Statistical Thermodynamic Theory of Liquid Water

Kiyoshi Arakawa, Kazuo Tokiwano,* and Kazumitsu Kojima
Research Institute of Applied Electricity, Hokkaido University, Sapporo 060
** Faculty of Engineering, Hokkaido University, Sapporo 060*

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A new statistical thermodynamic theory is presented for a model of liquid water, which consists of two components, *i.e.*, tetrahedrally-coordinated pentamers and non-hydrogen-bonded monomers. In the model the two components are assumed to be immersed in a uniform background potential which results from electrostatic, induction, and dispersion forces between water molecules. A partition function is given without assuming any specified lattice. A translational partition function is written into a simple and explicit expression which is derived from the Lebowitz solution of the Percus-Yevick equation for hard sphere mixtures. The mole fraction of each component and the density are determined by solving two equations, *i.e.*, the condition of free energy minimization and the equation of state derived from the partition function, simultaneously. Various thermodynamic quantities are calculated and the values determined are compared with those observed. Some discussions are carried out, together with the criticism of the earlier theories.

Various kinds of statistical thermodynamic theories of liquid water[1-3] have been proposed for about a decade since the presentation of the earlier theory by Némethy and Scheraga (1962). Many new experimental results have also been accumulated for nearly the same period of time and added a great deal of contributions to the knowledge of the structure of liquid water,[4] though no decisive conclusion about it has been obtained at present.[5]

Concerning the structure theories of liquid water, the situations are diversified nowadays certainly, but, as to the theoretical methods and models used, several distinguishable features are found in the studies carried out recently. Those are classified into three groups: 1) lattice and cell theories, 2) applications of the recent progress in the theory of liquids, *i.e.*, the Percus-Yevick and HNC equations *etc.*, 3) results in computer experiments, *i.e.*, molecular dynamics and Monte Carlo calculations.

Among the first group of studies we find lattice theories presented by Bell and others[6] and by Fleming and Gibbs,[7] a cell theory by Weissmann and Blum,[8] and an order-disorder theory by the authors.[9] Some of these theories[6,7,9] treated the theme of the cooperative character in the structure of liquid water, that is, the cooperative formation and breakage of the hydrogen-bonded structure, but the success of those is only qualitative, subjected to the limitation which is associated with the essential nature of the lattice theory. The studies in line with the second group are mainly promoted by Ben-Naim and others.[10] There seems to be a fair prospect of success of these theories, but the greatest problem lies in mathematical difficulties of solving integral equations for correlation functions. The most remarkable results in the third group are those of molecular dynamics given by Rahman and Stillinger.[11] They have made important contributions to the determination of the structure model for water. All the results described above give new possibilities, surely, to solve the important but difficult problem of the liquid structure of water. However, their successes remain to be qualitative and limited ones on the whole.

From the quantitative view-point of results, recent two theories presented by Weres and Rice[12] and by Scheraga and coworkers[13] are intensely interesting. The former one is a kind of lattice theory and the latter one is based on a mixture model (cluster model). They made a further forward step to the quantitative explanation of the equilibrium behavior of water. However, they are too solid-like. For example, it has been found in the calculation by Weres and Rice that the value of configurational entropy with respect to the arrangement of water molecules in basic cells remains quite unchanged throughout the temperature range from 0 to 100 °C. In the calculation by Scheraga *et al.* also, it has been found that $U_{\text{vib.}}$, the internal energy resulting from the intermolecular vibrational structure, increases from the value of 3.33 kcal/mol to 3.87 kcal/mol throughout the same range of temperature while $U_{\text{trans.}}$, the energy for translational motion, is very small, being within the range from 0.18 to 0.28 kcal/mol. These features of the two theories clearly show the too solid-like character, though it is found to be more intense in the theory by Weres and Rice than in the one by Scheraga *et al.*

Thus, the authors have attempted to propose a statistical thermodynamic theory of liquid water based on the recent progress in studies of liquids, in order to give the more adequate explanation of the properties of water. Details of the results are reported in the following sections.

Description of the Model

Since the proposition by Bernal and Fowler in 1933, the tetrahedral coordination has been considered to dominate in the local structure in liquid water. The results of X-ray studies from Morgan and Warren's (1938) to the recent Narten, Danford, and Levy's[14] has ascertained that the average coordination number in liquid water is slightly larger than four at ordinary temperatures, indicating the predominance of the local tetrahedral geometry. Recent spectroscopical studies by Walrafen[15] and others has also confirmed that the tetrahedrally-coordinated hydrogen-bonded configurations with C_{2v} symmetry constitute most of the structures present in water. This feature should be taken into consideration firstly in the formulation of the theoretical model for water.

In the recent presentation of a statistical thermodynamic theory for water, Lentz, Hagler, and Scheraga

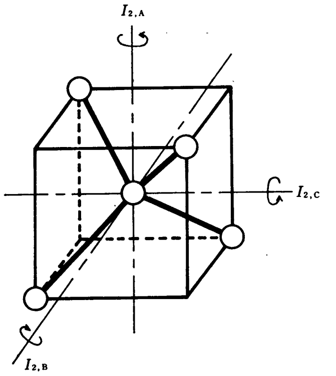

Fig. 1. Tetrahedrally-coordinated pentamer.

have used a model consisting of a distribution of small clusters from 1 to 9,[13] admitting the criticisms against the earlier theory of Némethy and Scheraga[16] (1962) that it used a model with very large clusters.

It is desirable that the basic model underlying a theory is as simple as possible if the theory can explain the behavior of the substance as objects with a sufficient accuracy. Thus, the authors assume that liquid water consists of two species which are tetrahedrally hydrogen-bonded pentamers (Fig. 1) and unbonded monomers. The character of the structure supposed to be intrinsic of water is attributed to the presence of the pentamers, and liquid water is regarded as an equilibrium mixture of the monomers and the pentamers.

In the formulation of the total partition function, we assume that attractive forces between molecules give rise to a uniform background potential, taking into consideration the treatment made first by Longuet-Higgins and Widom for liquid Argon,[17] by Scheraga and others for water,[13,18] and by the authors for normal liquid.[19] The magnitude of the background potential is determined by a direct calculation as described in later sections, while it was treated as an adjustable parameter in the calculation of Scheraga and others.

In order to give a translational partition function we regard the two species as hard spheres with diameters R_1 and R_2 ($R_1 < R_2$), respectively, which are immersed in the background potential, and the translational partition function is derived from the analytical solution of the Percus-Yevick equation for hard sphere mixtures. Its details are described later.

The Partition Function

For the model used the total partition function is expressed as a product,

$$Z = Q_{\text{trans.}} Q_{\text{rot.}} Q_{\text{int.}} Q_{\text{BG}}, \tag{1}$$

in terms of the translational, rotational, internal, and background potential contribution, respectively.

i) Translational Partition Function. We can write the translational partition function $Q_{\text{trans.}}$ at given V and T for an assembly of N_1 non-hydrogen-bonded monomers (the mass m_1 and the diameter R_1) and N_2 pentamers (the mass m_2 and diameter R_2). The formula is derived from the analytical and explicit solution of the generalized Percus-Yevick equation given first by Lebowitz.[20,21] The details of the derivation are described in Appendix I.

$Q_{\text{trans.}}$ is expressed as

$$Q_{\text{trans.}} = \left[\left(\frac{2\pi m_1 kT}{h^2}\right)^{3/2} e v_1 f\right]^{N_1} \left[\left(\frac{2\pi m_2 kT}{h^2}\right)^{3/2} e v_2 f\right]^{N_2}, \tag{2}$$

and

$$f = (1-\xi)\exp\left[-\frac{9}{\pi}\frac{V}{N_1+N_2}\frac{1}{(1-\xi)^2}(2XY-2XY\xi+X^3)\right], \tag{3}$$

where

$$v_1 = V/N_1 = \rho_1{}^{-1},\ v_2 = V/N_2 = \rho_2{}^{-1},$$

$$X = \frac{\pi}{6}\rho_1 R_1{}^2 + \frac{\pi}{6}\rho_2 R_2{}^2,\ Y = \frac{\pi}{6}\rho_1 R_1 + \frac{\pi}{6}\rho_2 R_2,$$

and the packing fraction is

$$\xi = \frac{\pi}{6}\rho_1 R_1{}^3 + \frac{\pi}{6}\rho_2 R_2{}^3.$$

The Eqs. 2 and 3 are a generalization of Eqs. 4 and 6 in the previous paper[19] for an one component fluid into the formulas for a mixture of hard spheres, where ξ corresponds to y in the paper. Equation 2 is seen to have a form identical with that given in the free volume theory in general. Thus, $f \equiv$ Eq. 3 is defined as a generalized equivalent free volume fraction, which is similar to the case of an one component fluid.[19] This is extended to the general case for an m-component fluid as described in Appendix I. In the presentation of our theory no lattice is assumed, and the theory derived is free from the criticism against the lattice theory in general in its application to liquids.

ii) Rotational Partition Function. The contribution $Q_{\text{rot.}}$ from the rotational motions to the total partition function becomes

$$Q_{\text{rot.}} = \left[\frac{\pi^{1/2}}{\sigma_1}\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2}(I_{1,\text{A}} I_{1,\text{B}} I_{1,\text{C}})^{1/2}\right]^{N_1} \times \left[\frac{\pi^{1/2}}{\sigma_2}\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2}(I_{2,\text{A}} I_{2,\text{B}} I_{2,\text{C}})^{1/2}\gamma\right]^{N_2}, \tag{4}$$

where $I_{i,\text{A}}$, $I_{i,\text{B}}$, $I_{i,\text{C}}$, and σ_i are the moment of inertia and symmetry factor, respectively, of an i-th particle. γ is a reduction factor which results from the restriction of the over-all free rotation for a larger particle such as a pentamer. Though this factor γ is expected to be smaller than 1 for the pentamer, we take it as 1, for it is impossible to compute the reduced number of rotational configurations. Symmetry factors σ_1 and σ_2 are taken to be 2, as usual.

iii) Internal Partition Function. The internal partition function $Q_{\text{int.}}$ is

$$Q_{\text{int.}} = Q_{\text{vib.}} \exp\left(\frac{-4N_2\varepsilon}{kT}\right), \tag{5}$$

where $Q_{\text{vib.}}$ is the contribution from the vibrational degrees of freedom from N_2 pentamers and ε is the energy of hydrogen bonding within pentamers. In each pentamer four hydrogen bonds are formed between the central molecule and four tetrahedrally-coordinated molecules. We write the vibrational contribution $Q_{\text{vib.}}$ as

$$Q_{\text{vib.}} = \left[\prod_{j=1}^{24}\left\{\frac{\exp(-h\nu_j/2kT)}{1-\exp(-h\nu_j/kT)}\right\}\right]^{N_2}, \tag{6}$$

where ν_j is the frequency of intermolecular vibrational mode within a pentamer. $24(=6\times 5-6)$ degrees of freedom are considered for the modes.

iv) Backbround Potential. The contribution Q_{BG} from the uniform background potential term to the total partition function becomes

$$Q_{\mathrm{BG}} = \exp(-U_{\mathrm{BG}}/kT) \tag{7}$$

As described in the previous section, each hard sphere molecule is assumed to be immersed in a uniform background potential U_{BG}, and no specific interactions are considered between hard spheres. U_{BG} for a molecule is considered to result from the dipole-dipole, dipole-induced dipole, and dispersion interactions between the molecule and all the other molecules as its medium. U_{BG} is expressed as inversely proportional to the volume of the liquid in the same way as Longuet-Higgins and Widon assumed,17) and is written into a simple form as $U_{\mathrm{BG}}=aN^2/V$, where a is a constant. This presupposes that, concerning electrostatic, induction, and dispersion interactions, water molecules behave similarly with each other, whether they are within pentamers or in unbonded state.

The dipolar interaction between permanent point dipoles is expressed as

$$U_{\mu\mu} = \frac{\mu^2}{\tilde{R}^3}[\sin\theta_{\mathrm{A}}\sin\theta_{\mathrm{B}}\cos(\phi_{\mathrm{A}}-\phi_{\mathrm{B}})-2\cos\theta_{\mathrm{A}}\cos\theta_{\mathrm{B}}], \tag{8}$$

where $\tilde{R}$ is the separation between a dipole A and a dipole B, θ_{A} and θ_{B} the polar angles for A and B (the line connecting A and B is regarded as a polar axis), and ϕ_{A} and ϕ_{B} the angles formed by the plane including the dipole and the polar axis with a reference plane. $U_{\mu\mu}$ is averaged for all configurations of two dipoles A and B with respects to angles θ_{A}, θ_{B}, ϕ_{A}, and ϕ_{B}, and the averaged value $<U_{\mu\mu}>$ becomes a function of $\tilde{R}$ only.

$$\langle U_{\mu\mu}\rangle = \int U_{\mu\mu}\exp(-U_{\mu\mu}/kT)\mathrm{d}\Omega \Big/ \int \exp(-U_{\mu\mu}/kT)\mathrm{d}\Omega, \tag{9}$$

where $\mathrm{d}\Omega=\sin\theta_{\mathrm{A}}\sin\theta_{\mathrm{B}}\,\mathrm{d}\,\theta_{\mathrm{A}}\,\mathrm{d}\,\theta_{\mathrm{B}}\,\mathrm{d}\,\phi_{\mathrm{A}}\,\mathrm{d}\,\phi_{\mathrm{B}}$.

The dipole-induced dipole interaction $U_{\mu\alpha}$ becomes

$$U_{\mu\alpha} = -\frac{2\mu^2\bar{\alpha}}{\tilde{R}^6}, \tag{10}$$

where $\bar{\alpha}$ is a average molecular polarizability, and the dispersion interaction between two molecules is

$$U_{\mathrm{disp.}} = -\frac{c}{\tilde{R}^6}, \tag{11}$$

The background potential U_{BG} is determined by integration of the sum of Eqs. 9, 10, and 11 multiplied by $g(\tilde{R})$. The $g(\tilde{R})$ is a molecular correlation function22) obtained from the observed radical distribution function by substracting intramolecular contributions.

Then, U_{BG} is written as

$$U_{\mathrm{BG}} = \frac{N^2}{2V}\int[\langle U_{\mu\mu}\rangle + U_{\mu\alpha} + U_{\mathrm{disp.}}]g(\tilde{R})4\pi\tilde{R}^2\mathrm{d}\tilde{R}. \tag{12}$$

A Monte Carlo method is used in the calculation of $<U_{\mu\mu}>$. The details in the procedure of calculation of U_{BG} are described in Appendix II.

Thermodynamic Variables

In the present model the following equilibrium at given T is established in water,

$$5(\mathrm{H_2O}) \rightleftharpoons (\mathrm{H_2O})_5, \tag{13}$$

where the total number of water molecules N remains constant,

$$N = N_1 + 5N_2. \tag{14}$$

The free energy F is obtained from the total partition function Z (Eq. 1).

$$F = -kT\ln Z, \tag{15}$$

where N_1, N_2, and molar volume V^0 (density ρ) at equilibrium are determined at given T and N from the condition of Z maximization and the equation of state derived from Z. Under the association equilibrium condition (Eqs. 13 and 14), the following relation holds.23)

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \left(\frac{\partial F}{\partial T}\right)_{V,N_1,N_2}, \quad \left(\frac{\partial F}{\partial V}\right)_{T,N} = \left(\frac{\partial F}{\partial V}\right)_{T,N_1,N_2}. \tag{16}$$

This relation simplifies the formulas for various thermodynamic variables which are derived from Eq. 15.

The equation of state is given as

$$pV = \frac{kT}{(1-\xi)^3}\Big[(N_1+N_2)(1+\xi+\xi^2) - \frac{\pi N_1N_2}{2V}(R_2-R_1)^2 \times\left\{R_1+R_2+\frac{\pi}{6}\left(\frac{N_1R_1{}^2+N_2R_2{}^2}{V}\right)R_1R_2\right\}\Big] + \frac{aN^2}{V}, \tag{17}$$

where the first term in the right of Eq. 17 is the same as that derived by Lebowitz20) for hard sphere mixtures, and the second term comes from the background potential term.

The entropy S is expressed24) as

$$S = S_{\mathrm{trans.}} + S_{\mathrm{rot.}} + S_{\mathrm{int.}}, \tag{18}$$

$$S_{\mathrm{trans.}} = k\ln Q_{\mathrm{trans.}} + \frac{3}{2}(N_1+N_2)k$$

$$S_{\mathrm{rot.}} = k\ln Q_{\mathrm{rot.}} + \frac{3}{2}(N_1+N_2)k$$

$$S_{\mathrm{int.}} = k\ln Q_{\mathrm{vib.}} + kT\frac{\partial\ln Q_{\mathrm{vib.}}}{\partial T} = S_{\mathrm{vib.}}.$$

The internal energy $U=F+TS$ is obtained from F and S as

$$U = 3(N_1+N_2)kT + 4N_2\varepsilon + kT^2\left(\frac{\partial\ln Q_{\mathrm{vib.}}}{\partial T}\right) + \frac{aN^2}{V}. \tag{19}$$

$$U_{\mathrm{trans.}} = U_{\mathrm{rot.}} = \frac{3}{2}(N_1+N_2)kT$$

$$U_{\mathrm{kin.}} = U_{\mathrm{trans.}} + U_{\mathrm{rot.}}$$

$$U_{\mathrm{vib.}} = kT^2\left(\frac{\partial\ln Q_{\mathrm{vib.}}}{\partial T}\right)$$

$$U_{\mathrm{HB}} = 4N_2\varepsilon$$

$$U_{\mathrm{BG}} = \frac{aN^2}{V}.$$

The heat capacity at constant pressure, C_p, is derived as follows,

$$\begin{aligned}C_p &= \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \\ &= \left(\frac{\partial U}{\partial T}\right)_{p,N_1,N_2} + \left(\frac{\partial U}{\partial N_2}\right)_{p,T}\left(\frac{\partial N_2}{\partial T}\right)_{p,N} + p\left(\frac{\partial V}{\partial T}\right)_p \\ &= 3(N_1+N_2)k + 2kT\left(\frac{\partial \ln Q_{\text{vib.}}}{\partial T}\right) + kT^2\left(\frac{\partial^2 \ln Q_{\text{vib.}}}{\partial T^2}\right) \\ &\quad + \left(\frac{\partial U_{\text{BG}}}{\partial T}\right)_p + \left[-12kT+4\varepsilon+kT^2\left(\frac{\partial \ln q_{\text{vib.}}}{\partial T}\right)\right] \\ &\quad \times \left(\frac{\partial N_2}{\partial T}\right)_{p,N} + p\left(\frac{\partial V}{\partial T}\right)_p, \qquad (20)\end{aligned}$$

where $(q_{\text{vib.}})=(Q_{\text{vib.}})^{1/N_2}$ is a molecular vibrational partition function for a pentamer.

Numerical Computations

i) Determination of Molecular Parameters. For the purpose of calculating thermodynamic quantities, the following values of molecular parameters are used, which have been determined from various sources. The magnitudes of hard sphere diameters and moments of inertia are tabulated in Table 1.

TABLE 1. MOLECULAR PARAMETERS

	Unbonded monomers	Pentamers
Diameter of hard spheres		
	$R_1=3.10$ Å	$R_2=5.50$ Å 5.55 Å
Polarizability $\bar{\alpha}$	1.44×10^{-24} cm^3	O–H···O distance 2.82 Å
Dipole moment μ	1.84 D	
Moments of inertia	(10^{-40} g cm^2)	
	$I_{1,\text{A}}=1.0220$ $I_{1,\text{B}}=1.9187$ $I_{1,\text{C}}=2.9376$	$I_{2,\text{A}}=I_{2,\text{B}}$ $=I_{2,\text{C}}=634.332$

The R_1 is considered to correspond to the van der Waals diameter for water, which is used in the molecular dynamics calculation by Stillinger and Rahman.[11] The magnitudes of moments of inertia for monomers are those determined by Benedict and others[25] and cited by Eisenberg and Kauzmann.[26] Those of moments of inertia for a pentamer are calculated for the configuration shown in Fig. 1, where the hydrogen-bonded distance in liquid water is taken to be 2.82 Å[14,27] and the mass of four tetrahedrally-bonded molecules is assumed to be concentrated at their centers of mass. Calculated values of the moments of inertia for three rectangular axes shown in Fig. 1, *i.e.*, $I_{2,\text{A}}$, $I_{2,\text{B}}$, and $I_{2,\text{C}}$ are all equal in their magnitudes. This equality of these three moments of inertia shows high degree of symmetry of that configuration, which supports the idea that the pentamer is treated as a sphere in this work. Some uncertainly attaches to the determination of R_2. Lentz, Hagler and Scheraga[13] used about 5.3—5.4 Å as the values of R_2 for a pentamer. They determined the value by measuring the displaced volume of "foil-wrapped space-filling models" (by immersion of the models into liquid). Their values are those for "clusters as compact as possible, consistent with a maximum value of hydrogen bonding", and supposed to be a little smaller than that for the pentamer shown in Fig. 1. Thus, we have carried out calculations for two values of R_2, *i.e.* 5.50 and 5.55 Å.

As to the energy of the formation of hydrogen-bonding, the value of 2.5 kcal per mole of hydrogen bonds is used, various experimental sources of which are given in Table 2. This value of ε is assumed to correspond to the energy for the process of hydrogen-bond breakage during which the separation of the hydrogen-bonded pair of molecules remains nearly unchanged. The values determined by various different experimental techniques are seen to agree with each other. Davis and Litovitz used the value of 2.55 kcal/mol in their calculation.[27]

TABLE 2. THE ENERGY OF HYDROGEN-BONDING ε (kcal/mol)

	ε	Authors	Bonding
R[a]	2.5_5	Walrafen[15]	O–H···O
IR[b]	2.5	Worley and Klotz[28]	O–H···O
R	2.4—2.5	Lindner[15]	O–D···O
IR	2.3	Senior and Verrall[29]	O–D···O
N[c]	≈2.5	Safford[15]	O–H···O
Average	2.5		

a) R: Raman. b) IR: infrared. c) N: neutron scattering.

Concerning the assignment of the frequency ν_j, there is still some uncertainty. We have assigned the values tabulated in Table 3 to each normal mode frequency $\nu_j (j=1—24)$, which are grouped as seen in the table. These values are taken from the sources[13,15,30,31] cited in Table 3 and are used as rounded-up values.

TABLE 3. NORMAL MODE FREQUENCIES ν_j FOR PENTAMERS

	ν_j (cm^{-1})	Number of modes[a]
ν_L[b]	700	3
ν_L'	550	4
ν_L''	450	4
ν_T	200	3
ν_T'	150	3
$\nu_\text{tor.}$	100	2
ν_b	60	3
ν_b'	40	2

a) Refs. 13, 15, 30, 31. b) Suffix L, L′, L″ are those for librational modes, T and T′ for translational ones, tor. for torsional one, and b and b′ for bending modes.

ii) Determination of Mole Fraction x for Hydrogen-Bonded Molecules and the Density of Liquid Water. In advance of calculating various thermodynamic quantities we must determine the equilibrium distribution for N_1 and N_2 at given T and V for a given total number N of molecules (Eq. 14). This can be carried out using the condition of the maximization of Z with respect to N_2, where the number of independent variables is only one under the condition of Eq. 14 for a given value of N and we take N_2 for the independent variable for convenience.

Thus,

$$\left(\frac{\partial F}{\partial N_2}\right)_{V,T} = \left(\frac{\partial F}{\partial N_2}\right)_{N_1,V,T} + \left(\frac{\partial F}{\partial N_1}\right)_{N_2,V,T}\left(\frac{\partial N_1}{\partial N_2}\right)_{V,T} = 0.$$

From Eq. 14 for a constant value of N,

$$\left(\frac{\partial N_1}{\partial N_2}\right)_{V,T} = -5.$$

Inserting this into the equation described above, we obtain

$$\left(\frac{\partial F}{\partial N_2}\right)_{N_1,V,T} = 5\left(\frac{\partial F}{\partial N_1}\right)_{N_2,V,T} \tag{21}$$

or

$$\mu_2 = 5\mu_1, \tag{21'}$$

where μ_1 and μ_2 is the chemical potential for each species, respectively. Eq. 21 (*i.e.* Eq. 21′) is the condition of thermodynamic equilibrium between pentamers and unbonded monomers.

In order to determine the density for the liquid theoretically, the equation of state, which is expressed as Eq. 17, is used, where the left hand side (pV) is safely regarded as zero under ordinary pressures (the so-called "vanishing external pressure condition"[19,32]).

The two procedures for the determination of the mole fraction and the density (*i.e.* molar volume) must be carried out simultaneously, because the two kinds of values to be determined are interrelated to each other in the two equations.

We use $x=5N_2/N$ as an independent variable instead of N_2, which is the mole fraction for hydrogen-bonded molecules in water. The following two equations are used in the determination of x and V for practical use. Eq. 21 becomes

$$\begin{aligned}
&-\left[\ln\left\{\left(\frac{2\pi m_2kT}{h^2}\right)^{3/2}\frac{V}{N}\frac{5}{x}\right\} + \ln(1-\xi)\right.\\
&-\frac{1}{(1-\xi)}\frac{\pi}{6}\frac{N}{V}\left(1-\frac{4}{5}x\right)R_2^3 - \frac{3}{(1-\xi)}(R_2^2Y+R_2X)\\
&\left.-\frac{3}{(1-\xi)^2}\left(R_2^3XY+\frac{3}{2}R_2^2X^2\right) - \frac{3R_2^3X^3}{(1-\xi)^3}\right]\\
&-\left[\ln\left\{\frac{\pi^{1/2}}{\sigma_2}\left(\frac{8\pi^2kT}{h^2}\right)^{3/2}(I_{2,A}I_{2,B}I_{2,C})^{1/2}\gamma\right\}\right.\\
&\left.+\ln\left\{\prod_{j=1}^{24}\frac{\exp(-h\nu_j/2kT)}{1-\exp(-h\nu_j/kT)}\right\} - \frac{4\varepsilon}{kT}\right]\\
&+5\left[\ln\left\{\left(\frac{2\pi m_1kT}{h^2}\right)^{3/2}\frac{V}{N}\frac{1}{(1-x)}\right\} + \ln(1-\xi)\right.\\
&-\frac{1}{(1-\xi)}\frac{\pi}{6}\frac{N}{V}\left(1-\frac{4}{5}x\right)R_1^3 - \frac{3}{(1-\xi)}(R_1^2Y+R_1X)\\
&\left.-\frac{3}{(1-\xi)^2}\left(R_1^3XY+\frac{3}{2}R_1^2X^2\right) - \frac{3R_1^3X^3}{(1-\xi)^3}\right]\\
&+5\left[\ln\left\{\frac{\pi^{1/2}}{\sigma_1}\left(\frac{8\pi^2kT}{h^2}\right)^{3/2}(I_{1,A}I_{1,B}I_{1,C})^{1/2}\right\}\right] = 0,
\end{aligned} \tag{22}$$

$$\xi = \frac{\pi}{6}\frac{N}{V}\left[R_1^3(1-x)+R_2^3\frac{x}{5}\right]$$

$$X = \frac{\pi}{6}\frac{N}{V}\left[R_1^2(1-x)+R_2^2\frac{x}{5}\right]$$

$$Y = \frac{\pi}{6}\frac{N}{V}\left[R_1(1-x)+R_2\frac{x}{5}\right],$$

and, from Eq. 17 with the vanishing external pressure condition, we obtain

$$\frac{kT}{(1-\xi)^3}\left[N\left(1-\frac{4}{5}x\right)(1-\xi)^2 + \frac{18}{\pi}V\{XY(1-\xi)+X^3\}\right] + U_{BG} = 0 \tag{23}$$

after some calculations (see Appendix I). For given values of various molecular parameters, the two simultanious equations are solved numerically to determine the values of x and V (*i.e.*, the density ρ).

iii) Numerical Calculations of Thermodynamic Variables. The computations of thermodynamic variables, F, U, S, C_p are carried out for each temperature, using the values of U_{AB} given in Appendix II as well as those of x and V determined according to the procedures in the previous section. The values of F, U, S, C_p are tabulated in Table 4 for the case of R_2=5.50 Å, including observed values. The calculated values of x and ρ also are given in Table 5.

We have taken the state of ice at 0 K in its ground intermolecular and intramolecular vibrational levels as the thermodynamic standard states. The values of U_{BG} have been calculated employing the state of infinitely dilute vapor at 0 K as the zero of energy. Then, we have added the value of 11.3−1.4=9.9 kcal/mol to those of U and F calculated from Eqs. 15 and 19, where

TABLE 4. CALCULATED AND EXPERIMENTAL THERMODYNAMIC PROPERTIES OF WATER

Temp (°C)	F (kcal/mol)		U (kcal/mol)		S (cal/deg mol)		C_p (cal/deg mol)	
	Calcd	Obsd[a]	Calcd	Obsd[a]	Calcd	Obsd[a]	Calcd	Obsd[b]
0	−1.07	−1.44	3.30	2.71	16.0_5	15.2	29.6	18.2
10	-1.16_5	−1.59	3.60_5	2.89	16.8_5	15.8	29.1	18.1
20	−1.34	−1.75	3.89_5	3.07	17.9	16.4	28.4	18.0
30	−1.59	−1.92	4.17_5	3.25	19.0	17.1	26.9	18.0
40	-1.95_5	−2.09	4.42	3.43	20.3	17.6	25.2	18.0
50	−2.35	−2.27	4.68	3.61	21.7	18.2	25.3	18.0
60	-2.65_5	−2.46	4.95_5	3.79	22.8	18.8	26.2	18.0
70	-2.89_5	−2.65	5.23	3.97	23.7	19.3	27.3	18.0
80	-3.09_5	−2.84	5.50	4.15	24.3_5	19.8	27.8	18.1
90	−3.28	−3.04	5.77_5	4.33	24.9_5	20.3	28.0	18.1
100	−3.47	−3.25	6.03_5	4.52	25.4_5	20.8	28.1	18.2

a) Ref. 13 and N.E. Dersey "Properties of Ordinary Water Substances," ACS Monograph, No. 81, Reinhold, New York (1940). b) G.S. Kell, *J. Chem. Eng. Data,* **12**, 66 (1967).

TABLE 5. MOLE FRACTION OF HYDROGEN-BONDED MOLECULES x AND DENSITY ρ

Temp (°C)	x	ρ (g/cm^3) Calcd	ρ (g/cm^3) Obsd
0	0.790	1.147	0.9998
10	0.729	1.121	0.9997
20	0.645	1.089	0.9982
30	0.529	1.049	0.9957
40	0.362	0.996	0.9922
50	0.200	0.943	0.9880
60	0.091	0.901	0.9832
70	0.040	0.870	0.9778
80	0.019	0.847	0.9718
90	0.009	0.826	0.9653
100	0.005	0.808	0.9584

11.3 kcal/mol is the value of sublimation energy from ice at 0 K[33] and 1.4 kcal/mol is the shift in intramolecular zero-point energy[34] for the process of sublimation.

Results and Discussion

i) Temperature Dependence of x *and* ρ. Values of x calculated are plotted against temperature in Fig. 2, where the two calculations for $R_2=5.50$ Å (Table 5) and for $R_2=5.55$ Å are given. The curves given in Fig. 2 shows that magnitude of x, which is regarded as a measure of the "structure" in liquid water, is large at lower temperatures (about 80% for $R_2=5.50$ Å and about 60% for $R_2=5.55$ Å) and decreases rapidly with increase of temperature. The inflection point where $\partial^2x/\partial T^2=0$ and the decreasing rate is maximum is about 40 °C for $R_2=5.50$ Å. This supports the idea that the structure of water varies a great deal at about 40—50 °C. It is observed experimentally that compressibility becomes minimum near about the temperatures and also that the third peak of the radial distribution curve nearly disappeares above the temperatures.[14,35] The rapid decrease of x at the temperatures is supposed to be associated with those observed facts. The calculation for $R_2=5.50$ Å is expected to give a more adequate result than that for $R_2=5.55$ Å.

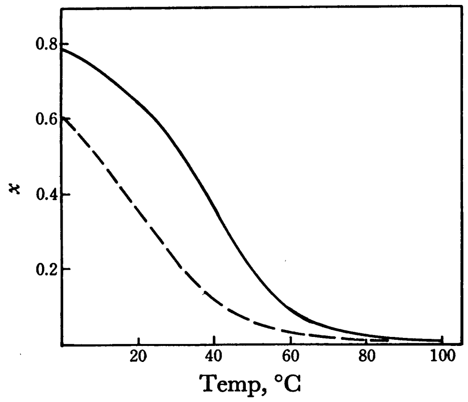

Fig. 2. The temperature dependence of mole fraction of hydrogen-bonded molecules.
——: $R_2=5.50$ Å,
------: $R_2=5.55$ Å.

The mole fraction of unbroken hydrogen bonds, x_{HB}, which is calculated from the value of x, is given in Table 6, and is compared with the values of Lentz, Hagler and Scheraga[13] (LHS) and those of Weres and Rice[12] (WR). Our values decrease more rapidly and are found to be smaller than those of LHS and WR. The values of WR are seen to be constant throughout the range of temperature from 0 to 100 °C, and those of LHS also are nearly constant. This is unreasonable, considering from the variation of various properties of water with temperature, *i.e.*, the disappearance of some features in the radial distribution curve at higher temperatures, *etc.* The temperature dependence of x_{HB} found in our work may be reasonably accepted as showing the behavior of water, though the magnitudes are too small at higher temperatures.

TABLE 6. MOLE FRACTION OF UNBROKEN HYDROGEN BONDS x_{HB}

Temp (°C)	This work ($R_2=5.50$ Å)	LHS	WR
0	0.32	0.47	0.68[a]
20	0.26	0.46	
40	0.14_5	0.45	
100	0.00_2	0.43	

a) Nearly constant from 0 to 100 °C.

Values of ρ calculated are plotted against temperature in Fig. 3 in comparison with observed values. The temperature dependence in the calculated ρ *vs.* T curve is seen to be too large compared with that observed. The curve becomes fairly flat at about 0—10 °C range ($R_2=5.50$ Å), though the temperature of maximum density (TMD) is not observed.

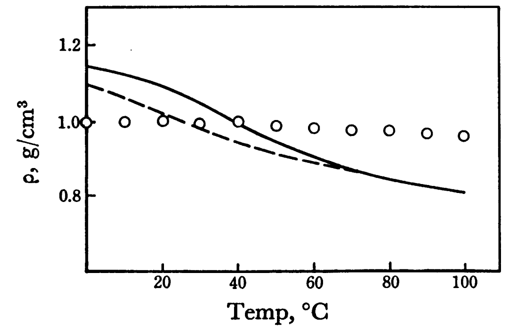

Fig. 3. The temperature dependence of density ρ.
——: $R_2=5.50$ Å,
------: $R_2=5.55$ Å,
○: observed values.

In the recent study by Lentz, Hagler, and Scheraga[13] they did not calculate the density and used the observed values as given ones in their calculation. Weres and Rice gave a calculated ρ *vs.* T curve (in Fig. 6 in their paper[12]), but their values of ρ is determined only semi-empirically as a direct result of their assumption that "the dimensions of the basic cell vary linearly with temperature."

In our calculation the density is determined theoretically without any additive assumptions by solving directly a simultaneous equation (Eqs. 22 and 23). The agreement of the calculated values of ρ with observed ones is fairly good on the whole, which proves the essential usefulness of the procedures for the determination of ρ in this work.

Fleming and Gibbs[7] have presented a lattice gas theory of water and carried out a theoretical determination of ρ. Their values are found to be too large by a factor of 1.4. They also have not succeeded in giving TMD in the range of temperatures from 0 to 100 °C, though a possibility of the presence of TMD below 0 °C has been stated. To give TMD in the calculated ρ *vs.* T curve is the problem of further studies.

ii) Temperature Dependence of Thermodynamic Variables. The values of F, U, and S are plotted against temperature in Figs. 4, 5, and 6, including the values calculated for the case of $R_2=5.55$ Å and those observed for comparison. The calculated F *vs.* T curve is seen to be in good agreement with the observed curve. Concerning the S *vs.* T given in Fig. 6, the deviation from the observed curve is small at lower temperatures, and it ascends more rapidly with temperature, being above the observed curve through all the range of temperatures from 0 to 100 °C. The behavior is similar to the U *vs.* T curve as given in Fig. 5. As clearly seen in Figs. 2—5, the calculation for $R_2=5.50$ Å gives better results than that for $R_2=5.55$ Å.

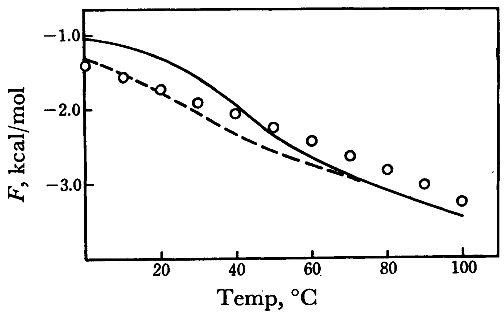

Fig. 4. The temperature dependence of free energy F.
——: $R_2=5.50$ Å,
------: $R_2=5.55$ Å,
○: observed values.

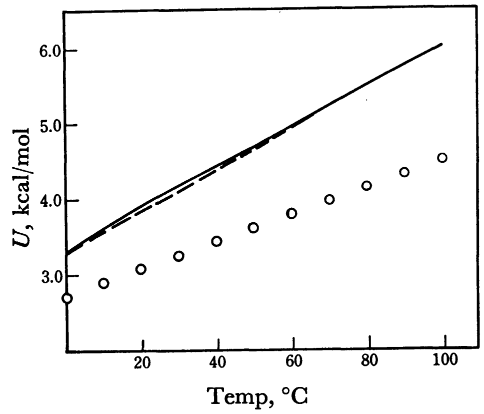

Fig. 5. The temperature dependence of internal energy U.
——: $R_2=5.50$ Å,
------: $R_2=5.55$ Å,
○: observed values.

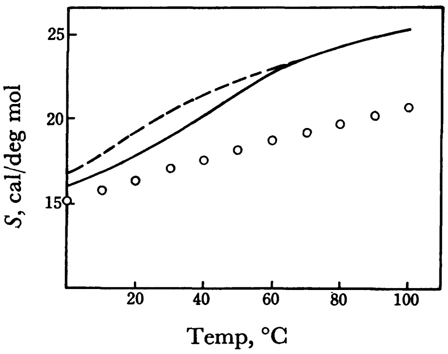

Fig. 6. The temperature depencence of entropy S.
——: $R_2=5.50$ Å,
------: $R_2=5.55$ Å,
○: observed values.

As expressed in Eqs. 18 and 19, the thermodynamic quantities calculated are regarded as consisting of several terms which are attributed to various kinds of degrees of freedom. Those are tabulated in Tables 7 and 8. It is very interesting to investigate the variation of the contribution from each degree of freedom with temperature, in order to compare the features of various theories.

Thus, our results (Tables 7 and 8) are compared with those of LHS[13] (Table 9) and WR[12] (Table 10) in

TABLE 7. VALUES OF VARIOUS TERMS IN Eq. 18 (cal/deg mol)

Temp (°C)	$S_{\text{trans.}}$	$S_{\text{rot.}}$	$S_{\text{int.}}$ a)	S_{total}
0	1.9	6.5	7.6_5	16.0_5
10	2.7_5	6.8_5	7.2_5	16.8_5
20	4.0_5	7.3	6.5_5	17.9
30	5.6	7.9	5.5	19.0
40	7.7	8.7_5	3.8_5	20.3
50	9.8_5	9.6_5	2.2	21.7
60	11.5	10.3	1.0	22.8
70	12.6	10.6_5	0.4_5	23.7
80	13.3	10.8_5	0.2	24.3_5
90	13.8_5	11.0	0.1	24.9_5
100	14.3_5	11.0_5	0.0_5	25.4_5

a) In our calculation $S_{\text{int.}}$ is identical with $S_{\text{vib.}}$.

TABLE 8. VALUES OF VARIOUS TERMS IN Eq. 19 (kcal/mol)

Temp (°C)	$U_{\text{kin.}}$	$U_{\text{vib.}}$	U_{HB}	U_{BG}	U_{total}
0	0.60	2.70	−1.58	−8.32	3.30
10	0.70_5	2.54_5	-1.45_5	−8.09	3.60_5
20	0.84_5	2.30	−1.29	−7.86	3.89_5
30	1.04_5	1.92_5	-1.05_5	−7.64	4.17_5
40	1.32_5	1.35	-0.72_5	−7.41	4.42
50	1.62	0.76	−0.40	−7.20	4.68
60	1.84	0.35_5	−0.18	−6.96	4.95_5
70	1.98	0.16	−0.08	−6.73	5.23
80	2.07_5	0.07_5	−0.04	−6.51	5.50
90	2.15	0.03_5	−0.02	−6.29	5.77_5
100	2.21_5	0.02	−0.01	−6.09	6.03_5

a) 9.9 kcal/mol has been added to the sum in order to obtain U_{total}.

Table 9. Thermodynamic properties calculated by Lentz, Hagler, and Scheraga[13)]

	0 °C	100 °C
U (kcal/mol)		
$U_{\rm kin.}$[a)]	0.542	0.868
$U_{\rm vib.}$	3.331	3.866
$U_{\rm HB}$	2.541	3.096
$U_{\rm total}$[b)]	2.914	4.331
S (cal/deg mol)		
$S_{\rm trans.}$	4.16	5.54
$S_{\rm rot.}$	2.50	3.14
$S_{\rm vib.}$	8.73	10.81
$S_{\rm H}$	0.63	0.53
$S_{\rm total}$	16.02	20.02

a) $U_{\rm kin.}=U_{\rm trans.}+U_{\rm rot.}$. b) The intermolecular zero point energy, 3.500 kcal/mol, has been substracted from the sum to obtain $U_{\rm total}$.

Table 10. Thermodynamic properties calculated by Weres and Rice[12)]

	0 °C	100 °C
$H=U$ (kcal/mol)		
Lattice	−8.296	−8.088
Translational vib.	1.729	2.290
Librational	2.517	2.858
Nonbonded neighbor	−1.325	−1.271
Long range	−1.190	−1.166
Intramolecular zero point	−0.900	−0.694
Total[a)]	3.835	4.509
S (cal/deg mol)		
Configurational	4.48	4.48
Orientational	1.70	1.69
Translational vib.	7.12	9.28
Librational	2.00	3.44
Nonbonded neighbor	−1.17	−0.95
Vibrational	0.26	0.26
Total	14.39	18.20

a) The sublimation energy at 0 K, 11.3 kcal/mol, has been added to the sum to obtain $U_{\rm total}$.

details. It is noticed that as to the entropy, each term in our theory corresponds to that in LHS theory when $S_{\rm int.}$ of ours is regarded as equivalent to $(S_{\rm vib.}+S_{\rm H})$ in LHS, and also noticed that it is not the case in the comparison with WR theory.

It is easily seen that the temperature dependence of entropy in our results is greater than that in WR and LHS theories. In the case of WR the calculated values of $S_{\rm total}$ are smaller than observed, being in sharp contrast to the authors' values. At lower temperatures the largest contribution to $S_{\rm total}$ comes from the vibrational motion in all three theories, but the behaviors are different at higher temperatures. In the authors calculation, $S_{\rm trans.}$ increases fairly rapidly and amounts to about a half of the total entropy at about 50—60 °C, while $S_{\rm trans.}$ in LHS theory increases only slightly with increasing temperature. As to the internal energy, the similar behavior is observed in the comparison between $U_{\rm kin.}$ in our calculation and that in LHS.

We can see another noticeable feature in the comparison of $S_{\rm vib.}$ and $U_{\rm vib.}$, the contributions from the vibrational degrees of freedom. They both decrease with increasing temperature in our calculation, while in the calculations by LHS as well as WR they increase on the contrary.

From the two features described above, it is tentatively said that the theory of LHS as well as that of WR is possessed of too solid-like character so far as the temperature dependence of thermodynamic variables is concerned.

In the calculation of WR, the configurational entropy which is attributed to the number of ways for the arrangement of molecules within a basic unit cell is kept constant throughout the range of temperatures from 0 to 100 °C. This is unreasonable, because it shows that the local structure in liquid water remains thoroughly unchanged with the variation of temperatures.

In our calculation the magnitudes of $U_{\rm vib.}$, $S_{\rm int.}=S_{\rm vib.}$, $U_{\rm HB.}$, and $S_{\rm trans.}$ vary most rapidly at 40—50 °C with increasing temperature. This is ascribed to the rapid decrease of the mole fraction of water molecules forming pentamers, as seen in Fig. 2, at the temperatures.

iii) Heat Capacity. In using Eq. 20 for the calculation of C_p, the term $p(\partial V/\partial T)_p=pV\alpha$ has been safely ignored in comparison with the term $(\partial U/\partial T)_p$, where $pV<1$ cal/mol and the thermal expansion coefficient $\alpha\lesssim10^{-3}$ deg.$^{-1}$. Among the remaining terms in Eq. 20, the temperature derivatives of $x=5N_2/N$ and $U_{\rm BG}$ are determined graphically using the curves given in Figs. 2 and AII-2, respectively, and the terms including $Q_{\rm vib.}$ are calculated using Eq. 6.

Our values (the eighth column in Table 4) becomes 27.3_5 cal/deg mol in the average throughout the range of temperatures, 0—100 °C, which is about 9 cal/deg mol larger than the average of $C_{p.{\rm obsd}}$. This is in sharp contrast to the feature found in the calculations of LHS[13)] and WR,[12)] where $C_{p.{\rm calcd}}$ is smaller than $C_{p.{\rm obsd}}$.

It is noted that a shallow minimum is observed at about 40 °C in the $C_{p.{\rm calcd}}$ *vs.* T relation in this work. This corresponds to the presence of a minimum at about 35 °C in the $C_{p.{\rm obsd}}$ *vs.* T relation. In the calculation of LHS and WR, $C_{p.{\rm calcd}}$ *vs.* T curves are monotonously increasing throughout the range of temperatures, 0—100 °C. The contribution to C_p from each degree of freedom can be determined from the corresponding values of internal energy (Eq. 19) given in Table 8. Each contribution averaged in the range 0—100 °C is shown in Table 11.

Table 11. Average contributions to the total heat capacity C_p (cal/deg mol)

Kinetic	16.1_5
Vibrational	−26.8
Hydrogen-Bonding	15.7
Background Potential	22.3
$C_{p.{\rm total}}$	27.3_5

iv) Equivalent Free Volume Fraction f. In the formulation of our theory we have used Eq. 2 as the translational partition function. The partition function has a form which is similar in its appearance to the formula used in cell theories of fluid mixtures. Then, we have defined f (Eq. 3) as an equivalent free volume fraction, which is a generalization of the authors' proposition[19] with respect to a pure liquid into multi-component fluids. In our theory no lattice which is necessary for cell theories is assumed.

The translational partition function for hard sphere mixtures is shown as a comparatively simple explicit expression similar to usual free volume theories. This is expected to give a good promise for further use.

We have calculated the values of f according to Eq. 3 and the values are compared with those calculated by Weissmann and Blum[8] for water using the Monte Carlo method. The values are given in Table 12. Our values are found to be larger than those of Weissmann and Blum. However, in their calculations, the contribution from the rotational degree of freedom is included, and the magnitude of f is expected to be of nearly the same order compared with ours if that contribution to the phase integral is substracted as stated in their paper.

TABLE 12. FREE VOLUME FRACTION f AND PACKING FRACTION ξ

Temp (°C)	f		ξ	
	This work	Weissmann-Blum[8]	R_2=5.50 Å	5.55 Å
4	5.80×10^{-5}	0.60×10^{-7}	0.64_5	0.61
50	7.14×10^{-3}	0.34×10^{-6}	0.50	0.48
100	2.95×10^{-2}	1.19×10^{-6}	0.42	0.42

As for the magnitudes of the packing fraction ξ given together in Table 12, the large value of ξ at 4 °C is supposed to result from the too large value of ρ_{calcd} obtained at the temperature.[19,36]

Concluding Remarks

The purpose of this paper has been to formulate a statistical thermodynamic theory for liquid water without using adjustable parameters to obtain the best fit with observed data as ordinarily carried out. We have used a model consisting of tetrahedrally hydrogen-bonded pentamers and unbonded monomers which are immersed in a uniform background potential. The feature in the theory and its results are outlined as follows: (a) the translational partition function for the model has been derived from the analytical solution of the Percus-Yevick equation for hard sphere mixtures, (b) U_{BG} has been calculated directly as the sum of dipole-dipole, dipole-induced dipole, and dispersion interactions, (c) the mole fraction x of hydrogen-bonded species and the density ρ have been determined by solving a simultaneous equation numerically, and calculated values of ρ are found to be of the right order in their magnitudes, compared with observed values, though the TMD is not observed, (d) the magnitude of x is found to be large (about 80%) at 0 °C which shows the predominance of the "structure" in liquid water at lower temperatures, (e) calculated thermodynamic properties are found to vary rapidly at 40—50 °C with increase in temperature, which is attributed to the rapid decrease of x at the range of temperatures, (f) the magnitude of x becomes very small above about 60 °C (Table 5).

The success in the present theory, though it is qualitative and limited, has put a support to the so-called small cluster model, and the better fit of results with observed data is expected through making some improvements of the model used. The first of those is an introduction of one more species, *i.e.* "hydrogen-bonded ring hexamer" as a structure unit. In that model, water is assumed to be a mixture of unbonded monomers, tetrahedrally-coordinated pentamers, and ring hexamers immersed in a uniform background potential. This three-component model is expected to improve the results.

Appendix I. An Analytical Expression of the Partition Function for the Mixture of Hard Spheres

For a system consisting of m components with number densities ρ_i, $i=1,\cdots\cdots m$,

$$F = G - pV = \sum_{i=1}^{m} N_i\mu_i - pV, \tag{AI-1}$$

where μ_i is the chemical potential of the i-th species and $N_i=\rho_i V$. The exact analytical solution of the generalized Percus-Yevick equation for the mixture of hard spheres was given by Lebowitz, and the μ_i becomes, following Lebowitz and Rowlinson,[20]

$$\beta\mu_i = \ln\left[\frac{\rho_i h^3}{(2\pi m_i kT)^{3/2}}\right] - \ln(1-\xi) + \frac{\pi}{6}\beta p R_i^3 + \frac{3}{(1-\xi)}(R_i^2 Y + R_i X) + \frac{9}{2}\frac{R_i^2 X^2}{(1-\xi)^2}, \tag{AI-2}$$

where R_i is the diameter of a particle of the i-th species and $\beta=1/kT$, and

$$\xi = \sum_{i=1}^{m}\frac{\pi}{6}\rho_i R_i^3,\quad X = \sum_{i=1}^{m}\frac{\pi}{6}\rho_i R_i^2,\quad Y = \sum_{i=1}^{m}\frac{\pi}{6}\rho_i R_i.$$

Substitution of Eq.AI-2 into Eq.AI-1 gives

$$F = \beta^{-1}\sum_{i=1}^{m}\ln\left[\frac{\rho_i h^3}{(2\pi m_i kT)^{3/2}}\right]^{N_i} - \beta^{-1}\ln(1-\xi)^{\sum_i N_i} + \frac{9}{\pi}\beta^{-1}V\frac{1}{(1-\xi)^2}\left[-\frac{\pi}{9}\beta p(1-\xi)^3 + 4XY - 4XY\xi + 3X^3\right]. \tag{AI-3}$$

The equation of sate (Eq. 2.8 in Ref. 20) which was given associated with the generalized compressibility relation is

$$\beta p = \frac{1}{(1-\xi)^3}\left[\left(\sum_{i=1}^{m}\rho_i\right)(1+\xi+\xi^2) - \frac{\pi}{2}\sum_{i<j}\rho_i\rho_j(R_i-R_j)^2(R_i+R_j+R_iR_jX)\right]. \tag{AI-4}$$

Using the relations,

$$\frac{\pi}{2}\sum_{i<j}\rho_i\rho_j(R_i-R_j)^2(R_i+R_j) = 3\xi\left(\sum_i\rho_i\right) - \frac{18}{\pi}XY$$

and

$$\frac{\pi}{2}\sum_{i<j}\rho_i\rho_j(R_i-R_j)^2R_iR_j = \frac{18}{\pi}(Y\xi-X^2),$$

we obtain from Eq. AI-4

$$\beta p = \frac{1}{(1-\xi)^3}\left[\left(\sum_i\rho_i\right)(1-\xi)^2 + \frac{18}{\pi}(XY - XY\xi + X^3)\right]. \tag{AI-5}$$

Inserting Eq. AI-5 into Eq. AI-3, we obtain

$$F = \beta^{-1}\sum_i \ln\left[\frac{\rho_i h^3}{(2\pi m_i kT)^{3/2}}\right]^{N_i} - \beta^{-1}\ln(1-\xi)^{\sum_i N_i}$$
$$-\beta^{-1}\sum_i N_i + \frac{9}{\pi}\beta^{-1}V\frac{1}{(1-\xi)^2}(2XY-2XY\xi+X^3). \tag{AI-6}$$

From Eq. AI-6 we give the following partition function Z which is expressed as a form with the equivalent free volume fraction f for an m-component mixture of hard spheres,

$$Z = \exp(-\beta F) = \prod_{i=1}^{m}\left[\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} ev_i f\right]^{N_i}$$
$$= \frac{(\sum_i N_i)!}{\prod_i N_i!}\prod_{i=1}^{m}\left[\left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} evf\right]^{N_i} \tag{AI-7}$$

where f has the form

$$f = (1-\xi)\exp\left[-\frac{9}{\pi}\frac{v}{(1-\xi)^2}(2XY-2XY\xi+X^3)\right], \tag{AI-8}$$

and $v_i = V/N_i, v = V/\sum_i N_i$.

For a one-component system, Eqs. AI-7 and AI-8 lead us to the same analytical expression as given in the previous paper by the two of the authors,[19)] in which the concept of an equivalent free volume was proposed on the basis of Wertheim's solution for the Percus-Yevick equation of pure liquid.

Appendix II. The Calculation of the Background Potential

Two steps of numerical integrations are required in carrying out the calculation of the background potential U_{BG}. The first step is the integration in obtaining $\langle U_{\mu\mu}\rangle$ (Eq. 9), as follows,

$$\langle U_{\mu\mu}\rangle = \int_0^\pi\int_0^\pi\int_0^{2\pi}\int_0^{2\pi} d\theta_A d\theta_B d\phi_A d\phi_B \exp\left[-\frac{U_{\mu\mu}(\theta_A,\theta_B,\phi_A,\phi_B)}{kT}\right]$$
$$\times U_{\mu\mu}\sin\theta_A\sin\theta_B \Big/ \int_0^\pi\int_0^\pi\int_0^{2\pi}\int_0^{2\pi} d\theta_A d\theta_B d\phi_A d\phi_B$$
$$\times\exp\left[-\frac{U_{\mu\mu}(\theta_A,\theta_B,\phi_A,\phi_B)}{kT}\right]\sin\theta_A\sin\theta_B, \tag{AII-1}$$

where

$$U_{\mu\mu} = \frac{\mu^2}{\tilde{R}^3}[\sin\theta_A\sin\theta_B\cos(\phi_A-\phi_B)-2\cos\theta_A\cos\theta_B].$$

The numerical evaluation of multidimentional integral such as Eq. AII-1 is usually carried out by means of the Monte Carlo method which gives as an estimate for the integral the sum,

$$\langle U_{\mu\mu}\rangle = \frac{1}{M}\sum_{i=1}^{M}\exp\left[-\frac{U_{\mu\mu}(\theta_{A_i},\phi_{A_i},\theta_{B_i},\phi_{B_i})}{kT}\right]U_{\mu\mu}\sin\theta_{A_i}\sin\theta_{B_i}\Big/$$
$$\frac{1}{M}\sum_{i=1}^{M}\exp\left[-\frac{U_{\mu\mu}(\theta_{A_i},\phi_{A_i},\theta_{B_i},\phi_{B_i})}{kT}\right]\sin\theta_{A_i}\sin\theta_{B_i}, \tag{AII-2}$$

where M is the number of the points X_i $(\theta_{A_i}, \phi_{A_i}, \theta_{B_i}, \phi_{B_i})$, and θ_{A_i}, ϕ_{A_i}, θ_{B_i}, and ϕ_{B_i} are chosen at random in the range of integration.

The error of such an estimate is of the order of $M^{-1/2}$ as a standard deviation. In carrying out the evaluation we have used the Monte Carlo method using the technique devised by Haselgrove.[37)] It is shown that the error in the method is convergent asymptotically to the order of $O(M^{-1})$ and $O(M^{-2})$ under certain conditions, and also shown that the method is superior to the usual Monte Carlo method. The magnitude of M has been taken as 15000, when the convergence in the integration is very well.

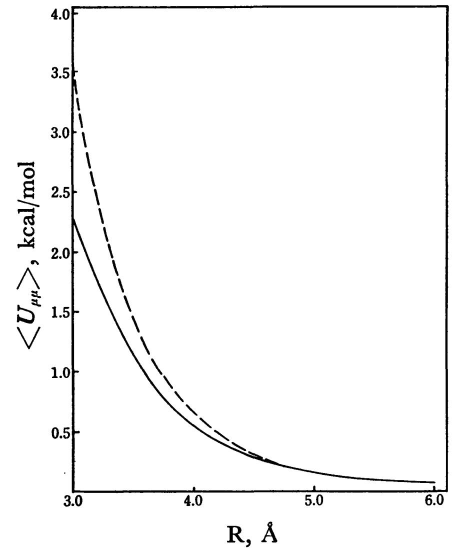

Fig. AII-1. $\langle U_{\mu\mu}\rangle$ *vs.* R curves at 25 °C.
——: Exact, ------: approximated (Eq. AII-3).

The calculated values of $\langle U_{\mu\mu}\rangle$ for 25 °C are plotted against the separation $\tilde{R}$ in Fig. AII-1, including the values calculated from the following approximate formula which should be used under the condition that kT is much greater than the difference of the maximum and minimum value of $U_{\mu\mu}$.

$$\langle U_{\mu\mu}\rangle = -\frac{2}{3kT}\frac{\mu^4}{\tilde{R}^6} \tag{AII-3}$$

The curve for this approximate formula is observed to deviate from the exact curve discriminately within the range of $\tilde{R}$ smaller than 4—5 Å.

The second step is the numerical evaluation of the integral in Eq. 12, where the magnitudes of $\bar{\alpha}$ and μ are given in Table 1 and the value of c is taken to be 60×10^{-60} erg cm^6.[38)]

Then, the background potential is

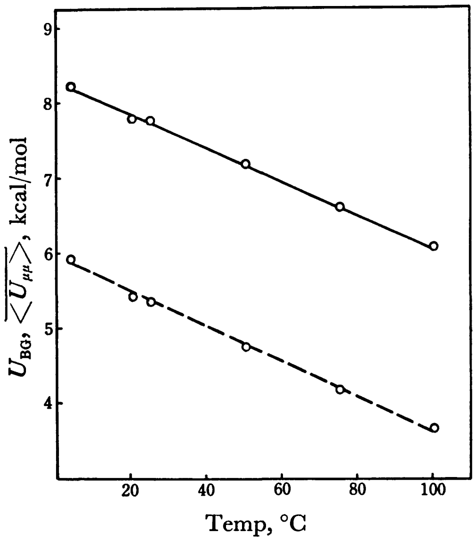

Fig. AII-2. The temperature dependence of U_{BG} and $\overline{\langle U_{\mu\mu}\rangle}$.
——: U_{BG}, ------: $\overline{\langle U_{\mu\mu}\rangle}$.

$$U_{\mathrm{BG}} = \frac{N^2}{2V}\int_{\tilde{R}_0}^{\infty}[\langle U_{\mu\mu}\rangle + U_{\mu\alpha} + U_{\mathrm{disp.}}]g(\tilde{R})4\pi\tilde{R}^2\mathrm{d}\tilde{R}$$
$$= \overline{\langle U_{\mu\mu}\rangle} + \bar{U}_{\mu\alpha} + \bar{U}_{\mathrm{disp.}}, \qquad \text{(AII-4)}$$

where the value of $\tilde{R}_0$ is taken to be 3.1 Å.[3,11] We have estimated the integral by means of the Simpson rule. The values of U_{BG} and $\overline{\langle U_{\mu\mu}\rangle}$ thus calculated are given in Fig. AII-2. Throughout the range of temperatures from 0°C to 100 °C, the values of $\bar{U}_{\mu\alpha}$ and $\bar{U}_{\mathrm{disp.}}$ are found to remain constant within the range of 0.34 ± 0.01 and 2.05 ± 0.05 kcal/mol, respectively.

References

1) R. A. Horne, Ed., "Water and Aqueous Solution," Wiley-Interscience, New York (1972).

2) F. H. Stillinger, *Adv. Chem. Phys.*, **31**, 1 (1975).

3) K. Arakawa, *Kagaku No Ryoiki Zokan*, No. **106**, 15 (1974); *Kagaku Sosetsu*, No. **11**, 35 (1976).

4) F. Franks, Ed., "Water" Vol. 1—5, Plenum, New York (1972—1975).

5) H. S. Frank, "Water" (Ed., F. Franks) Vol. 1, Plenum, New York (1972) Chapt. 14.

6) G. M. Bell, *J. Phys.*, **C**, **5**, 889 (1972).

7) P. D. Fleming and J. H. Gibbs, *J. Statist. Phys.*, **10**, 157, 351 (1974).

8) M. Weissmann and L. Blum, *Trans. Faraday Soc.*, **64**, 2605 (1968).

9) K. Arakawa and K. Sasaki, *Bull. Chem. Soc. Jpn.*, **40**, 3048 (1970).

10) A. Ben-Naim, *J. Chem. Phys.*, **52**, 5531 (1970); **57**, 3605 (1972); "Water and Aqueous Solutions," Plenum, New York (1974).

11) A. Rahman and F. H. Stillinger, *J. Chem. Phys.*, **55**, 3336 (1971); F. H. Stillinger and A. Rahman, *ibid.*, **57**, 1281 (1972); **60**, 1545 (1974); **61**, 4973 (1974); A. Rahman and F. H. Stillinger, *J. Am. Chem. Soc.*, **95**, 7943 (1973).

12) O. Weres and S. A. Rice, *J. Am. Chem. Soc.*, **94**, 8983 (1972).

13) B. R. Lentz, A. T. Hagler, and H. A. Scheraga, *J. Phys. Chem.*, **78**, 1531 (1974).

14) A. H. Narten, M. D. Danford, and H. A. Levy, *Discuss. Faraday Soc.*, **43**, 97 (1967).

15) G. E. Walrafen, "Water," ed by F. Franks, Vol. 1. Chapt. 5; "Hydrogen-Bonded Solvent Systems," ed by A. K. Covington and P. Jones, Taylor and Francis, London (1968), p. 9.

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

17) H. C. Longuet-Higgins and B. Widom, *Mol. Phys.*, **8**, 549 (1964).

18) A. T. Hagler, H. A. Scheraga, and G. Némethy, *J. Phys. Chem.*, **76**, 3229 (1972).

19) K. Arakawa and K. Kojima, *Bull. Chem. Soc. Jpn.*, **48**, 26 (1975).

20) J. L. Lebowitz, *Phys. Rev.*, **133A**, 895 (1964); J. L. Lebowitz and J. S. Rowlinson, *J. Chem. Phys.*, **41**, 133 (1964).

21) Scheraga and coworkers used the results of the studies by Lebowitz and Rowlinson only numerically and could not give an analytical expression of $Q_{\mathrm{trans.}}$ described in the present text.

22) A. H. Narten and H. Levy, *J. Chem. Phys.*, **55**, 2263 (1971).

23) δF is written as

$$\delta F = \left(\frac{\delta F}{\delta T}\right)_{V,N_1,N_2}\delta T + \left(\frac{\delta F}{\delta V}\right)_{T,N_1,N_2}\delta V$$
$$+ \left(\frac{\delta F}{\delta N_1}\right)_{V,T,N_2}\delta N_1 + \left(\frac{\delta F}{\delta N_2}\right)_{V,T,N_1}\delta N_2,$$

for small variations δT, δV, δN_1, and δN_2. We obtain $\delta N_1 + 5\delta N_2 = 0$ from Eq. 14 for a given N. Then, at the equilibrium condition of Eq. 13 for a given N,

$$(\delta F)_N = \left(\frac{\delta F}{\delta T}\right)_{V,N_1,N_2}(\delta T)_N + \left(\frac{\delta F}{\delta V}\right)_{T,N_1,N_2}\delta(V)_N.$$

Thus, we obtain Eq. 16.

24) In Eq. 18, the contribution from the temperature variation of a is ignored. The magnitude of a was determined from the values of U_{BG} (Table 8) and those of V° obtained from ρ_{calcd} (Table 4). It was found to be $-(1.35\pm0.03)\times10^5$ cal cm^3/mole^2 throughout the range of temperatures, 0—100 °C. Thus, the assumption, $\partial a/\partial T = 0$ is considered to be adequate.

25) W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.*, **24**, 1139 (1956).

26) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford Univ. Press, New York (1969).

27) C. Davis and T. Litovitz, *J. Chem. Phys.*, **42**, 2563 (1965).

28) J. D. Worley and I. M. Klotz, *J. Chem. Phys.*, **45**, 2868 (1966).

29) W. A. Senior and R. E. Verrall, *J. Phys. Chem.*, **73**, 4242 (1969).

30) B. R. Lentz, A. T. Hagler, and H. A. Scheraga, *J. Phys. Chem.*, **78**, 1844 (1974).

31) J. C. Owicki, L. L. Shipman, and H. A. Scheraga, *J. Phys. Chem.*, **79**, 1794 (1975).

32) K. Arakawa and O. Kiyohara, *Bull. Chem. Soc. Jpn.*, **43**, 975 (1970).

33) Ref. 26, p. 101.

34) E. Whalley, *Trans. Faraday Soc.*, **53**, 1578 (1957).

35) Ref. 26, p. 157.

36) J-P. Hansen and L. Verlet, *Phys. Rev.*, **184**, 151 (1969); D. J. Adams and A. J. Matheson, *J. Chem. Phys.*, **56**, 1989 (1972).

37) C. B. Haselgrove, *Math. Comput.*, **15**, 323 (1961).

38) Ref. 26, p. 44.