

## 액체 물에 관한 이론

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## Theory of Liquid Water

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요 약. 액체분자는 고체 및 기체와 같은 자유도를 갖는다는 가정하에 물에 관한 이론을 얻었다. 고체와 같은 분자의 진동수를 알아내는 데에 분광학적인 데이터를 이용하였다. 몰부피, 증기압, 엔트로피, 증발 엔트로피, 팽창률, 압축률, 일정한 부피 및 일정한 압력하에서의 열용량, 표면장력, 임계점등을 계산한 결과 모두가 실험치와 아주 잘 일치하였다.

**ABSTRACT.** A theory of liquid water is developed by assuming that the molecules in the liquid state have solid-like and gas-like degrees of freedom. The spectroscopic data are used in assigning the vibrational frequencies of solid-like molecules. The calculated values of molar volume, vapor pressure, entropy, entropy of vaporization, expansion coefficient, compressibility, heat capacities at constant volume and at constant pressure, surface tension and critical point properties are all in excellent agreements with the observed data.

### 1. INTRODUCTION

Liquid water has higher heat capacity, heat of vaporization and surface tension than would be normally expected from the hydrogen compounds of the other members of the oxygen family. The decrease of the volume of water with temperature rise between 0 and 4°C is the well known abnormal property of water.

A great number of models have been proposed to explain the physical properties of water. The models are grouped into mixture model, uni-

formist model and interstitial model.

The mixture models of Jhon, Grosh, Ree and Eyring<sup>1</sup> and Pak and Chang<sup>2</sup> are based on the significant structure theory of liquid, and succeed in fitting a large variety of data. However, the approximation of using single  $\theta$  to represent three degrees of translational and three degrees of librational freedom in Einstein oscillator functions places a limit to the extent of elucidation of actual molecular behavior. A more elaborate treatment of the mixture is that of Némethy and Sheraga<sup>3</sup>. They assigned that

the intermolecular vibrational frequencies for 4- and 3-hydrogen bonded molecules with  $210\text{ cm}^{-1}$  band and 2- and 1-hydrogen bonded molecules with  $160\text{ cm}^{-1}$  band. In this theory, however, there exist some logical inconsistencies.

Bernal<sup>4</sup> has proposed a uniformist model of water based on his concept of a liquid as an intrinsically irregular structure, and some detailed machine calculations of classical models for water have been undertaken by Rahman and Stillinger<sup>5</sup> using a molecular dynamic approach and by Barker and Watts<sup>6</sup> using Monte Carlo procedure. All of these calculations assume the potential energy of the water to be the simple sum of the potentials of pairs of molecules. Therefore, they cannot include effects arising from the energetic interaction between the several hydrogen bonds into which a single  $\text{H}_2\text{O}$  can enter nor can they any cognizance of broken bond.

Samoilov<sup>7</sup> thought that the increase in density when ice melts arises from the invasion of interstitial molecules into some of the empty spaces in the ice lattice. Danford and Levy<sup>8</sup> have refined the interstitial model by employing the computerized least-square methods of X-ray crystallographer. With this model, however, quantitative illustration of the physical properties of water cannot be performed.

In the present paper it is emphasized that liquid water is also a liquid. Although liquid water has some abnormal properties, the molecular state of the aggregate are not greatly different from the other liquids. As the other liquids, liquid water can have interface of various shape according to the container and has high fluidity.

Based on significant structure model, Pak<sup>9</sup> has proposed a simple theory of liquid by assuming that molecular size holes are introduced into the liquid and that the molecules jumping into the holes are gas-like degrees of freedom

and the molecules which vibrating at the equilibrium position have solid-like degrees of freedom. This theory can be applied to water without modification by only consideration of the hydrogen bonding in the liquid.

## 2. STRUCTURE OF LIQUID WATER

According to Pak's treatment of liquid<sup>3</sup> it is assumed that  $N(V-V_s)/V_s$  holes of molecular size are distributed at random in one mole of liquid water, where  $N$  is Avogadro's number and  $V_s$  and  $V$  are the molar volumes of the solid-like molecules and that of the liquid, respectively. If a molecule is neighbored to the hole it can jump into the hole with gas-like degrees of freedom, and the number of the gas-like molecules becomes  $N(V-V_s)/V$ . The remaining  $N(V_s/V)$  molecules are assumed to oscillate much like as the molecules in the solid state.

The solid-like molecules are linked by hydrogen bonds making somewhat distorted network. Therefore, nine intermolecular vibrations must be considered — the intramolecular vibrations are excluded<sup>10</sup>. Of the nine intermolecular vibrations, six refer to restricted translations and three to restricted rotations.

Two of the six restricted translations are equivalent to the hydrogen bond bending motions.<sup>11</sup> They are the totally symmetric deformations. The two hydrogen bending vibrations are unresolved and are assumed to occur at  $170\text{ cm}^{-1}$ . The remaining four restricted translations are the hydrogen bond stretching motions.<sup>11</sup> These stretching vibrations are also unresolved and the vibrational frequencies are assumed to be  $230\text{ cm}^{-1}$ .

Raman scattering from liquid water yields a broad weak band centered near  $60\text{ cm}^{-1}$ , and the intensity of it has been observed to decrease with temperature rise<sup>12</sup>. Infrared absorption

from liquid water also provide evidence suggestive of a broad weak component near  $60\text{ cm}^{-1}$ . In addition a component near  $60\text{ cm}^{-1}$  has been reported from neutron inelastic scattering studies<sup>13</sup>, and the intensity of anti-Stokes component in the spectrum has also been observed to decrease with increasing temperature<sup>14</sup>. A broad infrared absorption has also been observed for liquid water near  $170\text{ cm}^{-1}$ .<sup>15</sup> Further, neutron inelastic scattering spectra from liquid water indicate a component near  $170\text{ cm}^{-1}$  and the intensity has also been observed to decrease with increasing temperature<sup>13,14</sup>.

If  $60\text{ cm}^{-1}$  and  $170\text{ cm}^{-1}$  band are assigned to the vibrational frequencies equivalent to the hydrogen bond bending and to the hydrogen bond stretching, respectively, the calculated values of the heat capacity and the entropy of liquid water are too high compared with the experimental data. Accordingly,  $170\text{ cm}^{-1}$  band is assigned to the two hydrogen bond bending motions and  $230\text{ cm}^{-1}$  band is assigned to the four hydrogen bond stretching motions. The  $60\text{ cm}^{-1}$  band is considered to occur from the results of the energy exchange between the hydrogen bond stretching mode and the hydrogen bond bending mode.

The three restricted rotational bands occur near  $470$ ,  $590$ , and  $766\text{ cm}^{-1}$ , respectively<sup>10,11,16,17</sup>.

The three fundamental intramolecular vibrational frequencies of the gas-like molecule are  $1595$ ,  $3652$  and  $3756\text{ cm}^{-1}$ ,<sup>18</sup> and the three principal moments of inertia  $I_A$ ,  $I_B$  and  $I_C$  are  $1.0243 \times 10^{-40}$ ,  $1.9207 \times 10^{-40}$  and  $2.9470 \times 10^{-40}\text{ g} \cdot \text{cm}^2$ ,<sup>18</sup> respectively.

The potential energy of the gas-like molecules is assumed to be proportional to  $(V_s/V)^2$  as like the other liquids<sup>9</sup> and the proportionality constant obtained is  $\epsilon = 5544.2\text{ cal/mole}$ , which is about equal to the energy of the hydrogen

bonding. This indicates that the gas-like molecules are not free as in the vapor state but under a strong field of the hydrogen bonding.

Generally, the average intermolecular distance in the liquid is liable to increase with increasing temperature. In liquid water, however, the volume decrement is observed with temperature rise between  $0$  and  $4^\circ\text{C}$ . This fact indicates that there is a factor to shorten somewhat the average intermolecular distance in liquid water with increasing temperature. The intensity weakening and the broadening of the Raman bands for the hydrogen bond bending and the stretching motions with temperature rise indicate also that the degrees of breaking and of distortion of the hydrogen bond increase with temperature rise.

According to Pak's theory of liquid, the higher the temperature the more holes should be introduced into the liquid. The increment of the probability of existence of the holes near the neighborhood of the molecule should affect the hydrogen bond network, and therefore some distortion of the hydrogen bond should occur. The distortion of the hydrogen bond may give some decrement of the average van der Waals radius of the molecule. Therefore, the molar volume of the solid-like molecules exhibits some decrement with temperature rise. The volume depends also on the external pressure. Thus, an empirical formula for the volume is presented as follows.

$$V_s = V_s^* \{1 + (a/T)^3 - bp^n\} \quad (1)$$

The parametric values obtained are  $V_s^* = 15.093\text{ cm}^3$ ,  $a = 124.34^\circ\text{K}$ ,  $b = 2.5 \times 10^{-5} (\text{bar})^{-n}$  and  $n = 0.9$ . The last correction term  $bp^n$  can be neglected under the ordinary equilibrium vapor pressure and the proportionality constant  $b$  is the order of magnitude of the compressibility of ice.

Owing to the distortion of the hydrogen bond,

the ground state energy for the solid-like molecules should also depend on the temperature. The dependency is represented by the following empirical formula.

$$E_s = E_s^* - ct^2 \quad (2)$$

where  $t$  is the temperature in centigrade and the proportionality constant is  $c=0.00273$  cal/(mole $\cdot$ °C $^2$ ) and  $E_s^*$  is found to be 11150.5 cal/mole.

### 3. PARTITION FUNCTION

According to Pak's theory of liquid,  $N_s = N(V_s/V)$  solid-like molecules are distributed at random and the total available sites for the solid-like molecules is  $N_t = N(V/V_s)$ . The remaining  $N_g = N(V - V_s)/V$  molecules have the opportunity to jump into the neighboring holes under the potential energy  $E_g = \epsilon(V_s/V_s)^2$ .

The partition function of liquid water can be given as follows just like that of the other liquids.

$$Q = \frac{N_t!}{N_s!(N_t - N_s)!} \left[ \frac{e^{E_s/RT}}{\prod_{i=1}^9 (1 - e^{-h\nu_i/kT})} \right]^{N_t} \left[ \frac{(2\pi mkT)^{3/2} (V - V_s) e^{E_g/RT}}{h^3} \frac{\pi^{1/2} (8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{2h^3 \prod_{j=1}^3 (1 - e^{-h\nu_j/kT})} \right]^{N_g} \frac{1}{N_g!} \quad (3)$$

The partition function is rearranged as follows to give the convenient form for the calculation of the thermodynamic properties.

$$\frac{1}{N} \ln Q = \frac{1}{x} \left[ x^2 \ln x^2 - (x^2 - 1) \ln(x^2 - 1) + (x - 1) \ln x + \frac{g}{x} \left( 1 - \frac{1}{x} \right) + \delta \right] + \xi \quad (4)$$

where

$$\xi = \ln \left[ \frac{(2\pi mkT)^{3/2} e^{V_s}}{h^3 N} \frac{\pi^{1/2} (8\pi^2 kT)^{3/2} (I_A I_B I_C)^{1/2}}{2h^3 \prod_{j=1}^3 (1 - e^{-h\nu_j/kT})} \right]$$

$$\delta = \frac{E_s}{RT} - \sum_{i=1}^9 \ln(1 - e^{-h\nu_i/kT}) - \xi,$$

$$g = \frac{\epsilon}{RT},$$

and

$$x = \frac{V}{V_s}.$$

As indicated in the previous paper for the theory of liquid<sup>9</sup>, the fraction of the gas-like molecules should not be less than 1/12, and therefore,  $x=12/11$  is taken at 273.16°K, which is the lowest temperature that liquid water can exist under its own vapor pressure. At the triple point, the molar volume of liquid water is 18.018 cm $^3$  and thus  $V_s=16.5165$  cm $^3$  is obtained at the temperature. Using the thermodynamic equilibrium condition,  $G_l=G_g$ , between the phases of the liquid and the vapor, and by introducing the observed data of the molar volumes of the liquid and the vapor pressures at the temperatures of 273.16 and 277.15°K, the parametric values can be found, where  $G_l$  and  $G_g$  are the Gibbs free energies for the liquid and the vapor, respectively.

### 4. MOLAR VOLUME AND VAPOR PRESSURE

Introducing the equation to the statistical thermodynamic relation,  $A = -kT \ln Q$ , vapor pressure equation (the equation of state for liquid water) is obtained as follows.

$$P = \frac{RT}{Vx} \left[ x^2 \ln x^2 - (x^2 + 1) \ln(x^2 - 1) + \ln x + x - 1 + \frac{g}{x} \left( \frac{3}{x} - 2 \right) - \delta \right] \quad (5)$$

From the equation and the thermodynamic equilibrium condition,  $G_l=G_g$ , the molar volume of liquid water and the equilibrium vapor pressure are found simultaneously. The calculated values are compared with the observed data in the Table 1. The percent deviations are also

included.

### 5. ENTROPY AND ENTROPY OF VAPORIZATION

By using the equation (4) the third law entropy of liquid is obtained as follows.

$$S = \frac{R}{x} \left\{ x^2 \ln x^2 - (x^2 - 1) \ln (x^2 - 1) + \sum_{i=1}^9 \left\{ -\ln (1 - e^{-u_i}) + \frac{u_i}{e^{u_i} - 1} \right\} + (x-1) \left\{ \xi + 3 + \ln x + \sum_{j=1}^3 \frac{u_j}{e^{u_j} - 1} \right\} \right\} \quad (6)$$

where

$$u_i = \frac{h\nu_i}{kT} \quad \text{and} \quad u_j = \frac{h\nu_j}{kT}$$

If the molar volume of the vapor instead of that of the liquid is introduced into the equation the

entropy of the vapor phase is found. Then, from the difference between the entropies of the vapor and of the liquid the entropy of vaporization is obtained. The calculated values of the liquid entropy and the entropy of vaporization are compared in the Table 2. The percent deviations are also included.

### 6. COMPRESSIBILITY AND EXPANSION COEFFICIENT

The isothermal compressibility of liquid water is obtained from the equation (5) as follows.

$$\beta = - \left( \frac{1}{V} \frac{\partial V}{\partial P} \right)_T = - \frac{1}{x} \left( \frac{\partial x}{\partial P} \right)_T - \frac{1}{V_s} \left( \frac{\partial V_s}{\partial P} \right)_T = \beta' + \frac{33.95 \times 10^{-5}}{V_s} P^{-0.1} (\text{bar}^{-1}) \quad (7)$$

Table 1. The molar volume of liquid water and the vapor pressure.

T°K	V <sub>calc</sub> cm <sup>3</sup>	V <sub>obsd</sub> cm <sup>3</sup> (19)	Δ %	P <sub>calc</sub> atm	P <sub>obsd</sub> atm (19)	Δ %
273.16	18.018	18.018	0.00	0.00603	0.00603	0.00
277.15	18.016	18.016	0.00	0.00803	0.00803	0.00
283.15	18.021	18.021	0.00	0.01213	0.01212	0.08
293.15	18.048	18.048	0.00	0.02315	0.02307	0.35
313.15	18.161	18.157	0.02	0.07335	0.07279	0.77
343.15	18.448	18.425	0.13	0.3109	0.3075	1.11
373.15	18.850	18.798	0.28	1.0098	1.0000	0.98
423.15	19.731	19.640	0.46	4.691	4.698	-0.15

Table 2. The entropy of liquid water and the entropy of vaporization

T°K	S <sub>calc</sub> <sup>eu</sup>	S <sup>eu</sup> S <sup>*obsd</sup> (19)	Δ %	ΔS <sub>calc</sub> <sup>vpu</sup>	ΔS <sub>obsd</sub> <sup>vpu</sup> <sup>19</sup>	Δ %
273.16	15.04	15.15	-0.73	39.49	39.40	0.23
277.15	15.29	15.41	-0.78	38.78	38.67	0.28
283.15	15.65	15.80	-0.89	37.77	37.65	0.32
293.15	16.27	16.42	-0.91	36.15	35.02	0.36
313.15	17.45	17.61	-0.91	33.21	33.07	0.42
343.15	19.12	19.26	-0.73	29.40	29.27	0.44
373.15	20.69	20.77	-0.39	26.15	26.03	0.46
423.15	23.11	23.07	0.17	21.68	21.49	0.88

\*The entropy of liquid water at 25°C is 16.723 eu. See reference 10.

where

$$\beta' = \frac{V_x}{2RT} \left\{ \frac{2x^2}{x^2-1} - \ln \frac{x^2-1}{x} + \frac{x-3}{2} + \frac{3g}{x} \left( \frac{2}{x} - 1 \right) - \delta \right\}^{-1} \quad (7')$$

The isobaric expansion coefficient of liquid water can also be found from the equation as follows.

$$\begin{aligned} \alpha &= \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{x} \left( \frac{\partial x}{\partial T} \right)_P + \frac{1}{V_s} \left( \frac{\partial V_s}{\partial T} \right)_P \\ &= \beta' \left( \frac{\partial P}{\partial T} \right)_x + \frac{1}{V_s} \left( \frac{\partial V_s}{\partial T} \right)_P \\ &= \beta' \left[ \frac{P}{T} + \frac{R}{V_x} \left\{ \frac{Es}{RT} + \frac{2ct}{R} + 3 - \sum_{i=1}^9 \frac{u_i}{e^{u_i}-1} \right. \right. \\ &\quad \left. \left. + \sum_{j=1}^3 \frac{u_j}{e^{u_j}-1} - \frac{g}{x} \left( \frac{3}{x} - 2 \right) - 3 \left( 1 - \frac{V_s^*}{V_s} \right) \right\} \right] \\ &\quad - \frac{3}{T} \left( 1 - \frac{V_s^*}{V_s} \right) \quad (\text{°K}^{-1}) \end{aligned} \quad (8)$$

The calculated values of the compressibility and the expansion coefficient of liquid water are

compared in the Table 3. The differences between the calculated values and the observed data are included in the Table 3.

### 7. HEAT CAPACITIES AT CONSTANT VOLUME AND AT CONSTANT PRESSURE

The heat capacity at constant volume of liquid water is obtained from the equation (6) as follows.

$$\begin{aligned} C_v &= \frac{R}{x} \left[ \sum_{i=1}^9 \frac{u_i^2 e^{u_i}}{(e^{u_i}-1)^2} \right. \\ &\quad \left. + (x-1) \left\{ 3 + \sum_{j=1}^3 \frac{u_j^2 e^{u_j}}{(e^{u_j}-1)^2} \right\} + \left( 1 - \frac{V_s^*}{V_s} \right) \right. \\ &\quad \left\{ x^2 \ln x^2 - (x^2+1) \ln (x^2-1) + \ln x + \xi + 3 \right. \\ &\quad \left. - \sum_{i=1}^9 \left( -\ln(1-e^{-u_i}) + \frac{u_i}{e^{u_i}-1} \right) \right. \\ &\quad \left. \left. + \sum_{j=1}^3 \frac{u_j}{e^{u_j}-1} \right\} \right] \end{aligned} \quad (9)$$

Table 3. The expansion coefficient and the compressibility of liquid water

$T$ °K	$10^5 \alpha_{\text{calc}}^{\text{°K}^{-1}}$	$10^5 \alpha_{\text{obsd}}^{\text{°K}^{-1}}$ <sup>(19)</sup>	$10^5 \Delta$	$10^5 \beta_{\text{calc}}^{\text{bar}^{-1}}$	$10^5 \beta_{\text{obsd}}^{\text{bar}^{-1}}$ <sup>(19)</sup>	$10^5 \Delta$
273.16	-5.38	-6.81	1.43	5.11	5.10	0.01
277.15	0.55	0.03	0.52	5.06	4.96	0.10
283.15	8.84	8.79	0.05	5.00	4.79	0.21
293.15	21.17	20.66	0.51	4.91	4.59	0.32
313.15	41.59	38.54	3.05	4.82	4.42	0.40
343.15	64.75	58.40	6.35	4.83	4.52	0.31
373.15	82.80	75.00	7.80	5.00	4.89	0.11

Table 4. The heat capacities at constant volume and at constant pressure of liquid water.

$T$ °K	$C_{v,\text{calc}}^{\text{cal}/(\text{mole} \cdot \text{°K})}$	$C_{v,\text{obsd}}^{\text{cal}/(\text{mole} \cdot \text{°K})}$ <sup>(19)</sup>	$\Delta$ %	$C_{p,\text{calc}}^{\text{cal}/(\text{mole} \cdot \text{°K})}$	$C_{p,\text{obsd}}^{\text{cal}/(\text{mole} \cdot \text{°K})}$ <sup>(19)</sup>	$\Delta$ %
273.16	19.29	18.14	6.34	19.30	18.15	6.34
277.15	19.02	18.09	5.14	19.02	18.09	5.14
283.15	18.64	18.02	3.44	18.66	18.04	3.44
293.15	18.09	17.88	1.17	18.25	17.99	1.45
313.15	17.19	17.52	-1.88	17.68	17.98	-1.67
343.15	16.24	16.89	-3.85	17.55	18.03	-2.66
373.15	15.57	16.21	-3.95	17.88	18.14	-1.43

The heat capacity at constant pressure can be found from the equations (7), (8) and (9) according to following relation.

$$C_p = C_v + \frac{TV\alpha^2}{\beta} \quad (10)$$

The calculated values of the heat capacities at constant volume and at constant pressure of liquid water are compared with the observed data in the Table 4. The percent deviations are also included in the Table 4.

### 8. SURFACE TENSION

The surface tension of liquid water can be calculated by using the iteration method which has been proposed by Chang *et al.*<sup>20</sup> They considered that the surface is a gradual transition region which is composed of several molecular layers. Assuming the most dense molecular plane appears in the surface region, the following relation for surface tension can be obtained.

$$\gamma = \sum_i \frac{0.9165}{V_i} \left( \frac{V_i}{N} \right)^{1/3} (G_i - G_s) \quad (11)$$

where  $G_i$  and  $V_i$  are the molar Gibbs free energy and the molar volume of the  $i$ -th layer from the top surface layer, respectively. In calculating these values by using the partition function of liquid water, the ground state ener-

gy for the solid-like molecule should be corrected. In correction of the ground state energy the intermolecular dispersion energy is assumed to be proportional to the number density of the neighboring molecules. The intermolecular dispersion energy is assumed to be  $E_d = (E_s - \epsilon)$ , since  $\epsilon$  corresponds to the field resulted by the hydrogen bond and by some long range forces of the dipole interaction. Thus, the ground state energy for the solid-like molecules in the  $i$ -th layer can be given as follows.

$$E_{si} = E_d \left[ \frac{3}{12} \frac{\rho_{i+1}}{\rho_i} + \frac{6}{12} \frac{\rho_i}{\rho_i} + \frac{3}{12} \frac{\rho_{i-1}}{\rho_i} \right] + \epsilon \quad (12)$$

where  $\rho_i$  is the number density of the  $i$ -th layer. This density can be obtained according to the method of Chang *et al.*

The calculated values of surface tension of liquid water are compared with the observed data in the Table 5, in which the percent deviations are included. The percent contribution of each layer to the surface tension are also listed in the Table 5.

### 9. CRITICAL POINT

The critical point properties can be obtained from the equation (5) by using the following

Table 5. The surface tension of liquid water.

T °K	$\gamma$ dyne/cm calc	% contribution of the layers			$\gamma^*$ dyne/cm obsd <sup>21</sup>	$\Delta$ %
		first	second	third		
273.16	76.11	(94.47	5.26	0.25)	76.1	0.01
277.15	75.66	(94.39	5.36	0.25)	75.5	0.21
283.15	74.97	(94.26	5.48	0.26)	74.6	0.50
293.15	73.73	(94.08	5.65	0.27)	73.0	1.00
313.15	71.12	(93.64	6.05	0.31)	69.9	1.75
343.15	66.85	(92.99	6.64	0.37)	65.2	2.53
373.15	62.38	(92.24	7.29	0.47)	60.5	3.11

\*The observed data are linear extrapolated values according to the equation of reference 21. These data are slightly higher (about 1 dyne/cm in average) than the values found in reference 19.

relations.

Table 6. The critical point properties of water.

	Calculated	Observed <sup>(19)</sup>	$\Delta$ %
$T_C$ °K	594.8	647.4	-8.10
$P_C$ atm	294.1	218.3	34.7
$V_C$ cm <sup>3</sup>	50.5	55.4	-8.83

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \quad (13)$$

If it is assumed that the numerical value of the partition function for the solid-like molecule and of that for the gas-like molecule coincide at the critical point, the following relations can be derived for any liquid.

$$(V_C/V_S) = 3.3166, \quad (P_C V_C)/(RT_C) = 0.3044, \\ \epsilon/(RT_C) = 0.09783, \quad \delta = 1.2195. \quad (14)$$

From the above relations the critical point properties of water can easily be found. The calculated values are compared with the observed data in the Table 6. The percent deviations are also included.

## 10. DISCUSSIONS

All the calculated values are in excellent agreements with the observed data. In applying the theory to liquid water the molar volume of the solid-like molecule and the ground state energy is considered to be given by the equations (1) and (2), respectively. However, further study on the hydrogen bond distortion would give the better formulas for  $V_s$  and  $E_s$ . The value of  $\epsilon$  becomes 115.7 cal/mole at the critical point. This means that nearly all the hydrogen bond break up at the critical point. Further improvements may give better agreement of the fraction of gas-like molecules with the data of the absorption spectroscopic studies<sup>22, 23</sup>.

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