BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 303—308 (1969)

The Structure Theory of Water. I. Two State Theory

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(Received March 29, 1968)

A statistical thermodynamic theory was successfully applied to liquid water, based on the two state model which consists of an ice-like structure (class I) and unbonded monomers (class II). The resulting partition function was formulated and calculated using the two quantities, the energy difference between class I and class II, ε, and the free volume per molecule, v_f, as the adjustable parameters which were varied within the physically-reasonable range. The magnitudes of ε and v_f were estimated to be 3 kcal/mol and 4.0×10^{-25} cm^3 respectively to give the best fit of calculated values to the experimental data. From the partition function obtained, the Helmholtz energy, the internal energy, the entropy, and the specific heat were calculated. The agreement between the calculated values and the experimental data was found to be satisfactory. From the obtained result it may be concluded that the simple two state model is adequate to explain the thermodynamical data for liquid water.

A number of studies have been made on the structure of liquid water since Bernal and Fowler[1] proposed a pseude crystal model based on the tetragonal structure in water. However, many problems are left unsolved at present. Morgan and Warren[2] gave the radial distribution curve for water from their X-ray diffraction data, and estimated the average number of first nearest neighbors to be 4.4—4.9 at temperatures from 1.5 to 83°C.

The approach to the structure theory of water based on the ice-like structure, as made by Bernal and Fowler, that is, the approach from the viewpoint that the main structure of liquid water is solid-like, has been taken by many workers. The bent-hydrogen-bonding chain theory given by Pople[3] and the structure theory of Davis and Litovitz[4] are typical of the solid-like theory. However, these theories were found to be able to explain the properties of water only partly. On the other hand, Eucken[5] proposed an association theory, in which water was supposed to be an equilibrium mixture of monomer, dimer, tetramer and octamer.

In 1948, Hall[6] presented a two state theory of water, which was based on the assumption that liquid water was composed of an ice-like structure ("open structure") and unbonded water molecules ("close-packed structure"), in order to explain the ultrasonic absorption data. Hall's theory succeeded in the interpretation of ultrasonic absorption data, but was pointed out by Litovitz and Carnevale[7] to be unsatisfactory for the explanation of the pressure dependence of ultrasonic absorption. Since then, the two state theory of liquid water has been developed in various ways by a number of authors. Some of them, the theories of Samoilov,[8] Frank and Quist,[9] *etc.* were found to emphasize the solid-like structure. On the other hand Frank and Wen[10] proposed a flickering cluster model based on the cooperative nature of hydrogen bonding formation, and pointed out the life time of the cluster to be as short as 10^{-10} or 10^{-11} sec from the relaxation data. According to the suggestion of Frank and Wen, Némethy and Scheraga[11] have presented a refined statistical theory, in which water is assumed to be an equilibrium mixture of flickering clusters and unbonded molecules. The clusters are supposed to be composed of tetra-, tri-, di-, and singly-hydrogen-bonded water molecules, and therefore, Némethy and Scheraga's theory is also regarded as a five state theory.

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

[2] J. Morgan and B. E. Warren, *ibid.*, **6**, 666 (1938).

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

[4] C. M. Davis and T. A. Litovitz, *J. Chem. Phys.*, **42**, 2563 (1965).

[5] A. Eucken, *Zeit. für Elektrochemie*, **52**, 255 (1948).

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

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

[8] O. Ya. Samoilov and T. A. Nosova, *Zh. Strukt. Khim.*, **6**, 798 (1965).

[9] H. S. Frank and A. S. Quist, *J. Chem. Phys.*, **34**, 604 (1961).

[10] H. S. Frank and W-Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957); H. S. Frank, *Proc. Roy. Soc.*, **A247**, 481 (1958).

[11] G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).

After the proposition of Némethy and Scheraga's theory, several studies have been made along this line. Vand and Senior have recently presented a nine-state theory,[12] and, proposed further an energy band theory. Vand and Senior introduced an additional assumption of the energy band into the structure theory of water without any theoretical explanation. This assumption means a continuous distribution of energy for water molecules and also means the introduction of a very large number of states since the energy changes continuously. It is questionable that, when the life time of the hydrogen-bonded region is known to be as short as 10^{-11}—10^{-10} sec, a number of different states within the hydrogen-bonded region could be distinguished each other, for a "state" has to be regarded as corresponding to a "structure." The assumption of the presence of a number of distinguishable states with as short a life time as 10^{-11}—10^{-10} sec may be doubtful, when the energy difference between the states is as small as the energy of thermal motion. It may be generally said that, on constituting the theory, the number of states assumed is desirable to be as small as possible, so long as the increase in the number of states means the increase in the number of parameters.

Therefore, the authors have made a theoretical investigation on the structure of water based on the two state model, and investigated the effectiveness and the limitation of the two state theory.

Theory

Two State Model. It is assumed that liquid water is an equilibrium mixture of two classes of molecules. Class I is constituted by hydrogen-bonded molecules (open structure or ice-like structure) and class II is constituted by unbonded monomers (close-packed structure). The molecules in each class are assumed to be in a uniform state on the average, and the energy level of the molecules in class II is ε ($\varepsilon > 0$), taking the level of those in class I as the ground level. A molecule changes its state fluctuationally with lapse of time, and the life time during which a molecule stays in the state of class I is of the order of 10^{-11}—10^{-10} sec, as pointed out by Frank and Wen[10] based on relaxational data concerning the life time of flickering clusters. It is assumed that a molecule acts as in a solid phase while it stays in the state of class I, and that it acts as in a gaseous phase while in class II.

Statistical Treatment. The formulation of the partition function, $\mathcal{Z}$, for the mixture of $\mathcal{N}x$ molecules in class I and $\mathcal{N}(I-x)$ molecules in class II is made as follows,

$$\mathcal{Z} = \frac{\mathcal{N}!}{(\mathcal{N}x)!\,\{\mathcal{N}(1-x)\}!}(f_{\rm I})^{\mathcal{N}x}(f_{\rm II}\,{\rm e}^{-\varepsilon/RT})^{\mathcal{N}(1-x)}, \qquad (1)$$

where $f_{\rm I}$ and $f_{\rm II}$ are partition functions for each species. The partition function $\mathcal{Z}$ for the equilibrium mixture is equated to the maximum term as usual regarding x as a parameter. The mole fraction x for class I in the equilibrium mixture is determined by the maximization of $\mathcal{Z}$ concerning x as a variable, using Stirling's approximation,

$$\frac{\partial \ln \mathcal{Z}}{\partial x} = 0. \qquad (2)$$

Introducing Eq. (1) to Eq. (2), we obtain Eq. (3) for the equilibrium value of x,

$$x = \frac{f_{\rm I}}{f_{\rm I} + f_{\rm II}\,{\rm e}^{-\varepsilon/RT}}, \qquad (3)$$

and, introducing Eq. (3) into Eq. (1), the partition function, $\mathcal{Z}$ for the equilibrium mixture, is represented as follows,

$$\mathcal{Z} = (f_{\rm I} + f_{\rm II}\,{\rm e}^{-\varepsilon/RT})_{\mathcal{N}}\,. \qquad (4)$$

The Helmholtz energy, A is obtained from the following equation (5),

$$A = -\,kT\ln\mathcal{Z} = -\,\mathcal{N}kT\ln(f_{\rm I} + f_{\rm II}\,{\rm e}^{-\varepsilon/RT}) \qquad (5)$$

and the energy and entropy can be calculated by Eqs. (6) and (7).

$$\begin{aligned} E &= kT^2\,\frac{\partial \ln \mathcal{Z}}{\partial T} \\ &= \mathcal{N}kT^2\left(\frac{\partial f_{\rm I}}{\partial T} + \frac{\partial f_{\rm II}}{\partial T}\,{\rm e}^{-\varepsilon/RT} + \frac{\varepsilon}{RT^2}\,{\rm e}^{-\varepsilon/RT}f_{\rm II})\right)/ \\ &\quad (f_{\rm I} + f_{\rm II}\,{\rm e}^{-\varepsilon/RT}) \end{aligned} \qquad (6)$$

$$S = (E-A)/T \qquad (7)$$

The specific heat, C_V, is derived from the energy, E.

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad (8)$$

The partition functions of each species, $f_{\rm I}$ and $f_{\rm II}$, are given in the following equations, Eq. (9) and Eq. (10),

$$f_{\rm I} = \prod_{i=1}^{6}\left(\frac{1}{1-{\rm e}^{-h\nu_i/kT}}\right) \qquad (9)$$

$$f_{\rm II} = \left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2} v_f\right\}\left\{\frac{(8\pi^2kT)^{3/2}(\pi ABC)^{1/2}}{2h^3}\right\}, \qquad (10)$$

where ν_i is the frequency of translational vibrations and librations in the state of class I, v_f is the free volume[13] available to a molecule in the state of class II, and A, B and C are the principal moments of inertia of water molecule. The factor in the first bracket of $f_{\rm II}$ corresponds to the translational degrees of freedom and that in the second bracket to the rotational ones. The contribution from intramolecular vibrations into $f_{\rm I}$ and $f_{\rm II}$ is ignored, because it may be safely regarded as 1 at temperatures from 0 to 100°C.

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[12] V. Vand and W. A. Senior, *J. Chem. Phys.*, **43**, 1869, 1873, 1878 (1965).

[13] A. Bondi, *J. Phys. Chem.*, **58**, 929 (1954).

Results

Determination of Parameters. The energy difference between two states, ε, and the free volume, v_f, which is available to a molecule in the state of class II, are two main parameters used in this theory. It is impossible to determine the magnitude of ε and v_f precisely from theory at present, and therefore, they have been treated as the adjustable parameters to give the best fit of calculated values to experimental data. The variation of parameters was, of course, limited within the physically reasonable range. In the earlier treatment based on the two state model the magnitude of ε has been estimated to be within the range of 2.5—3.0 kcal/mol. Smith and Lawson estimated the magnitude of ε to be 2.6 kcal/mol from their sound velocity data,[14] and Lawson *et al.* estimated it to be 3 kcal/mol from their thermal conductivity data.[15] Wada used the value of 2.51 kcal/mol in his treatment.[16]

Taking account of the heat of fusion of ice in addition to the estimation described above, we have taken the range of ε to be 2.75—3.15 kcal/mol.

The magnitude of v_f has been found to be of order of 1% of the volume per molecule (molecular volume) for many liquids.[13,17] Némethy and Scheraga used the value of 4.4×10^{-25} cm^3 which was about 1.5% of the molecular volume of water.[11] The magnitude of v_f calculated from the heat of vaporization of water[13] was 1.1×10^{-25} cm^3 (about 0.35%), and the magnitude of "fluctuation volume" calculated from the distance at the second peak in the Morgan and Warren's radial distribution curve[11,13] was 2.6×10^{-25}—4.6×10^{-25} cm^3, when that distance was taken to be 3.1—3.2 Å. Therefore, calculations have been made within the range of v_f from 1.1 to 4.6×10^{-25} cm^3 as the adjustable parameter. It has been found that the best fit of the calculated to the experimental data has been obtained when the magnitudes of ε and v_f have been taken to be 3 kcal/mol and 4.0×10^{-25} cm^3 (about 1.3% of the molecular volume) respectively.

As for the frequencies which have been attributed to intermolecular vibrations a tentative assignment has been made referring to the data from the infrared and Raman spectroscopy: 210 cm^{-1} for three modes of translational vibrations[11,18,19] and 500 cm^{-1} for three modes of librations on the average.[18,20),*1] The principal moments of inertia have been given to be the same as in the vapor state:[21] $A=1.024\times10^{-40}$, $B=1.921\times10^{-40}$, and $C=2.947\times10^{-40}$.

Calculations of Thermodynamic Variables. Using the values of parameters described above calculations of thermodynamic functions have been made over the temperature range from 0—100°C at 10°C intervals. The calculated values of the Helmholz energy, A, the internal energy, E, the entropy, S, and the specific heat at constant volume, C_V, are given in Table 1, and are plotted against temperature in Fig. (1)—(4). The results calculated are compared with the experimental data for water, which are taken from Dorsey.[11,22] The agreement between the observed and the calculated results is very good for the free energy, and is fairly good for the internal energy and the entropy. The values of E and S calculated are a little larger than the observed. The maximum deviation in the energy is 300 cal/mol, which amounts to 10% of the observed, and that in the entropy is 0.8 e.u., which is 4.7% of the observed. The agreement is found to be better at higher temperatures than at lower temperatures for A, E, and S. The circumstances are a little different for the specific heat, C_V. The curve calculated is found to cross at about 40°C with the experimental curve. The maximum percent deviation in C_V is 17%, which is observed at the boiling point. The agreement between the calculated and the observed specific heat is, however, better than for the curve given by Némethy and Scheraga's theory,[11] as it is seen in Fig. 4.

The magnitude of the mole fraction x has been calculated from Eq. (3), and given in Table 2, together with those given by Némethy and Scheraga,[11] and Buijs and Choppin.[23]

Molar Volume of Water. Concerning the molar volume of water, we assume that it is represented by the linear summation of the volume

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

[15] A. W. Lawson, R. Lowell and A. L. Jain, *ibid.*, **30**, 643 (1959).

[16] G. Wada, This Bulletin, **34**, 955 (1961).

[17] J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolyte," ACS Monograph No. 17 (Reinhold, New York (1950), 3rd ed., p. 76).

[18] P. A. Giguére and K. B. Harvey, *Can. J. Chem.*, **34**, 798 (1956).

[19] P. C. Cross, J. Burnham and P. A. Leighton, *J. Am. Chem. Soc.*, **59**, 1134 (1937).

[20] C. H. Cartwright, *Phys. Rev.*, **49**, 470 (1936).

[*1] Calculations on the basis of another assignment (lit. (18)—(20), Walrafen, *J. Chem. Phys.*, **47**, 114 (1967)), in which 200 cm^{-1} for translational vibrations and 500, 650, and 750 cm^{-1} for librations, have been made for comparison. Practically the same results have been obtained. The magnitude of x has been found within the deviation of ±0.01 from the results given in Table 2.

[21] R. P. Marchi and H. Eyring, *J. Phys. Chem.*, **68**, 221 (1964).

[22] N. E. Dorsey, "Properties of Ordinary Water Substances," ACS Monograph No. 81 (Reinhold, New York (1940)).

[23] K. Buijs and G. R. Choppin, *J. Chem. Phys.*, **39**, 2035 (1963).

TABLE 1. THERMODYNAMIC VARIABLES

Temp. (°C)	$A_{\text{calc.}}$ (kcal/mol)	$A_{\text{obs.}}$[11,22] (kcal/mol)	$E_{\text{calc.}}$ (kcal/mol)	$E_{\text{obs.}}$[11,22] (kcal/mol)	$S_{\text{calc.}}$ (cal/deg·mol)	$S_{\text{obs.}}$[11,22] (cal/deg·mol)	$(C_V)_{\text{calc.}}$ (cal/deg·mol)	$(C_V)_{\text{obs.}}$[11,12] (cal/deg·mol)
0	−1.06	−1.20	3.04	2.75	15.0	14.5	19.1	18.1_5
10	−1.28	−1.35	3.14	2.93	15.6	15.1	18.9	18.0_3
20	−1.44	−1.50	3.31	3.11	16.3	15.7	18.9	17.8_8
30	−1.61	−1.66	3.54	3.29	17.0	16.3	18.8	17.7_2
40	−1.78	−1.83	3.70	3.47	17.7	16.9	17.6	17.5_4
50	−1.97	−2.00	3.93	3.65	18.3	17.5	16.9	17.2_9
60	−2.15	−2.17	4.09	3.83	18.7	18.1	16.3	17.1_2
70	−2.35	−2.36	4.26	4.01	19.3	18.6	15.5	16.8_9
80	−2.54	−2.55	4.40	4.20	19.7	19.1	14.7	16.5_9
90	−2.74	−2.74	4.54	4.36	20.1	19.6	13.8	16.3_2
100	−2.94	−2.94	4.64	4.55	20.3	20.0	13.5	16.1_8

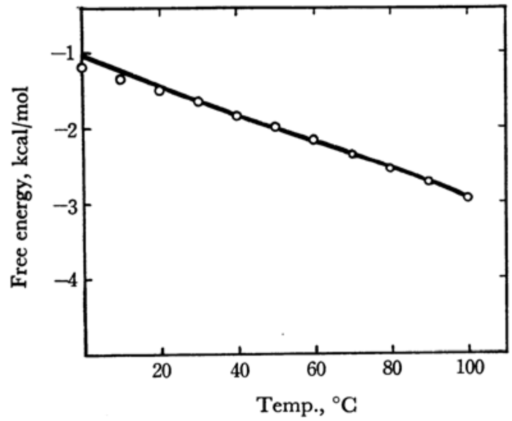

Fig. 1. Free energy, A, for water. Circle, observed; Solid line, calculated

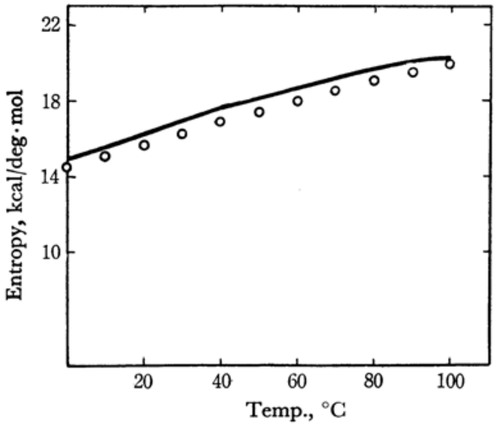

Fig. 3. Entropy, S, for water. Circle, observed; Solid line, calculated

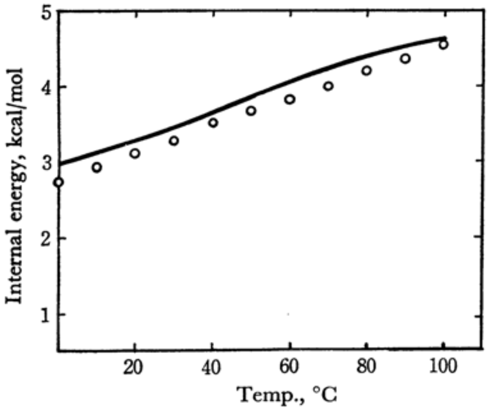

Fig. 2. Internal energy, E, for water. Circle, observed; Solid line, calculated

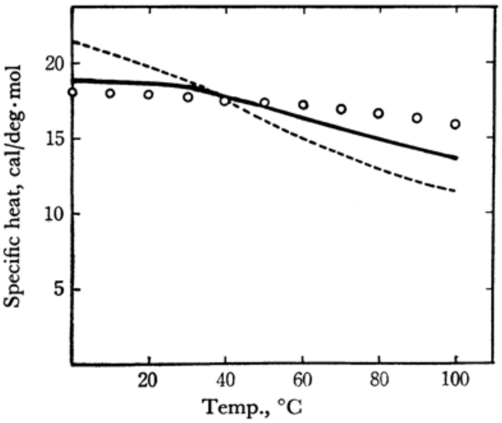

Fig. 4. Specific heat at constant volume, C_V. Circle, observed; Solid line, calculated by authors; Dotted line, calculated by Némethy & Scheraga[11]

of two classes of molecules as described below.

$$V = xV_{\text{I}}(1+\alpha_{\text{I}}t) + (1-x)V_{\text{II}}(1+\alpha_{\text{II}}t) \qquad (11)$$

where $V_{\text{I}} \times 19.657$, and $\alpha_{\text{I}} = 1.55 \times 10^{-4}$ which are the values for ice[11,22]; $V_{\text{II}} \times 16.252$, $\alpha_{\text{II}} = 1.50 \times 10^{-3}$, where V_{II} has been determined by fitting the Eq. (11) to the experimental data at the melting point and α_{II} has been determined in order to obtain the best fit as a parameter. The values of the molar volume calculated are given in Fig. 5

in comparison with the experimental data. The calculated curve is seen to have a minimum at about 4°C. The magnitudes of V_{II} and α_{II} which are for the close-packed structure have been found of reasonable ones,[*2] compared with those used by other authors.[11)]

TABLE 2. FRACTION OF HYDROGEN-BONDED PORTION, x

Temp. (°C)	Authors	Némethy & Scheraga[11)]	Buijs & Choppin[23)]
0	0.520	0.528	0.53
10	0.464	0.493	
20	0.415	0.462	
30	0.368	0.434	
40	0.327	0.409	
50	0.293	0.388	0.42
60	0.262	0.370	
70	0.239	0.356	
80	0.215	0.344	
90	0.197	0.334	
100	0.179	0.325	0.35

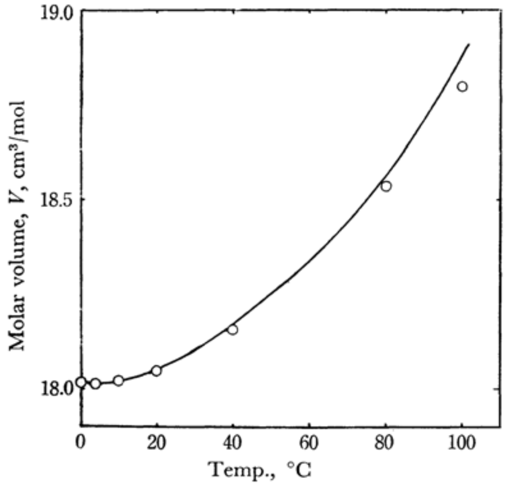

Fig. 5. Molar volume of water.
Solid line, calculated; Circle, observed

Discussions

As seen in Figs. (1)—(5), the results of calculations are found to be satisfactory on the whole, taking into account the simplicity of the model used. This fact supports the idea that the two state model used is an adequate representation of the structure of liquid water in order to describe the thermodynamical behavior. And it is also concluded that thermodynamic data are not sensitive to the detailed structure of each class and are governed by the average character on the whole.

Recently, Eyring and coworkers have proposed the significant structure theory for water.[21,24,26)] The earlier theory proposed by Marchi and Eyring[21)] used a two state model, but the monomer concentration at the melting point calculated was only 2.5 mol %. This is unreasonably small. The later theory presented by Jhon, Grosh, Ree, and Eyring[24)] was a three state theory which assumed that water consists of Ice-I-like structure, Ice-III-like structure, and monomers. The agreement to experimental data was certainly improved in the latter theory,[24)] compared with that in the former theory.[21)] However, additional assumptions were introduced into the latter theory.

The theory of Némethy and Scheraga may be said to be successful in the approximate description of thermodynamical behaviors of water. However, in the results calculated it is seen that several problems are found left unsolved in addition to the deviation of the magnitude of specific heat from the observed data. The one is the abnormally small magnitude of the mole fraction of di-hydrogen-bonded species, which is unreasonable.[12)] Further studies are required.

In the present theory the ice-like structure (class I) is regarded as a uniform state on the average without any further assumption to its structure. Though the present theory has turned out to be successful for the description of thermodynamical behaviors of water, it is, of course, necessary to introduce a further structural assumption concerning the structure of the ice-like region in order to describe the various kinds of relaxational behaviors. From the view-point of relaxational process, it has been proposed, as pointed out by Frank and Wen,[10)] that the ice-like structure is composed of flickering clusters.[10,11)] It is impossible to determine the size of clusters, exactly speaking, the distribution of the cluster size in the ice-like portion, using the theory based on the two state model which consists of each uniform-structure region, as in the present theory. For the purpose of determining the cluster size the introduction of third state, "the surface state on the cluster" is required, and the investigations by authors along this line are proceeding.

As for the calculation of the partition function concerning f_I (Eq. (9)), the frequency assignment used is, of course, an oversimplification, though the exact assignment has not been determined at

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[*2] The magnitude of V_{II} corresponds to the molar volume of spherical molecules with the diameter of 3.2 Å, arrayed in b.c.c. lattice, where the void fraction is assumed to be about 10%.

24) M. S. Jhon, J. Grosh, T. Ree and H. Eyring, *J. Chem. Phys.*, **44**, 1465 (1966).

25) H. Eyring and R. P. Marchi, *J. Chem. Educ.*, **40**, 562 (1963).

26) H. Eyring, T. Ree and N. Hirai, *Proc. Natl. Acad. Sci. Am.*, **44**, 683 (1958).

present. This deficiency will be supplemented in the further investigations.

Conclusion

A statistical thermodynamic theory based on the two state model has been successfully applied to liquid water. The two state model firstly proposed by Hall turned out to be an adequate description to the thermodynamical behaviors of water, in spite of its simplicity.

We wish to thank to Miss Yuko Endo for her cooperation in performing this study.