

## Transient State Theory of Significant Liquid Structure applied to Water

by

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액체구조에 관한 천이상태이론의 물에 대한 적용

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### 초 록

박형석, 안운선과 장세훈<sup>(\*)</sup>이 제안한 액체구조에 관한 천이상태이론을 물에 적용시켜 액체상태에 있는 물의 상태함수를 구했다.

이 이론은 액체의 분자가 고체와 같은 자유도, 천이상태의 자유도 및 기체와 같은 자유도를 갖는다는 것이다.

물은 4°C에서 그의 부피가 최소로 되는 등 특유한 성질들을 가졌지만 이 액체이론이 잘 적용된다.

이 이론을 써서 계산한 물의 몰부피, 증기압, 엔트로피, 증발열 및 일정한 압력에서의 비열 그리고 임계점에서의 성질 등은 실험치와의 좋은 일치를 보여준다.

### Abstract

The partition function for liquid water is developed according to the transient state theory of significant liquid structure proposed by Pak, Ahn and Chang<sup>(\*)</sup>. This theory assumes that the molecules may possess solid-like, transient and gas-like degrees of freedom in liquid state.

Although liquid water has several special properties, for example, minimum molar volume at 4°C, the general theory of liquid can be applied successfully.

The theoretically calculated values for thermodynamic properties at the liquid temperature range and for the critical properties are in good agreement with the observed values.

### Introduction

The structure of liquid water has long been a subject of great interest because of the several

unusual physical properties such as the high melting and boiling points, the high heat capacity, the high entropies of fusion and vaporization, the decrease of the molar volume on melting, and the subsequent contraction between

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0 and 4°C, etc.

Various qualitative models for water have been proposed to explain its properties and to elucidate its structure. The earlier workers<sup>(2-15)</sup> attempted to explain its anomalous properties by postulating the existence of hydrogen bond. However, none of these are satisfactory.

Recently, Némethy and Scheraga<sup>(16)</sup> have developed a partition function for liquid water, based on the "flickering cluster" model proposed by Frank and Wen<sup>(13)</sup> assuming a distribution of the H<sub>2</sub>O molecules over five energy levels, which represent from zero to four hydrogen bondings per molecule. The results from this model are in satisfactory agreement with the experimental values as to entropy, free energy and internal energy, but this model fails to explain the behavior of the specific heat of water. In addition, Vand and Senior<sup>(18)</sup> have pointed out that the concentration of the species derived by Némethy and Scheraga do not show a satisfactory correlation with the experimental results of Buijs and Choppin<sup>(17)</sup> determined by infrared techniques. Buijs and Choppin have observed three absorption bands in the near infrared spectrum of liquid water (in the region 1.1 to 1.3 $\mu$ ), whose intensities vary with temperature and electrolyte concentration. Vand and Senior<sup>(19, 20)</sup> have developed partition function for liquid water replacing Buijs and Choppin's concept of discrete energy level of water molecules by energy bands of water. They have assumed a Gaussian distribution of energy and expanded the partition function as a power series which involves many parameters to be determined using experimental data.

Marchi and Eyring<sup>(21)</sup> have developed a partition function based on significant liquid structure theory proposed by Eyring et al<sup>(22), (23)</sup>. They assumed two solid-like species, a non-rotating hydrogen bonded species and a rotating monomer. They further assumed that the monomer is capable to rotate in the interstitial sites of the hydrogen bonded species. But this is improbable

because the interstitial site of hydrogen bonded species does not have enough space for the free rotation of the monomer.

Authors<sup>(24)</sup> have previously developed a partition function for liquid water applying the modified theory of significant liquid structure proposed by Chang et al<sup>(25)</sup>. There, it is assumed that Ice-I like, Ice-III like and gas-like molecules exist in liquid water and the molecules of Ice-I like and Ice-III like, both of which are oscillating torsionally, are in thermodynamic equilibrium. The equilibrium constant has been taken equal to the ratio of the partition functions of the two species. Various thermodynamic properties and surface tension<sup>(26)</sup> of liquid water from the partition function was calculated in success.

Lately, Jhon, Grosh, Ree and Eyring<sup>(27)</sup> have modified the partition function proposed by Marchi and Eyring, assuming, that there exist two species of solid-like molecules; one, a cage-like cluster of about 46 molecules with the density of Ice-I, and the other, an Ice-III like monomer. They also assumed that the cage-like cluster is dispersed in Ice-III like monomer. However, the partition function for the cage-like cluster is not given explicitly.

Though various quantitative models have been proposed and the thermodynamic properties have been calculated successfully by many workers, no general theory of liquid has been applied to water yet. Surely, the structure and the physical properties of real liquids depend on the chemical properties of the composing particles and the nature of the interacting forces among these particles. And yet, a simple and clear model, which might be taken as a "zerth approximation" is absolutely essential for the further development of the liquid theory.

#### Application of transient state theory of significant liquid structure to water

Recently, Pak, Ahn and Chang<sup>(1)</sup> have developed a theory of liquid state and called it transient

state theory of significant liquid structure (Hereafter, it is called as transient state theory.). They have applied transient state theory to various liquids such as argon, nitrogen, benzene, chloroform and carbon disulfide with success.

In the theory it is assumed that liquid molecules are partitioned by three kinds of degrees of freedom, i. e., the solid-like, the transient, and the gas-like. And it is further assumed that the transition of the degrees of freedom from the solid-like to the gas-like does not occur directly, but the change takes place through a transient state, in which the molecules are in different energy state by acquiring strain energy due to the neighboring molecular-sized holes in the liquid, supposing that the molar volumes for the solid-like portion and the transient portion are same. Since the holes are molecular size,  $N \frac{V - V_s}{V_s}$  number of holes are introduced in liquid in random fashion, where  $N$  is Avogadro's number and  $V$  and  $V_s$  are molar volumes of liquid and solid-like molecules, respectively. Since the introduction of a molecular-sized hole requires an energy equal to heat of vaporization of a molecule, the molecules jumping into the holes should have the gas-like degrees of freedom. Then, the fraction of the molecules having the gas-like degrees of freedom becomes

$$\frac{\frac{V - V_s}{V_s} N}{\frac{V - V_s}{V_s} N + N} = (V - V_s) / V.$$

The remaining fraction  $V_s / V$  are partitioned among solid-like and transient degrees of freedom by portions,  $\alpha$  and  $1 - \alpha$ , respectively, The strain energy, the energy difference between the transient state and the solid-like state are proportional to the heat of sublimation and inversely proportional to the number of the vacant sites around a molecule,  $n(V - V_s) / V_s$ , where  $n$  is given by  $12(V_s / V_i)$ ,  $V_i$  being the molar volume

of the liquid at the triple point. Einstein's solid model is applied for both of the solid-like and the transient state. The frequency of the lattice vibration is, in general, less in the transient state than in the solid-like state, since the former is at the higher energy state by the amount of strain energy, and it is less in both states than in the solid state. In other words, the molecules in the solid-like and in the transient state do not have the same degrees of freedom and the same structure, and neither case, the molecular structure and the degrees of freedom have to be equal to solid. This is true especially in the molecules having molecular dissymmetry or high entropy of fusion as water molecules.

Therefore, in applying the transient state theory, the molecules in the solid-like and in the transient state may have different molar volumes, whose values are different from that of solid Ice-I, 19.65 cc. The molar volumes at the solid-like and the transient state,  $V_s$  and  $V_t$ , as calculated by trial and error method are 18.018cc and 16.095 cc, respectively.

Then, according to the transient state theory, partition function for liquid water is given as follows;

$$F = \frac{(N_s + N_t)!}{N_s! N_t!} f_s^N f_t^N f_g \frac{1}{N_g!} \\ = \frac{\left[ \frac{V_s}{V} N \right]^!}{\left[ \frac{V_s}{V} N \alpha \right]^! \left[ \frac{V_s}{V} N (1 - \alpha) \right]^!} \cdot \left[ \frac{e^{E_s / RT}}{(1 - e^{-\theta_s / T})^6} \prod_{i=1}^3 \frac{1}{1 - e^{-h\nu_i / kT}} \right]^{\frac{V_s}{V} \alpha N} \\ \left[ \frac{n \frac{V - V_s}{V_s} e^{(E_s - \epsilon) / RT}}{(1 - e^{-\theta_s / T})^6} \prod_{i=1}^3 \frac{1}{1 - e^{-h\nu_i / kT}} \right]^{\frac{V_s}{V} (1 - \alpha) N} \cdot \left[ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \right]^{\frac{V - V_s}{V} N} \\ \frac{\pi^{1/2} (8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{2h^3} \prod_{i=1}^3 \left[ \frac{1}{1 - e^{-h\nu_i / kT}} \right]^{\frac{V - V_s}{V} N} \dots\dots\dots(1)$$

where  $\theta$  is Einstein characteristic temperature;  $E_s$ , the sublimation energy of the solid-like molecule;  $V_s$ , the mean molar volume of the molecules in the solid-like and in the transient state,  $V_s = \alpha V_s + (1 - \alpha)V_t$ ; here subscripts  $s$ ,  $t$ , and  $g$  stand for the solid-like, the transient and the gas-like, respectively.

Due to the strong interactions among the molecules of liquid water, it is reasonable to assume that the molecules in the solid-like and in the transient state cannot rotate freely. In fact, Stevenson<sup>(28)</sup> has found that the rotating monomer concentration is very small. Therefore, it is assumed that the molecules in the solid-like and in the transient state oscillate torsionally with the frequencies equal to those of the respective vibrations corresponding to  $\theta_s$  and  $\theta_t$ .

Here, it is assumed that the molecules in the gas-like state behave like an ideal gas. The three principal moment of inertia found in the literature<sup>(29)</sup> are  $1.0243 \times 10^{-40}$ ,  $1.9207 \times 10^{-40}$ , and  $2.9470 \times 10^{-40}$  g·cm<sup>2</sup> for  $I_A$ ,  $I_B$ , and  $I_C$ , respectively.

The interatomic vibrational frequencies may be taken equal to those in the three states without appreciable error. They are also found in the literature<sup>(29)</sup>, i. e.,  $\bar{\nu}_1 = 1595$ ,  $\bar{\nu}_2 = 3652$ , and  $\bar{\nu}_3 = 3756$  cm<sup>-1</sup>.

**Determination of parameters in the partition function**

The values of  $\alpha$  can be calculated using the thermodynamic equilibrium condition;

$$\left(\frac{\partial A}{\partial \alpha}\right)_{T, V, N} = -kT \left(\frac{\partial \ln F}{\partial \alpha}\right)_{T, V, N} = 0 \dots (2)$$

From the above relation  $\alpha$  is obtained

$$\alpha = \frac{f_s}{f_s + f_t} \dots (3)$$

Introducing (3), and using Stirling's approximation, equation (1) becomes;

$$F = \left[ \frac{e^{E_s/RT}}{(1 - e^{-\theta_s/T})^6} (1 + \lambda(x-1) e^{-\frac{aE_s}{(x-1)RT}}) \right] \dots$$

$$\prod_{i=1}^3 \frac{1}{1 - e^{-h\nu_i/kT}} \left[ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \frac{\pi^{1/2}(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{2h^3} \prod_{i=1}^3 \frac{1}{1 - e^{-h\nu_i/kT}} \right]^{1/2} \left(1 - \frac{1}{x}\right)^N \dots (4)$$

where  $\lambda = n \left( \frac{1 - e^{-\theta_s/T}}{1 - e^{-\theta_t/T}} \right)^6 \dots (4a)$

and  $x = \frac{V}{V_s} \dots (4b)$

The parametric values,  $\theta_s$ ,  $\theta_t$ ,  $E_s$ , and "a" are determined at the triple point by the following method.

From the partition function the following equations can be derived.

$$\varphi \equiv \frac{A}{RT} = \frac{1}{N} \ln F = \frac{1}{x} [\sigma + y + (x-1)(\gamma + \ln x)] \dots (5)$$

where  $\sigma = \frac{E_s}{RT} - 6 \ln(1 - e^{-\theta_s/T}) - \sum_{i=1}^3 \ln(1 - e^{-h\nu_i/kT}) \dots (5a)$

$y = \ln \{1 + \lambda(x-1)e^{-\omega}\} \dots (5b)$

$\omega = \frac{aE_s}{n(x-1)RT} \dots (5c)$

and  $\gamma = \left[ \ln \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV_s}{N} \frac{\pi^{1/2}(8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{2h^3} \prod_{i=1}^3 \frac{1}{1 - e^{-h\nu_i/kT}} \right] \dots (5d)$

$$\frac{PV}{RT} = \frac{\lambda e^{-\omega}(1+\omega)}{1 + \lambda(x-1)e^{-\omega}} - \frac{1}{x} (\sigma - \gamma + 1 + y - \ln x - x) \dots (6)$$

The equilibrium condition at constant temperature and pressure between the liquid and its vapor is

$$F_l = A_l + PV_l = F_g = A_g + PV_g$$

By combining this with equations (5) and (6), and assuming the vapor behaves ideal, we obtain following equation;

$$Z \equiv \frac{\lambda(x-1)(1+\omega)e^{-\omega}}{1 + \lambda(x-1)e^{-\omega}} = (x-1) \left[ \ln \frac{RT}{PV} - 2 + \frac{2PV}{RT} + \frac{1}{x} \right] \dots (7)$$

The right-hand side of equation (7) is constant at a given temperature and pressure. It is independent on the values of  $\omega$  and  $\lambda$ . Therefore, differentiating both sides with respect to  $\omega$  at a constant temperature and pressure, one may obtain  $(\frac{\partial Z}{\partial \omega})_\lambda = 0$ , and thence we get the following equation;

$$\omega = \lambda(x-1)e^{-\omega} \dots \dots \dots (8)$$

From equation (7) and (8),  $w = z$ , and  $\lambda = \frac{\omega}{(x-1)e^{-\omega}}$  are obtained. The calculated values of  $\lambda$  and  $\omega$  at the triple point are 14.04 and 0.22435, respectively. By assigning appropriate value for  $\theta_v$ ,  $\theta_l$ ,  $E_s$ , "a" are obtained from equations, (4a), (5a), and (5c), respectively. The obtained parametric values are given as follows:

$$E_s = 10940 \text{ cal/mole, } a = 0.02618$$

$$\theta_v = 234.6^\circ \text{K, } \theta_l = 224.0^\circ \text{K}$$

$$V_v = 18.018 \text{cc, } V_l = 16.095 \text{cc}$$

The values of  $V_v$ ,  $V_l$  and  $\theta_l$  are assigned so as the calculated vapor pressure and the molar volume at 10 °C to coincide with the observed values.

**Calculation of thermodynamic properties and the results**

Vapor pressure and molar volume are obtained by plotting free energy,  $A$  vs  $V$  (22,23) as follows.

First, from equation (5),  $A$  are calculated at various  $V$  covering the liquid and vapor regions. Next, a common tangential line to the two regions is drawn. The slope of the line gives equilibrium vapor pressure and the tangential points give the molar volume of the liquid and the vapor.

The calculated and observed molar volumes of the liquid and its vapor pressures are given in table I and II, respectively.

Entropy is calculated from equation (5) as;

$$S = - \left( \frac{\partial A}{\partial T} \right)_v = \frac{R}{x} \left[ -6 \ln(1 - e^{-\theta_l/T}) \right.$$

**Table I, Molar volume of liquid water.**

$t^\circ\text{C}$	$V_{calc.} \text{ (cc)}$	$V_{obs.}^{30} \text{ (cc)}$	$\Delta\%$
0	18.019	18.019	0.00
4	18.018	18.017	0.01
10	18.021	18.021	0.00
20	18.035	18.048	-0.07
60	18.192	18.324	-0.72
100	18.498	18.799	-1.60
150	19.086	19.641	-2.83

**Table II, Vapor pressure of liquid water.**

$t^\circ\text{C}$	$P_{calc.} \text{ (atm.)}$	$P_{obs.}^{30} \text{ (atm.)}$	$\Delta\%$
0	0.006029	0.006029	0.00
4	0.008030	0.008028	0.02
10	0.01214	0.01212	0.17
20	0.02319	0.02307	0.52
60	0.1997	0.1966	1.58
100	1.020	1.000	2.00
150	4.766	4.698	1.45

$$+ \frac{1}{e^y} \frac{6\theta_l/T e^{-\theta_l/T}}{1 - e^{-\theta_l/T}}$$

$$+ \left(1 - \frac{1}{e^y}\right) \frac{6\theta_l/T e^{\theta_l/T}}{1 - e^{-\theta_l/T}} + y + \left(1 - \frac{1}{e^y}\right) \omega$$

$$+ (x-1)(\gamma + 3 + \ln x) \Big]$$

$$+ R \left\{ - \sum_{i=1}^3 \ln(1 - e^{-h\nu_i/kT}) + \sum_{i=1}^3 \frac{h\nu_i}{kT} \cdot \frac{e^{-h\nu_i/kT}}{1 - e^{-h\nu_i/kT}} \right\}$$

.....(9)

and thence heat of vaporization from the following relation,

$$\Delta H_v = T(S_g - S_l) \dots \dots \dots (10)$$

where  $S_g$  and  $S_l$  are entropies of the gas and the liquid at the temperature,  $T$ . The calculated and observed values of liquid entropy and heat of vaporization are given in table III and IV, respectively.

Heat capacity at constant pressure,  $C_p$  is obtained from the following equation,

$$C_p = C_v + \frac{TV\alpha^2}{\beta} = C_v + \frac{TV \left( \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \right)^2}{-\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T}$$

Table III, Entropy of liquid water.

$t^{\circ}\text{C}$	$S_{\text{calc.}}$ (e. u.)	$S_{\text{obs.}}$ (e. u.)	$\Delta\%$
0	14.92	15.2	-1.9
10	15.57	15.8	-1.5
20	16.18	16.4	-1.4
60	18.44	18.7	-1.4
100	20.50	20.8	-1.4

Table IV, Heat of vaporization of liquid water.

$t^{\circ}\text{C}$	$\Delta H_p^{\text{calc.}}$ (cal/mole)	$\Delta H_{\text{vobs.}}^{30}$ (cal/mole)	$\Delta\%$
0	10820	10740	0.74
10	10720	10640	0.75
20	10620	10540	0.76
60	10230	10150	0.79
100	9800	9720	0.82

$$\begin{aligned}
 &= T \left( \frac{\partial S}{\partial T} \right)_v - \frac{T \left( \frac{\partial P}{\partial T} \right)_v^2}{\left( \frac{\partial P}{\partial V} \right)_T} \\
 &= \frac{R}{x} \left\{ U_i + \left( 1 - \frac{1}{e^y} \right) (U_i - U_i + \omega) \cdot \right. \\
 &\quad \left. \left\{ \frac{1}{e^y} (U_i - U_i + \omega) + 1 \right\} \right. \\
 &\quad \left. + \frac{1}{e^y} U_i \left( \frac{\theta_i / T e^{-\theta_i / T}}{1 - e^{-\theta_i / T}} + \frac{\theta_i}{T} - 1 \right) \right. \\
 &\quad \left. + \left( 1 - \frac{1}{e^y} \right) U_i \left( \frac{\theta_i / T e^{-\theta_i / T}}{1 - e^{-\theta_i / T}} + \theta_i / T - 1 \right) \right. \\
 &\quad \left. - \left( 1 - \frac{1}{e^y} \right) \omega + 3(x-1) \right\} \\
 &+ R \sum_{i=1}^3 \frac{\left( \frac{h\nu_i}{kT} \right)^2}{(1 - e^{-h\nu_i/kT})^2} e^{-h\nu_i/kT} \\
 &+ R \frac{1}{x^2} \left\{ (U_i - U_i + \omega) \xi \left\{ \frac{(1+\omega)x}{e^y} - (x-1) \right\} \right. \\
 &\quad \left. \xi^2 \left( 2\omega + 1 - \frac{\omega^2}{e^y - 1} \right) x + \xi(1+\omega) \right. \\
 &\quad \left. + x(1+\xi) + 2 - \left\{ -6 \ln(1 - e^{-\theta_i / T}) + U_i + y \right\}^2 \right. \\
 &\quad \left. + \gamma + \ln x - (\sigma + y + 0.5) \right\} \dots \dots \dots (11)
 \end{aligned}$$

$$\text{where } U_i = \frac{6\theta_i / T e^{-\theta_i / T}}{1 - e^{-\theta_i / T}},$$

\*  $S_{\text{obs.}}$  are the values obtained from  $S_e - \Delta H_v / T$ , where  $S_e$  is the entropy of gas obtained from the spectroscopic data<sup>29</sup> and  $\Delta H_v$  is the observed heat of vaporization at the temperature  $T$ .

$$U_i = \frac{6\theta_i / T e^{-\theta_i / T}}{1 - e^{-\theta_i / T}}$$

$$\text{and } \xi = \frac{\lambda e^{-\omega}}{1 + \lambda(x-1)e^{-\omega}}$$

The calculated and observed values of  $C_p$  at various temperatures are compared in table V.

Table V, Heat capacity at constant pressure of liquid water.

$t^{\circ}\text{C}$	$C_p^{\text{calc.}}$ (cal/mole. $^{\circ}\text{K}$ )	$C_p^{\text{obs.}}^{30}$ (cal/mole. $^{\circ}\text{K}$ )	$\Delta\%$
0	18.60	18.15	2.48
10	17.93	18.04	-0.61
20	17.57	17.99	-2.33
60	18.26	18.01	1.39
100	18.40	18.14	1.43

Critical point properties are calculated using the conditions,

$$\left( \frac{\partial P}{\partial V} \right)_T = 0, \text{ and } \left( \frac{\partial^2 P}{\partial V^2} \right)_T = 0,$$

which are given in table VI.

Table VI, Critical point properties of water.

Property	Calculated	Observed	$\Delta\%$
$T_c$ $^{\circ}\text{K}$	745	647	15.1
$P_c$ atm.	410	218	88.1
$V_c$ cc	54.4	56.3	-3.37

### Discussion

The agreement between calculated and observed values are excellent in molar volume, vapor pressure, entropy, heat of vaporization and heat capacity at constant pressure.

It is known<sup>(31)</sup> that the calorimetrically measured entropy is less than the entropy obtained from the spectroscopic data by 0.81 e. u. This is due to the residual entropy. The calculated entropy of liquid is compared with the spectroscopic entropy which may be evaluated from the difference between the spectroscopic entropy of gas and the entropy of vaporization.

The calculated molar volume show the minimum at near  $4^{\circ}\text{C}$  and the heat capacity at constant pressure at near  $35^{\circ}\text{C}$ , which are in good

agreement with the experimental observation.

The calculated critical point properties deviate from the observed values as might be expected since transient state theory is one of the zeroth approximation.

Nevertheless, we may say that the application of transient state theory to the complicated molecular states of liquid water is successful.

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