occurrence of ionic recombination is more probable in ice. The fact that both the activation energy and the pre-exponential factor in water are lower than in ice as is seen in Eqs. 25 and 26, is thus qualitatively acknowledged on this reason as well.

When the proton jumps have once propagated successively along a chain of hydrogen bonds in the direction of electric field, all the molecules that proton jumps have taken place between the neighboring molecules must rotate in order to conduct electricity in the same direction once more. The rate-determining step of electric conduction of ice and water in a static field is, therefore, the process of molecular rotation, as in the case of ionization of water described in the last section, and the apparent activation energy during the overall process of electric conduction must be much higher than the height of the energy barrier for proton jumps.

Especially in case of liquid water, the matter is more complicated than in the case of ice, because, even if the electric conduction is mostly owing to the proton jumps in the icy state, rather than to the migration or diffusion of ions themselves, the fraction of the icy state decreases as the temperature rises, and this fact makes the apparent activation energy somewhat lower than in ice*.

Temperature of Maximum Density.—From Eq. 3, next relation can be derived,

$$\frac{\mathrm{d}v}{\mathrm{d}T}=(v_{\mathrm{i}}-v_{\mathrm{p}})\frac{\mathrm{d}x}{\mathrm{d}T}+x\alpha_{\mathrm{i}}v_{\mathrm{i}}{}^{0}+(1-x)\alpha_{\mathrm{p}}v_{\mathrm{p}}{}^{0} \quad (27)$$

where, at the temperature of the maximum density T_{m}, $\mathrm{d}v/\mathrm{d}T$ is equal to zero. Since the second and the third terms in the right-hand side of Eq. 27 are both positive, and $\mathrm{d}x/\mathrm{d}T$ in the first term is negative, one of the necessary conditions that an equilibrating liquid mixture of multicomponent system like liquid water has a maximum density at a certain temperature is generally $v_{\mathrm{i}}>v_{\mathrm{p}}$. Among many associating liquids, some might satisfy this condition, but unfortunately they can not be observed in practice, unless T_{m} is above the freezing points. Thus T_{m} can be known from Eq. 27 theoretically, inserting the relation $\mathrm{d}x/\mathrm{d}T=-x(1-x)\Delta H_{\mathrm{f}}/\boldsymbol{R}T^{2}$. But, for instance, an error of ±0.05 kcal. mol^{-1} in ΔH_{f} corresponds to that of about ±1°C in T_{m} in case of water, which is not so adequate as to predict T_{m} correctly.

When a small amount of a different substance is dissolved in water, the temperature of the maximum density of the solution is either raised or lowered from 3.98°C. This is because the balance of Eq. 1 fluctuates by either the hydration or the dehydration of water molecules surrounding the added molecules, according to the polarity of the latter. In the right-hand side of Eq. 27, ignoring the contribution of the second term compared with those of the first and the third terms, and admitting $v_{\mathrm{i}}-v_{\mathrm{p}}\approx v_{\mathrm{i}}{}^{0}-v_{\mathrm{p}}{}^{0}$ approximately, the following equation is obtained,

$$\frac{\Delta H_{\mathrm{f}}}{\boldsymbol{R}T_{\mathrm{m}}{}^{2}}\Bigg/\left[1+\exp\left(-\frac{\Delta G}{\boldsymbol{R}T_{\mathrm{m}}}\right)\right]\approx\frac{\alpha_{\mathrm{p}}v_{\mathrm{p}}{}^{0}}{v_{\mathrm{i}}{}^{0}-v_{\mathrm{p}}{}^{0}} \quad (28)$$

according to which, T_{m} is found to vary mainly as a function of ΔH_{f} and ΔS_{f}, if the density of the added substance does not affect seriously,

$$\left(\frac{\partial T_{\mathrm{m}}}{\partial\Delta H_{\mathrm{f}}}\right)_{\Delta S_{\mathrm{f}}}=\frac{\dfrac{\boldsymbol{R}T_{\mathrm{m}}{}^{2}}{(\Delta H_{\mathrm{f}})^{2}}\left[1+\exp\left(-\dfrac{\Delta G}{\boldsymbol{R}T_{\mathrm{m}}}\right)\right]+\dfrac{T_{\mathrm{m}}}{\Delta H_{\mathrm{f}}}\exp\left(-\dfrac{\Delta G}{\boldsymbol{R}T_{\mathrm{m}}}\right)}{\dfrac{2\boldsymbol{R}T_{\mathrm{m}}}{\Delta H_{\mathrm{f}}}\left[1+\exp\left(-\dfrac{\Delta G}{\boldsymbol{R}T_{\mathrm{m}}}\right)\right]+\exp\left(-\dfrac{\Delta G}{\boldsymbol{R}T_{\mathrm{m}}}\right)}>0 \quad (29)$$

$$\left(\frac{\partial T_{\mathrm{m}}}{\partial\Delta S_{\mathrm{f}}}\right)_{\Delta H_{\mathrm{f}}}=\frac{-\dfrac{T_{\mathrm{m}}{}^{2}}{\Delta H_{\mathrm{f}}}\exp\left(-\dfrac{\Delta G}{\boldsymbol{R}T_{\mathrm{m}}}\right)}{\dfrac{2\boldsymbol{R}T_{\mathrm{m}}}{\Delta H_{\mathrm{f}}}\left[1+\exp\left(-\dfrac{\Delta G}{\boldsymbol{R}T_{\mathrm{m}}}\right)\right]+\exp\left(-\dfrac{\Delta G}{\boldsymbol{R}T_{\mathrm{m}}}\right)}<0 \quad (30)$$

After all, T_{m} will be lowered by the dissolution of a substance which makes ΔH_{f} decrease or ΔS_{f} increase; namely, which inclines the

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* The electric conductance of ice and liquid water may be represented in another formula: $\kappa=en\mu$, where e is a protonic charge, and n and μ are the number and the mobility of charge carriers, respectively. n is closely related to the degree of ionization of water, which is affected by the energy of rotation of water molecules, while the factor which determines μ is the activation energy of a proton jump, or the height of the energy barrier in the potential curve of hydrogen bond.

equilibrium of Eq. 1 towards the right-hand side, and vice versa. In short, a part of the icy state is fused and the depression of T_m occurs. So far as observed experimentally, all the electrolytes[29] and general hydrophilic non-electrolytes lower T_m, while some alcohols such as *tert*-butyl alcohol raise T_m exceptionally[30]. The structure of water around ions or dissolved strange molecules will be discussed elsewhere.

Summary

Various characteristic properties of liquid water can be explained fairly well by a simple structural model proposing that water consists of an equilibrating mixture between two states: the icy state which possesses ice structure and appears and disappears locally and temporarily, and the packed state in which water molecules are closely packed without hydrogen bondings. Only assuming that the fraction of the icy state at 100°C is 0.2, the fractions and the equilibrium constants at various temperatures are calculated, and therefrom the heat and the entropy of fusion of ice, the specific heat and the heat of vaporization of liquid water are derived, which are all in good agreement with the observed values. The radial distribution function of water obtained by X-rays reveals the packed state to have a structure similar to the closest packing, and the surface tension of water tells that the surface of water is more abundant in the icy state than the bulk water is, positively adsorbed as if it were a kind of surfactants. The heat of ionization and the activation energy of electric conduction are qualitatively described by the rotation mechanism of water molecules in the icy state. A reasonable explanation concerning the existence of the temperature of the maximum density and the effects of different substances upon it are also offered.

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[30] G. Wada and S. Umeda, unpublished.