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# The Structure Theory of Water. III. The Order-Disorder Theory

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Taking into account the cooperative nature of cluster formation, we applied the order-disorder theory, using Bragg and Williams's approximation, to liquid water based on a two state model. The two state model consists of hydrogen-bonded molecules arrayed on $\alpha$-sites in a tetragonal lattice and non hydrogen-bonded molecules on $\beta$-sites in the lattice. A partition function was formulated and calculated. The calculated energy difference, $\varepsilon$, between the molecules on $\beta$-sites and those on $\alpha$-sites decreased continuously with the rise of temperature. Thermodynamic variables of liquid water were calculated at each temperature, where no adjustable parameter was used. Agreement between calculated values and observed ones is fairly good.

The structure of liquid water has been studied by many workers recently,[1,2] but conclusive results are still lacking. In advancing the structure theory of water, the models used are classified into two groups, a multi-state theory and a uniform-state theory. In the former, it has been assumed that liquid water consists of several distiguishable molecular species. Némethy and Scheraga[3] proposed a statistical theory of liquid water based on the model. Eyring and coworkers[4] applied a "significant structure theory" to water. In the preceding paper,[2] we stated that a simple two state theory could explain thermodynamic properties of water. Thus, we pointed out that the principal feature of multi-state theories was described by the two state theory. Existence of two different molecular species in liquid water has been supported experimantally by Luck[5] and Walrafen[6] from spectroscopic data.

Recently, Frank and Franks[7] have discussed the structural change of water caused by the presence of solute in aqueous solutions of urea, using a two state model. The application of two state theory to aqueous solutions has given fairly good results,

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[1] *Discuss. Faraday Soc.*, pp. 97—148 (1967).

[2] K. Arakawa and K. Sasaki, This Bulletin, **42**, 303 (1969).

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

[4] M. S. Jhon, J. Grosh, T. Ree and H. Eyring, *ibid.*, **44**, 1465 (1966).

[5] W. A. Luck, *Discuss. Faraday Soc.*, **43**, 115 (1967).

[6] G. E. Walrafen, *J. Chem. Phys.*, **48**, 244 (1968).

[7] H. S. Frank and F. Franks, *ibid.*, **48**, 4746 (1968).

as Holtzer and Emerson[8] and Ben-Neim and Stillinger[9] have reported. Our data of ultrasonic absorption[10] have shown that a two state model represents the structure of solvent water in aqueous solutions.

Studies based on the uniform-state model have been made since Pople[11] proposed a distored hydrogen-bond model. Einberg and Kauzmann[12] have pointed out the utility of distorted hydrogen-bond models. The "uniform nature" of the structure of water has been emphasized in the interpretation of spectroscopic data by Wall and Hornig,[13] Falk and Ford[14] and Franck and Roth.[15] However, no explanation of the origin of ultrasonic absorption such as made by Hall and others[16] using a two state model has been given by the uniform-state theory.

Though no decisive conclusion has been obtained, various attempts in the field of the structure theory of water have been made. However, one of the most important problems left unsolved at present is the direct introduction of the cooperative nature of the structure formation into theory. Thus, we attemped here an application of order-disorder theory[17] to explain thermodynamic properties of water on the basis of a two state model. The cooperative nature of "cluster" ("open-packed structure") formation are taken directly into account.

## Theory

**Model.** As pointed out recently by Narten *et al.*[18] from X-ray diffraction data, liquid water consists of an ice-like structure and unbonded molecules.[18–20] The ice-like structure is believed to be a partly-broken lattice linked tetragonally by hydrogen bonds. It is seen that the number of first nearest neighbours in liquid water varied from 4.4 to 4.9 at temperatures 1.5—83°C.[21]

In the formulation of the following statistical theory, we assume that all molecules are distributed in a body-centered cubic lattice,[22] and that water is an equilibrium mixture of molecules arranged in two kinds of sites, $\alpha$ and $\beta$, in the lattice, as shown in Fig. 1. Hydrogen-bonded molecules occupy $\alpha$-sites forming a tetragonal sub-lattice, and non-hydrogen-bonded molecules occupy $\beta$-sites. The energy level of molecules on $\beta$-sites is higher than that on $\alpha$-sites. At 0°K in a "completely-ordered state" all molecules occupy only $\alpha$-sites forming an ice-like structure. With the rise of temperature, population of $\alpha$-sites decreases and that on $\beta$-sites increases, causing patial break-down of the ice-I-like structure. At a "completely-disordered state," two kinds of sites are occupied with equal probability.

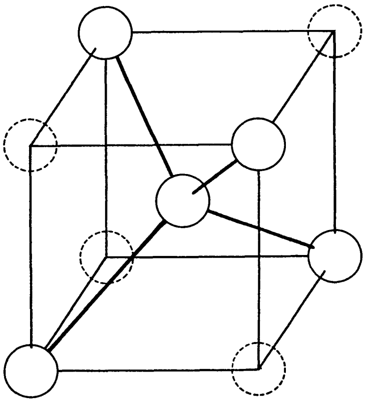

Fig. 1. $\alpha$ and $\beta$-site in a body-centered cubic lattice.
○ $\alpha$-site, ◌ $\beta$-site

**Application of Order-Disorder Theory.** The total partition function, $Z$, is given by

$$Z = Wf_{\alpha}^{N_{\alpha}}f_{\beta}^{N_{\beta}} \exp\left(-H/\boldsymbol{R}T\right) \tag{1}$$

where $W$ is a combinatorial factor, $H$ potential energy, $T$ temperature, $N_\alpha$ and $N_\beta$ are the number of molecules arranged in each site, and $f_\alpha$ and $f_\beta$ are the molecular partition functions for molecules in each site, respectively. The combinatorial factor and the potential energy are defined by

$$W = \frac{[\alpha]!}{N_\alpha!([\alpha]-N_\alpha)!}\cdot\frac{[\beta]!}{N_\beta!([\beta]-N_\beta)!} \tag{2}$$

$$H = N_\alpha V_\alpha + N_\beta V_\beta,\ N_\alpha + N_\beta = N \tag{3}$$

where $[\alpha]$ and $[\beta]$ are the number of each kind of lattice site ($[\alpha]=[\beta]=N$), $V_\alpha$ and $V_\alpha$ the potential

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[8] A. Holtzer and M. F. Emerson, *J. Phys. Chem.*, **73**, 26 (1969).

[9] A. Ben-Naim and F. H. Stillinger, *ibid.*, **73**, 900 (1969).

[10] K. Arakawa, N. Takenaka and K. Sasaki, This Bulletin, **43**, 636 (1970).

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

[12] D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford at Clarendon Press (1969).

[13] T. T. Wall and D. F. Hornig, *J. Chem. Phys.*, **43**, 2079 (1965).

[14] M. Falk and T. A. Ford, *Can. J. Chem.*, **44**, 1699 (1966).

[15] E. U. Franck and K. Roth, *Discuss. Faraday Soc.*, **43**, 108 (1967).

[16] L. Hall, *Phys. Rev.*, **73**, 775 (1948); T. A. Litovitz and E. H. Carnivale, *J. Appl. Phys.*, **26**, 816 (1955); A. H. Smith and A. W. Lawson, *J. Chem. Phys.*, **22**, 351 (1954).

[17] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambrige University Press (1939).

[18] A. H. Narten, M. D. Danford and H. A. Levi, *Discuss. Faraday Soc.*, **43**, 97 (1967).

[19] M. D. Danford and H. A. Levi, *J. Amer. Chem. Soc.*, **84**, 3965 (1962).

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

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

[22] C. M. Davis and T. A. Litovitz, *ibid.*, **42**, 2563 (1965).

energy of molecules on $\alpha$ and $\beta$-sites, respectively, and $N$ is the total number of molecules. We define as usual the degree of order, $s$, in relation to $N_\alpha$ and $N_\beta$.

$$N_\alpha = \frac{N(1+s)}{2},\ N_\beta = \frac{N(1-s)}{2} \tag{4}$$

Introducing Eq. (4) into Eq. (2), we obtain the combinatorial factor, *viz.*,

$$W = \left[\frac{N!}{\left\{\frac{N(1+s)}{2}\right\}!\left\{\frac{N(1-s)}{2}\right\}!}\right]^2 \tag{5}$$

The degree of order, $s$, is determined by minimization of the Helmholtz energy, $A$, with respect to $s$. Thus, in equilibrium, we have

$$\frac{\partial A}{\partial s} = 0 \tag{6}$$

where

$$A = -kT\ln Z \tag{7}$$

In carrying out calculation, Bragg and Williams's approximation17) concerning the relation between the energy for the exchange of molecules on different kinds of sites and the degree of order $s$ is applied.

When the approximation is made as usual, $V_\beta - V_\alpha$ should be proportional to $s$. Thus, we have

$$V_\alpha = \frac{V^0(1+s)}{2},\ V_\beta = \frac{V^0(1-s)}{2} \tag{8}$$

from the consideration that $V_{\alpha,s=0} = V_{\beta,s=0}$ in the completely-disordered state. This condition is regarded as a special case of $\mu_{\alpha,s=0} = \mu_{\beta,s=0}$ where $\mu_\alpha$ and $\mu_\beta$ are chemical potentials of the molecule on each site. Thus, in the present case, $V_{\alpha,s=0} \neq V_{\beta,s=0}$,[*1] because the molecular partition function $f_\alpha$ is not identical with $f_\beta$.

Let us put

$$V_\alpha = V_\alpha^0\left(\frac{1+s}{2}\right),$$
$$V_\beta = V_\beta^0\left(\frac{1-s}{2}\right) \tag{8'}$$

and $V_\alpha^0 \neq V_\beta^0$.

We assume that at boiling point a complete randomness is realized. Thus, $s$ should vanish at boiling point, and the chemical potential of the molecule on $\alpha$-site should be equal to that on $\beta$-site at that temperature, as follows:

$$\frac{V_\alpha^0}{2} - kT_b\ln(f_\alpha)_{T=T_b} = \frac{V_\beta^0}{2} - kT_b\ln(f_\beta)_{T=T_b} \tag{9}$$

and we have

$$V_\alpha^0 - V_\beta^0 = -2kT_b\ln\left(\frac{f_\beta}{f_\alpha}\right)_{T=T_b} \tag{9'}$$

where a subscript $b$ represents boiling point. When Eqs. (5), (7), (8') and (9') are inserted into Eq. (6), we obtain

$$\ln\left(\frac{1+s}{1-s}\right) = -\frac{1}{4kT}(V_\alpha^0 + V_\beta^0)\,s + \frac{1}{2}\left\{\frac{T_b}{T}\ln\left(\frac{f_\beta}{f_\alpha}\right)_{T=T_b} - \ln\left(\frac{f_\beta}{f_\alpha}\right)\right\} \tag{10}$$

Equation (10) is a fundamental equation which determines $s$ as a function of temperature. The second term on the right hand side of Eq. (10) vanishes at $s=0$ $(T=T_b)$ more rapidly with the decrease of $s$ than the first term. The usual procedure in the application of Bragg and Williams's approximation can be used. We have

$$V_\alpha^0 + V_\beta^0 = -8kT_b \tag{11}$$

and

$$V_\alpha^0 = -kT_b\left\{4 + \ln\left(\frac{f_\beta}{f_\alpha}\right)_{T=T_b}\right\} \tag{12}$$

$$V_\beta^0 = -kT_b\left\{4 - \ln\left(\frac{f_\beta}{f_\alpha}\right)_{T=T_b}\right\} \tag{12'}$$

Combining Eqs. (11) and (12) with Eq. (10), we have

$$\ln\left(\frac{1+s}{1-s}\right) = \frac{2T_b}{T}s + \frac{1}{2}\left\{\frac{T_b}{T}\ln\left(\frac{f_\beta}{f_\alpha}\right)_{T=T_b} - \ln\left(\frac{f_\beta}{f_\alpha}\right)\right\} \tag{13}$$

Eq. (13) is used for the calculation of $s$. Introducing Eqs. (4), (12) and (12') into Eq. (3), we have

$$H = -NkT_b(1+s^2) - \left\{\frac{NkT_b}{2}\ln\left(\frac{f_\beta}{f_\alpha}\right)_{T=T_b}\right\}s \tag{14}$$

Thus, we can calculate the Helmholtz energy $A$, internal energy $E$, and entropy $S$, from the following equations.

$$\begin{aligned} A = {} & -NkT\{2\ln2 - (1+s)\ln(1+s) - (1-s)\ln(1-s) \\ & + \frac{(1+s)}{2}\ln f_\alpha + \frac{(1-s)}{2}\ln f_\beta\} \\ & - NkT_b(1+s^2) - \left\{\left(\frac{NkT_b}{2}\right)\ln\left(\frac{f_\beta}{f_\alpha}\right)_{T=T_b}\right\}s \end{aligned} \tag{15}$$

$$\begin{aligned} E = {} & \frac{NkT^2}{2}\left\{\left(\frac{1+s}{f_\alpha}\right)\frac{\partial f_\alpha}{\partial T} + \left(\frac{1-s}{f_\beta}\right)\frac{\partial f_\beta}{\partial T}\right\} \\ & - NkT_b(1+s^2) - \left\{\frac{NkT_b}{2}\ln\left(\frac{f_\beta}{f_\alpha}\right)_{T=T_b}\right\}s \end{aligned} \tag{16}$$

$$S = \frac{(E-A)}{T} \tag{17}$$

The molecular partition function for each site, $f_\alpha$ and $f_\beta$, are given by the following equations.2)

$$f_\alpha = \prod_{i=1}^{6}\left\{1 - \exp\left(\frac{-h\nu_i}{kT}\right)\right\}^{-1} \tag{18}$$

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[*1] In an ordinary application of Bragg and Williams's approximation the difference between $f_\alpha$ and $f_\beta$ is not taken into account. Thus, from the equal probability for the occupation of each site at $s=0$, it necessarily follows from the general condition $\mu_{\alpha,s=0} = \mu_{\beta,s=0}$ that $V_{\alpha,s=0} = V_{\beta,s=0}$.

$$f_\beta = \prod_{i=1}^{3} \left\{1 - \exp\left(\frac{-h\nu'_i}{kT}\right)\right\}^{-1} \cdot \frac{(8\pi kT)^{3/2}(\pi ABC)^{1/2}}{2h^3} \tag{19}$$

$\nu_i$ is the frequency of intermolecular vibration for $\alpha$-site which includes translational and rotational ones. $\nu_i'$ is the frequency of translational vibrations for $\beta$-site. $A$, $B$ and $C$ are principal moments of inertia of water molecule. In the derivation of Eq. (19), the molecules on $\beta$-sites are assumed to be free rotators. In the calculations of $f_\alpha$ and $f_\beta$, the contribution from intramolecular vibrations is nearly 1 at temperatures 0—100°C, and thus ignored.

## Results

**Procedure of Calculation.** As seen in Eq. (12), $V_\alpha^0$ is the potential energy of water molecules on $\alpha$-sites at the completely-ordered state ($s=1$, 0°K) so that it is twice the energy for breaking hydrogen bond. The amount of energy can be calculated from Eq. (12) without any additional assumptions. The energy difference, $\varepsilon$, between the molecules on $\beta$-sites and those on $\alpha$-sites is obtained as follows.

$$\varepsilon = V_\beta - V_\alpha = NkT_b \left\{4s + \ln\left(\frac{f_\beta}{f_\alpha}\right)_{T=T_b}\right\} \tag{20}$$

We evaluated the magnitude of $\varepsilon$ at $s=1$ to be 4.33 kcal/mol and at $s=0$ 1.36 kcal/mol. The energy difference between two species of molecules for various treatments based on two state model is tabulated in Table 1. The values are distributed within the range 2.4—4.5 kcal/mol. Our value seems to be reasonable on the average compared with those by others.

Table 1. Energy difference between both sites

| Authors | Energy (kcal/mol) | Reference |
|---|---|---|
| Nemethy and Scheraga | 2.64 | (a) |
| Vand and Senior | 2.8 | (b) |
| Worley and Klotz | 2.4 | (c) |
| Walrafen | 2.5 | (d) |
| Scatchard *et al.* | 3.4 | (e) |
| Lawson *et al.* | 3 | (f) |
| Pauling | 4.5 | (g) |
| previous paper of authors | 3.0 | (h) |
| present paper $s=1$ | 4.33 | |
| $s=0.5$ | 2.85 | |
| $s=0$ | 1.36 | |

(a) Reference 3.
(b) Reference 32.
(c) J. D. Worley and I. M. Klotz, *J. Chem. Phys.*, **45**, 2868 (1966).
(d) G. E. Walrafen, *ibid.*, **48**, 244 (1968).
(e) G. Scatchard, G. M. Kavanagh and L. B. Tincknor, *J. Amer. Chem. Soc.*, **74**, 3715 (1952).
(f) A. W. Lawson, R. Lowell and A. L. Jain, *J. Chem. Phys.*, **30**, 643 (1959).
(g) L. Pauling, "The Nature fo the Chemical Bond," 3rd Ed., Cornell, Ithaca, New York (1960).
(h) Reference 2.

The degree of order, $s$, is within the range of 0—1 at temperatures from 100°C to 0°K. The equilibrium value of $s$ at a given temperarute is determined graphically using Eq. (13) as shown in Fig. 2, where the lines (a), (b) and (c) are the plot of the right hand side of Eq. (13) at 0, 50 and 100°C, respectively. The calculated values of $s$ are plotted against temperature in Fig. 3. The obtained value of $s$ at 0°C is 0.83.

In the assignment of intermolecular vibration of water molecules, there are some ambiguities.[1-3] For the three modes of translational vibrations on

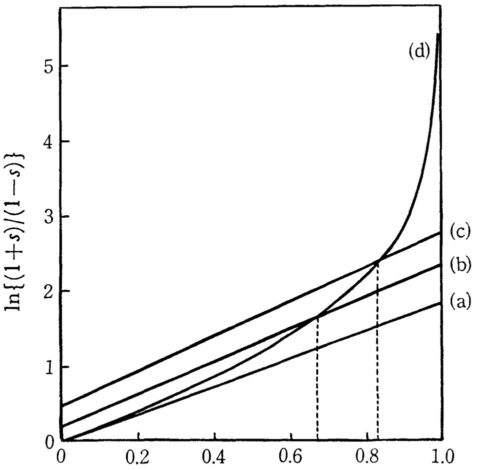

Fig. 2. Determination of the magnitude of $s$ at equilibrium.
(a) 0°C, (b) 50°C, (c) 100°C,
(d) $\ln\{(1+s)/(1-s)\}$

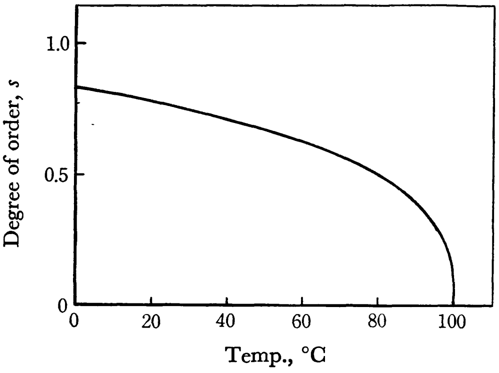

Fig. 3. Temperature dependence of degree of order $s$.

each site, a common value of 180 cm$^{-1}$ [23] is assigned, and 500, 650 and 750 cm$^{-1}$ are assigned[24,25,2] for each mode of librations for $\alpha$-site. The principal moments of inertia for a free rotator molecule is the same as in vapor state; $A=1.024\times10^{-40}$, $B=1.921\times10^{-40}$, and $C=2.947\times10^{-40}$ [2,26]

**Calculation of Thermodynamic Variables.** With the value of $s$ determined graphically, calculation of thermodynamic functions has been made over the temperature range 0—100°C at 10°C intervals. The obtained values of Helmholtz energy $A$, internal energy $E$ and entropy $S$ are given in Table 2, and are plotted against temperature in Fig. 4—6. The results calculated are compared with the observed data for water.[27] The fraction $x=(1+s)/2$ of the molecules on $\alpha$-sites is tabulated together with other thermodynamic variables in Table 2. The calculated value of $A$ are satisfactory on the whole. The calculated value of $E$ increases rapidly with increasing temperature at higher temperatures. This can be interpreted by the variation of $s$ with rising temperature, which falls off rapidly near boiling point. But deviation of the calculated results from experimental data is not so large. Agreement of thermodynamic functions calculated with observed values is satisfactory, taking into account the fact that no adjustable parameters are used in the present calculation as in the former theories.

TABLE 2. THERMODYNAMIC VARIABLES

| Temp. (°C) | $A_{calc.}$ | $A_{obs.}$ (kcal/mol) | $E_{calc.}$ | $E_{obs.}$ (kcal/mol) | $S_{calc.}$ | $S_{obs.}$ (cal/deg mol) | $x$ |
|---|---|---|---|---|---|---|---|
| 0 | −0.91 | −1.20 | 1.59 | 2.75 | 9.11 | 14.5 | 0.915 |
| 10 | −1.00 | −1.35 | 1.72 | 2.95 | 9.60 | 15.1 | 0.903 |
| 20 | −1.10 | −1.50 | 1.87 | 3.11 | 10.1 | 15.7 | 0.890 |
| 30 | −1.14 | −1.66 | 2.01 | 3.29 | 10.4 | 16.3 | 0.875 |
| 40 | −1.29 | −1.83 | 2.15 | 3.47 | 11.0 | 16.9 | 0.859 |
| 50 | −1.41 | −2.00 | 2.35 | 3.65 | 11.6 | 17.5 | 0.836 |
| 60 | −1.49 | −2.17 | 2.55 | 3.83 | 12.1 | 18.1 | 0.806 |
| 70 | −1.64 | −2.36 | 2.72 | 4.01 | 12.7 | 18.6 | 0.784 |
| 80 | −1.77 | −2.55 | 2.94 | 4.20 | 13.4 | 19.1 | 0.749 |
| 90 | −1.91 | −2.74 | 3.15 | 4.36 | 13.9 | 19.6 | 0.713 |
| 100 | −2.05 | −2.94 | 3.78 | 4.55 | 15.6 | 20.0 | 0.500 |

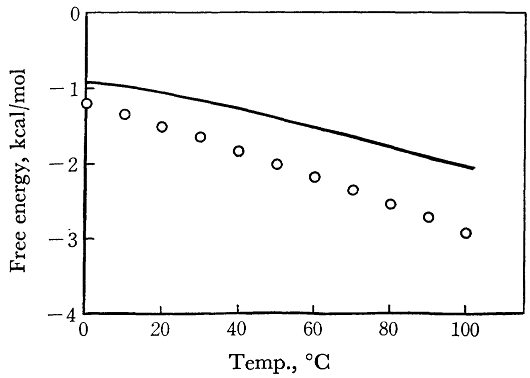

Fig. 4. Free energy, $A$, for water.
Circle, observed; Solid line, calculated

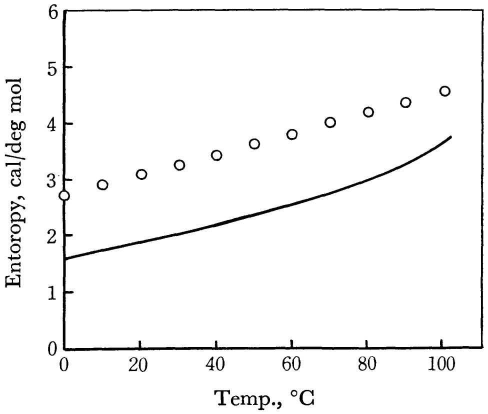

Fig. 5. Internal energy, $E$, for water.
Circle, observed; Solid line, calculated

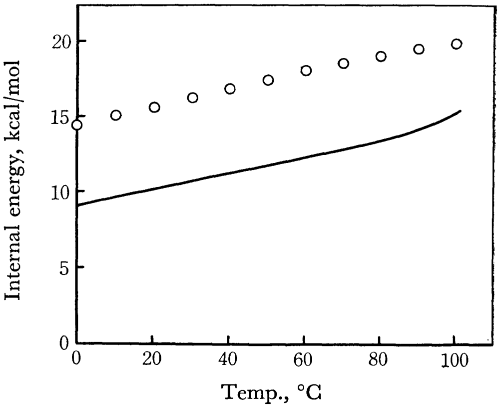

Fig. 6. Entropy, $S$, for water.
Circle, observed; Solid line, calculated

## Discussion

**Cooperative Formation and Destruction of Ice-like Structure in Liquid Water.** From various kinds of relaxational processes in water, Frank and Wen[28] pointed out that the lifetime of ice-like

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[23] M. Magat, *Discuss. Faraday Soc.*, **43**, 145 (1967).

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

[25] G. E. Walrafen, *J. Chem. Phys.*, **40**, 3249 (1964); P. C. Cross, J. Burnham and P. A. Leighton, *J. Amer. Chem. Soc.*, **59**, 1134 (1937).

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

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

[28] H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, **24**, 481 (1957).

structure in liquid water was the order of $10^{-11}$—$10^{-10}$ sec. The cooperative nature of the formation and destruction of ice-like structure (clusters) has been pointed out by many workers. However, the cooperative effect itself has never been directly treated theoretically in these studies. Consequently, the clusters in liquid water have been treated like a "solid". Gurikov[29] criticized Némethy and Scheraga's theory, in this respect. Perram and Levine[30] also pointed out an inadequate procedure in Némethy and Scheraga's theory in which geometrically impossible configurations of five species were included for the calculation of the combinatorial factor. In the present situation of the structure theory of water, it is emphasized that the cooperative process of cluster formation should be introduced directly in forming the theory. Thus, we have introduced the cooperative nature of cluster formation through the application of the order-disorder theory on the basis of a two state model.[19,20] This is an essential feature in the present theory.

**Parameters used in Theories.** In this study, the degree of order, $s$, has been used as only one parameter, which determines all thermodynamic variables of water. The value of $s$ at equilibrium has been determined by minimizing the free energy. Thus, this theory has no adjustable parameter practically. In Némethy and Scheraga's theory, free volume, $v_f$, and energy difference, $\varepsilon$, between the tetra-hydrogen-bonded state and the unbonded state were used as adjustable parameters. In our previous paper,[2] $v_f$ and $\varepsilon$ were used as adjustable parameters, which were determined to give the best fit to experimental data as made in Némethy and Scheraga's theory. Thus, the present theory has a merit that no adjustable semi-empirical parameters are used.

Weissmann and Blum[31] have recently reported a cell theory in which no adjustable parameter is used. However, their results are far from the observed data. The calculated values in the present theory are seen in fair agreement with observed ones.

**Two State Theory and Distorted Hydrogen Bond Theory.** The multi-state theories of water have been developed in various forms: Némethy and Scheraga's five species model, Vand and Senior's continuous energy band model[32] and Buijs and Choppin's three state model.[33] We pointed out previously that two state theory could explain most of the observed data as well as multi-state theories. Various multi-state theories are practically reduced to two state theories. The number of states corresponds to the number of parameters which are introduced in the theory. In constructing a theory, the number of parameters is desired to be as small as possible. In this respect, a two state model is superior to a multi-state model consisting of more than two species.

In the discussion of the first report of this series of studies, the authors referred to the presence of a "third state" or "surface state" on the cluster. However, the emphasis of "surface state" has turned out to be inadequate, considering the very short lifetime and the cooperative nature of cluster formation.

On the other hand, various uniform-state models (distorted hydrogen-bonded model) have been proposed by several workers since the presentation of Pople's theory.[11] Eisenberg and Kauzmann[12] have recently claimed that, with rising temperature, hydrogen bonds of water molecules are bent rather than broken. However, concerning the uniform-state model, there are several shortcomings in the explanation of the structure and properties of water. Firstly, the cooperative behavioı of cluster formation in liquid water can not be explained by the uniform-state theory. Secondly, the data of ultrasonic absorption have never been explained by the uniform-state theory, while Hall and others[16] succeeded in describing those data using a two state model.

Furthermore, the nature of "hydrophobic interaction" has never been explained by the uniform-state theory, but Némethy and Scheraga succeeded in explaining it by the multi-state theory.[34]

Thus, it may be said that the structure and properties of water have never been described successfully by any uniform-state theory.

**The Energy Difference $\varepsilon$ between Two States.** In our results, the energy difference between both sites continuously decreases as the degree of order decreases with increasing temperature. The magnitude of $\varepsilon$ (4.33 kcal/mol at $s=1$ and 1.36 kcal/mol at $s=0$) at each temperature is seem to be reasonable. Up to this time, the energy difference between two structures in the two state theories has been regarded as a constant value in the range of temperature 0—100°C. However, the circumstances of molecules vary with rising temperature, so that the energy difference should decrease as a result of cooperative process. The present theory has succeeded in describing the variation of $\varepsilon$ with rising temperature.

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29) Yu. V. Gurikov, *J. Struct. Chem.*, (translation of *Zh. Strukt. Khim.*), **6**, 786 (1966).

30) J. W. Perram and S. Levine, *Discuss. Faraday Soc.*, **43**, 131 (1967).

31) M. Weissmann and L. Blum, *Trans. Faraday Soc.*, **65**, 2605 (1969).

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

33) K. Buijs and G. R. Choppin, *ibid.*, **39**, 2035 (1963).

34) G. Némethy and H. A. Scheraga, *ibid.*, **36**, 3401 (1962).