

A New Approach to Significant Liquid Structure for Chemical Kinetics in Liquid Phase

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액체 용액에서의 화학 반응 속도론을 위한 액체 상태함의 유도

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박 형 석

이 연구는 동아일보사와 인촌 기념회가 주관하는 제 1회
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요 약

액체의 상태함을 유도하여 여러 가지 액체들에 적용하여 열역학적 성질들과 점성도를 계산하여 측정치와의 좋은 일치를 보았다. 그리고 이 상태함을 써서 여러 성분으로 된 액체 용액의 상태함을 얻었으며, 나아가서 액체 용액에서의 화학 반응 속도를 구할 수 있음을 보였다.

I. The reaction rate in liquid solution.

Kinetic studies of chemical reactions are usually based upon either a collision theory or an absolute reaction rate theory. Because of an advanced knowledge on the gaseous state, chemical reactions in the gaseous state have comparatively well developed. Reactions in the liquid, however, differ markedly from those in the gas phase because of the presence of solvent molecules, which are always in intimate contact with the reactants and, in fact, often interact strongly with them.

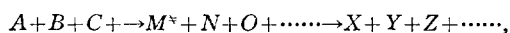
Recently, A. M. North⁽¹⁾ has studied collision theory

in liquids. However, a lot of difficult problems are unsolved in application of the theory to the actual chemical reactions.

The application of the absolute reaction rate theory to reactions in liquid solution is simple and can be reduced to collision theory. The major problem encountered in the application of the theory is that the properties of liquid should be given from molecular levels. If the properties can be given statistically from molecular levels, that is, if an accurate partition function of the liquid can be derived, it is theoretically possible to calculate the absolute rates of the reaction in the liquid solution.

The reaction between the reactants in the liquid solution can be thought of as occurring in three well-defined stages; (1) diffusion of initially separated reactant molecules to become neighbors, (2) the actual chemical transformation, and (3) diffusion of the products away from each other. Diffusion in a liquid has an activation energy which is less than the one accompanying the actual chemical transformation. The step (2) is consequently the rate-determining one for the most reactions between the dissolved substances.

Considering the above fact, H. Eyring⁽²⁾ derived a rate equation for the reaction in the liquid solution. The specific rate constant, k , of the general reaction



where M^* is a activated complex, N, O, \cdots are intermediates and X, Y, Z, \cdots are the final products, is given by the expression

$$k = \left(\kappa \frac{kT}{h} K^* \right) \frac{f_A f_B f_C \cdots}{f_{M^*} f_N f_O \cdots} \quad (1)$$

κ being a transmission coefficient. In deriving equation (1), a chemical equilibrium between the reactants and the activated complex, including the intermediates, is considered. K^* is the equilibrium constant and f 's are the activity coefficients of the respective species, both of which are obtainable according to the statistical thermodynamics only if we can develop the partition functions of the liquids. That is;

$$K^* = \frac{Q_{M^*} Q_N Q_O \cdots}{Q_A Q_B Q_C \cdots} \quad (2)$$

where Q 's are the total partition function for the respective liquid except Q_{M^*} , which is the partition function minus the translational degree of freedom in the reaction coordinate and corrected the zero level of energy to coincide with the ones for the reactants. The activity coefficients, f_i 's, are given by the following expressions:

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (3)$$

$$a_i = c_i f_i \quad (4)$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j \neq n_i} \quad (5)$$

where $i=A, B, \cdots, M^*, N, O, \cdots$. In the above equations, a_i , c_i , μ_i and μ_i° are activity, concentration, chemical potential and chemical potential at unit activity for component i , respectively. Helmholtz free energy for the solution, A , in equation (5) can be

found from the partition function for the solution, Q , *i. e.*,

$$A = -kT \ln Q \quad (6)$$

In this paper the partition function for the liquid is developed, which is the fundamental process for the theoretical derivation of chemical kinetics in the liquid solution.

II. Theory of liquid Structure.

A. Introduction.

It is very difficult to give a complete statistical mechanical description of liquids, since every molecule in liquids is in continuous interaction with a number of other molecules, and the molecules are partially ordered, *i. e.*, neither regular as in a solid nor at random as in a gas.

For the description of liquids, there are two fundamental ways. The one is the radial distribution function theory developed by J. G. Kirkwood *et al.*⁽³⁾. Although the theory is formal, the mathematical complication restricts the actual application of the theory scarcely to a simple liquid such as argon.

The other is a model approach, in which liquid model is visualized at first, and then transcribed into a mathematical form. Some of the model approaches to the liquid are free volume theories⁽⁴⁾, quasi-lattice theories⁽⁵⁾, and the significant structure theory developed by H. Eyring⁽⁶⁾. Among the theories the last one is very useful for the actual application to the various physical properties of the liquids.

Recently, the significant structure theory has been modified by S. Chang *et al.*⁽⁷⁾ and has been corrected some of the theoretical defects in it by H. Pak, W. Ahn and S. Chang⁽⁸⁾, which is named as the transient state theory of significant liquid structure.

A new formulation of the partition function, however, should be done to draw out the physical picture of the liquid more clearly.

B. The formulation of the partition function.

The experimental data of X ray diffraction⁽⁹⁾ indicate that the arrangement of the molecules in the liquid keeps short range order with about the same intermolecular distance in the solid, though about ten

percent volume increment is observed when the solid undergoes a phase change to form the liquid.

From these experimental facts, it can be assumed that $N(V - V_s)/V$, of molecular size holes are introduced at random in one mole of the liquid, where N is Avogadro's number, V and V_s are the molar volume of the liquid at the temperature under consideration and the one of the solid at the triple point, respectively. The random introduction of $N(V - V_s)/V$ holes into one mole of the solid to become the liquid requires about the same energy with the one of the sublimation of $N(V - V_s)/V$ molecules, $E_s(V - V_s)/V$, where E_s is the molar sublimation energy. Therefore, the average ground state energy for the liquid molecules becomes $-E_s + E_s(V - V_s)/V$, while that for the solid molecules is $-E_s$, being taken the energy zero as the energy the molecules have when they are infinitely separated and at rest.

All the liquid molecules should not exist in the same energy state because of the holes introduced among the molecules. Since the $N(V - V_s)/V_s$ holes are distributed at random among the N molecules, $N(V - V_s)/V_s \cdot \left(\frac{N}{N + N \frac{V - V_s}{V_s}} \right) = N(V - V_s)/V$ molecules can jump into them.

The molecules jumping into the holes have the gas-like degrees of freedom, i. e., they move around in the free volume $V - V_s$, which is the total volume of the holes.

The remaining molecules $N - N(V - V_s)/V = N(V_s/V)$ have the solid-like degrees of freedom, i. e., they vibrate at the stable positions just like Einstein oscillators in the solid.

The partition functions for the solid-like and for the gas-like molecule are expressed as

$$q_s = \frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \cdot b_s \dots \dots \dots (7),$$

and

$$q_g = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot (V - V_s) \cdot b_g \dots \dots \dots (8),$$

respectively, where θ is Einstein characteristic temperature, and b is the interatomic vibrational and the molecular rotational partition function. The subscripts s and g stand for the solid-like and the gas-like molecules, respectively.

Then, the partition function for the liquid becomes

$$Q = \frac{\left\{ N \frac{V}{V_s} \right\}!}{\left\{ N \frac{V_s}{V} \right\}! \left\{ N \frac{V}{V_s} - N \frac{V_s}{V} \right\}!} \left[\frac{e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \cdot b_s \right]^{\frac{V_s}{V} N} \cdot \left[\frac{(2\pi mkT)^{3/2}}{h^3} \cdot (V - V_s) \cdot b_g \right]^{\frac{V - V_s}{V} N} \frac{1}{\left\{ N \frac{V - V_s}{V} \right\}!} \dots \dots \dots (9)$$

In equation(9), the first combination factor is the positional degeneracy for the solid-like molecules, because the number of the total available sites for the $N(V_s/V)$ distinguishable solid-like molecules is $N + N(V - V_s)/V_s = N(V/V_s)$, and the last factor results from the indistinguishability of the gas-like molecules. The ground state energy for the solid-like molecules, E_s , is not a constant, but it slightly depends on the environment of the molecules as given by

$$E_s = E_c + E_d \dots \dots \dots (10)$$

where E_c is a constant which stands for the interaction energy due to the nearest neighboring molecules, and E_d stands for the interaction energy due to the second neighbors which are existed across the holes and therefore E_d is multiple proportional to the probability for the holes to come to the nearest neighboring positions of the molecule, $(V - V_s)/V$, and to the one for the other molecules to come to the neighboring positions of the holes which are already in contact with the molecule under consideration, V_s/V , i. e., E_d is proportional to $(V - V_s)/V \cdot (V_s/V)$. Then, equation(10) is expressed as

$$E_s = E_c + a(V - V_s)/V \cdot (V_s/V) \dots \dots \dots (11)$$

where a is the proportionality constant.

C. Calculation of the thermodynamic properties.

From equations(6) and(9) and by using Stirling's approximation for the factorials, Helmholtz free energy is obtained as

$$A = -kT \ln Q = -(RT/x) \{ C + y + (x-1)(D + \ln x) \} \dots \dots \dots (12)$$

where $x = V/V_s$, $C = E_c/(RT) - 3 \ln (1 - e^{-\theta/T}) + \ln b_s$, $D = \ln \left(\frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{e^{V_s}}{N} \right) + \ln b_g$, $y = x^2 \ln x^2 - (x^2 - 1) \ln (x^2 - 1) + \alpha(x-1)/x^2$ and $\alpha = a/(RT)$.

Vapor pressure and entropy are given as

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T, N} = \frac{RT}{V_s} \cdot \frac{1}{x^2} \left\{ \left(x^2 + \frac{1}{2} \right) \ln x^2 \right.$$

$$-(x^2+1)\ln(x^2-1)+\frac{3-2x}{x^2}\alpha+x \\ -(C-D\div 1)\} \dots\dots\dots(13)$$

and

$$S=-\left(\frac{\partial A}{\partial T}\right)_{V,N}=\frac{R}{x}\left\{-3\ln(1-e^{-\theta/T})+\frac{3\theta/T e^{-\theta/T}}{1-e^{-\theta/T}}\right. \\ \left.+\ln b_s+T\frac{\partial \ln b_s}{\partial T}+x^2\ln x^2-(x^2-1)\ln(x^2-1)\right. \\ \left.+(x-)(D+1.5+T\frac{\partial \ln b_g}{\partial T}+\ln x)\right\} \dots\dots\dots(14),$$

respectively.

The parameters E_s , θ and a can be obtained at a low temperature (such as triple point), at which the vapor in equilibrium with the liquid behaves as an ideal gas, by using the equations(12), (13) and (14) only if the observed data of the vapor pressure, the molar volume of the liquid and the entropy of the liquid at the chosen temperature are available, since the Helmholtz free energy of the liquid at the temperature can be obtained from the equilibrium condition between the liquid and the vapor

$$A_l+PV_l=A_g+PV_g \dots\dots\dots(15)$$

where the subscripts l and g stand for the liquid and the vapor, respectively.

Using equation(12), at an arbitrary temperature under consideration, Helmholtz free energy, A , is calculated for various values of volume, V , ranging from the liquid region to the vapor region and it is plotted against V . Then, the negative slope of the common tangential line between the two regions gives the vapor pressure at the temperature. And the tangential points at the liquid region and at the vapor region give the molar volumes of the liquid and the vapor, respectively, at the temperature. For a more accurate value of the liquid molar volume, the vapor pressure just

obtained is introduced into equation (13) and solved for V .

The entropies of the liquid and the vapor can easily be found from equation(14) only if the molar volumes are known. Then, the entropy of vaporization is given by the difference of the entropies,

$$\Delta S_{vapn}=S_g-S_l \dots\dots\dots(16)$$

At the critical point, the following conditions are satisfied simultaneously;

$$P=-\left(\frac{\partial A}{\partial V}\right)_{T,N}, \left(\frac{\partial P}{\partial V}\right)_{T,N}=0, \left(\frac{\partial^2 P}{\partial V^2}\right)_{T,N}=0 \\ \dots\dots\dots(17)$$

From equations (13) and (17), the following equations are obtained:

$$T=\frac{R}{a}\left\{0.5+0.25x-\frac{1+\frac{1}{x^2}}{\left(1-\frac{1}{x^2}\right)^2}\right\} \cdot \frac{x^2}{6-1.5x} \\ \dots\dots\dots(18)$$

$$C-D=\frac{2x^2}{x^2-1}-\ln\frac{x^2-1}{x}+\frac{1}{2}(x-3) \\ -\frac{3x-6}{x^2} \cdot \frac{a}{RT} \dots\dots\dots(19)$$

$$P=\frac{RT}{V_s}\left\{\ln\frac{x^2}{x^2-1}+\frac{x+1}{2x^2}-\frac{2}{x^2-1}\right. \\ \left.+\frac{x-3}{x^4} \cdot \frac{a}{RT}\right\} \dots\dots\dots(20)$$

Solving equations (18) and (19) simultaneously for T and V , critical temperature and critical volume can be found, and then, critical pressure is obtained from equation(20).

The calculated thermodynamic properties of various liquids, which are compared with the experimental data at the various temperatures, are listed in Tables 1 and 2.

TABLE 1. Molar Volume, Vapor Pressure and Entropy of Vaporization.

Temperature, ($^{\circ}$ K)	Molar volume, (cc)			Vapor pressure, (atm)			Entropy of vaporization. (eu)		
1. Argon (A).									
	$V_{calc.}$	$V_{obs.}^{10}$	$\Delta\%$	$P_{calc.}$	$P_{obs.}^{10}$	$\Delta\%$	$\Delta S_{calc.}$	$\Delta S_{obs.}^{11}$	$\Delta\%$
83.96(T_t)	28.03	28.03	0.00	0.6739	0.6739	0.00	19.43	19.43	0.00
87.49(T_b)	28.52	28.69	-0.59	1.0112	1.000	1.12	18.34	18.65	-1.66
97.76	30.40	30.15	0.83	2.754	2.682	2.68	15.38

$$^{10}V_s=24.98 \text{ cc}, E_s=1750.0 \text{ cal}, a=335.1 \text{ cal}, \theta=44.83^{\circ}\text{K}, b_l=b_g=1 \dots\dots\dots(21)$$

2. Benzen (C_6H_6).

	$V_{calc.}$	$V_{obs.}^{10}$	$\Delta\%$	$P_{calc.}$	$P_{obs.}^{11}$	$\Delta\%$	$\Delta S_{calc.}$	$\Delta S_{obs.}^{11}$	$\Delta\%$
278.675 (T_i)	87.29	87.29	0.00	0.04718	0.04718	0.00	29.78	29.78	0.00
328.15	93.33	92.80	0.57	0.4304	0.4302	0.05	23.65	23.40	1.07
353.25 (T_b)	96.94	95.92	1.06	1.0061	1.000	0.61	21.12	20.83	1.39
423.15	109.8	106.8	2.81	5.890	5.70	3.33	15.29	14.88	2.76

$$^{10}V_s=77.00 \text{ cc}, \quad E_s=9756.2 \text{ cal}, \quad a=3809.7 \text{ cal}, \quad \theta=50.03^\circ\text{K}, \quad ^{12}I_A I_B I_C=6.435 \times 10^{-114} \text{ g. cm}^2,$$

$$b_s = \frac{1}{(1-e^{-\theta/T})^3} \prod_{i=1}^{30} \frac{1}{1-e^{-h\nu_i/kT}} \quad \text{and} \quad b_g = \frac{\pi^{1/2}(8\pi^2 kT)^{3/2}(I_A I_B I_C)^{1/2}}{12 h^3} \prod_{i=1}^{30} \frac{1}{1-e^{-h\nu_i/kT}} \dots\dots\dots(22)$$

3. Acetone ($\text{CH}_3\text{--CO--CH}_3$).

	$V_{calc.}$	$V_{obs.}^{10}$	$\Delta\%$	$P_{calc.}$	$P_{obs.}^{11}$	$\Delta\%$	$\Delta S_{calc.}$	$\Delta S_{obs.}^{11}$	$\Delta\%$
178.35 (T_i)	63.64	63.48	0.25	2.60×10^{-5}	48.82
273.15	71.49	71.49	0.00	0.09133	0.09133	0.00	28.64	28.64	0.00
329.35 (T_b)	77.69	77.44	0.32	1.0097	1.000	0.97	21.88	21.96	-0.36
373.15	83.80	83.81	-0.01	3.722	3.67	1.42	17.81	17.56	1.42

$$^{10}V_s=59.96 \text{ cc}, \quad E_s=9398.1 \text{ cal}, \quad a=4647.4 \text{ cal}, \quad \theta=48.66^\circ\text{K}, \quad ^{13}I_A I_B I_C=1.398 \times 10^{-114} \text{ g. cm}^2, \quad B=920 \text{ cal},$$

$$I'=5.3 \times 10^{-40} \text{ g. cm}^2,$$

$$b_s = \frac{1}{(1-e^{-\theta/T})^3} \prod_{i=1}^{22} \frac{1}{1-e^{-h\nu_i/kT}} \cdot \frac{8\pi^2 I' kT}{9h^3} \cdot \pi \cdot e^{B/RT} \quad \text{and} \quad b_g = \frac{\pi^{1/2}(8\pi^2 kT)^{3/2}(I_A I_B I_C)^{1/2}}{2h^3} \prod_{i=1}^{22} \frac{1}{1-e^{-h\nu_i/kT}} \cdot \frac{8\pi^2 I' kT}{9h^2} \cdot \pi \cdot e^{B/RT} \dots\dots\dots(23)$$

4. Chloroform (CHCl_3).

	$V_{calc.}$	$V_{obs.}^{10}$	$\Delta\%$	$P_{calc.}$	$V_{obs.}^{10}$	$\Delta\%$	$\Delta S_{calc.}$	$\Delta S_{obs.}^{11}$	$\Delta\%$
209.65 (T_i)	72.32	72.60	-0.39	0.000895	39.72
273.15	78.22	78.22	0.00	0.08026	0.08026	0.00	28.28	28.28	0.00
334.35 (T_b)	85.53	84.75	0.92	1.0165	1.000	1.65	21.12	21.07	0.24
373.15	91.34	89.99	1.50	3.116	3.197	-2.53	17.61	17.66	-0.28

$$^{10}V_s=67.00 \text{ cc}, \quad E_s=9327.5 \text{ cal}, \quad a=4096.1 \text{ cal}, \quad \theta=31.20^\circ\text{K}, \quad ^{14}I_A I_B I_C=3.286 \times 10^{-113} \text{ g. cm}^2,$$

$$b_s = \frac{1}{(1-e^{-\theta/T})^3} \prod_{i=1}^9 \frac{1}{1-e^{-h\nu_i/kT}} \quad \text{and} \quad b_g = \frac{\pi^{1/2}(8\pi^2 kT)^{3/2}(I_A I_B I_C)^{1/2}}{3h^3} \prod_{i=1}^9 \frac{1}{1-e^{-h\nu_i/kT}} \dots\dots\dots(24)$$

5. Carbon disulfide (CS_2).

	$V_{calc.}$	$V_{obs.}^{10}$	$\Delta\%$	$P_{calc.}$	$P_{obs.}^{11}$	$\Delta\%$	$\Delta S_{calc.}$	$\Delta S_{obs.}^{11}$	$\Delta\%$
223.15	55.47	55.74	-0.48	0.00931	0.00934	-0.32	32.12
273.15	58.88	58.88	0.00	0.1675	0.1675	0.00	24.92	24.92	0.00
310.40 (T_b)	62.54	62.27	0.43	1.0095	1.000	0.95	20.13	20.05	0.40
373.15	67.67	67.65	0.03	4.383	4.42	-0.84	15.86	15.41	2.92

$$^{10}V_s=49.00 \text{ cc}, \quad E_s=8104.6 \text{ cal}, \quad a=4396.9 \text{ cal}, \quad \theta=34.11^\circ\text{K}, \quad ^{12}I=626.2 \times 10^{-40} \text{ g. cm}^2,$$

$$b_s = \frac{1}{(1-e^{-\theta/T})^2} \prod_{i=1}^4 \frac{1}{1-e^{-h\nu_i/kT}} \quad \text{and} \quad b_g = \frac{8\pi^2 I kT}{2h^2} \prod_{i=1}^4 \frac{1}{1-e^{-h\nu_i/kT}} \dots\dots\dots(25)$$

6. Chlorine (Cl₂)

	$V_{calc.}$	$V_{obs.}^{10}$	$\Delta\%$	$P_{calc.}$	$P_{obs.}^{11}$	$\Delta\%$	$\Delta S_{calc.}$	$\Delta S_{obs.}^{10}$	$\Delta\%$
172.12 (T_i)	41.57	41.57	0.00	0.01374	0.01374	0.00	31.69	31.69	0.00
193.15	43.00	42.58	0.99	0.07634	0.07606	0.37	27.40
239.05 (T_b)	46.65	45.45	2.64	1.0040	1.000	0.40	20.51	20.41	0.49
273.15	50.02	48.31	3.54	3.678	3.644	0.93	16.71

$^{10}V_s=37.32\text{cc}$, $E_s=6071.0\text{ cal}$, $a=2859.0\text{ cal}$, $\theta=45.50^\circ\text{K}$, $^{15}I=116.3\times 10^{-40}\text{ g. cm}^2$,

$$b_s = \frac{1}{(1-e^{-\theta/T})^3} \frac{1}{1-e^{-h\nu/kT}} \quad \text{and} \quad b_g = \frac{8\pi^2 I k T}{2h^2} \frac{1}{1-e^{-h\nu/kT}} \dots\dots\dots (26)$$

7. Ammonia (NH₃)

	$V_{calc.}$	$V_{obs.}^{11}$	$\Delta\%$	$P_{calc.}$	$P_{obs.}^{11}$	$\Delta\%$	$\Delta S_{calc.}$	$\Delta S_{obs.}^{11}$	$\Delta\%$
195.45 (T_i)	23.20	23.20	0.00	0.0605	0.0605	0.00	30.94	30.94	0.00
213.15	23.88	23.86	0.08	0.2178	0.2161	0.79	27.61	27.60	0.04
239.75 (T_b)	25.03	24.98	0.20	0.9977	1.000	-0.23	23.47	23.24	0.99
253.15	25.67	25.61	0.23	1.871	1.877	-0.32	21.67	21.37	1.40

$^{16}V_s=20.57\text{ cc}$, $E_s=6394.0\text{ cal}$, $a=3035.8\text{ cal}$, $\theta=165.35^\circ\text{K}$, $^{17}I_A I_B I_C=3.518\times 10^{-119}\text{ g. cm}^2$,

$$b_s = \frac{1}{(1-e^{-\theta/T})^3} \prod_{i=1}^6 \frac{1}{1-e^{-h\nu_i/kT}} \quad \text{and} \quad b_g = \frac{\pi^{1/2}(8\pi^2 k T)^{3/2}(I_A I_B I_C)^{1/2}}{3h^3} \prod_{i=1}^6 \frac{1}{1-e^{-h\nu_i/kT}} \dots\dots\dots (27)$$

8. Water (H₂O)

	$V_{calc.}$	$V_{obs.}^{11}$	$\Delta\%$	$P_{calc.}$	$P_{obs.}^{11}$	$\Delta\%$	$\Delta S_{calc.}$	$\Delta S_{obs.}^{11}$	$\Delta\%$
273.15 (T_i)	18.019	18.019	0.00	0.006029	0.006029	0.00	39.32	39.32	0.00
277.15	18.017	18.017	0.00	0.008020	0.008028	-0.10	38.60	38.57	0.08
283.15	18.028	18.021	0.04	0.01210	0.01212	-0.17	37.64	37.58	0.16
293.15	18.074	18.048	0.14	0.02303	0.02307	-0.17	36.07	35.95	0.33
333.15	18.494	18.324	0.93	0.1970	0.1966	0.20	30.63	30.47	0.53
373.15 (T_b)	19.161	18.799	1.93	1.0042	1.0000	0.42	26.24	26.05	0.73
423.15	20.258	19.641	3.14	4.693	4.696	-0.06	21.77	21.46	1.44

$V_\sigma=16.78\text{ cc}$, $E_s=10873\text{ cal}$, $a=3510.7\text{ cal}$, $\theta=233.24^\circ\text{K}$, $v=0.022811\text{ cc}$, $^{18}I_A I_B I_C=5.798\times 10^{-120}\text{ g. cm}^2$.

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 the boiling points compared with the other hydrides of oxygen family, the decrease of the molar volume upon melting and the subsequent contraction between 0 and 4°C etc.

Various models for liquid water have been proposed by many workers⁽¹⁹⁾. It has been considered that the anomalous physical properties are due to the existence

of hydrogen bond in liquid water just like in ice-I(20).

Due to the existence of the hydrogen bonds and the holes introduced among the molecules, which is considered in the present theory, the total number of available sites for the solid-like molecules can not be equal to $N(V/V_s)$, but it is equal to $N(V^*/V_\sigma)$, where V_s , V , V_σ and V^* are the molar volumes of ice-I-like, liquid water, ice-III-like and the one if each site in the liquid were occupied just as in the ice-III-like, respectively. $V-V^*$ is assumed to be inv-

ersely proportional to the number of holes, $N(V^*-V_g)/V_g$, introduced in the liquid,

$$V-V^*=v/(x^*-1) \dots\dots\dots(28)$$

where v is the proportionality constant, and

$$x^*=V^*/V_g \dots\dots\dots(29).$$

Since the numbers of the solid-like and the gas-like molecules become $N(1/x^*)$ and $N(1-\frac{1}{x^*})$, respectively, the partition function for liquid water is expressed as

$$Q = \frac{(Nx^*)!}{\left[N\frac{1}{x^*}\right]! \left[Nx^*-N\frac{1}{x^*}\right]!} \left[\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3} \cdot b_s \right]^{\frac{1}{x^*}N} \left[\frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{eV^*}{N} \cdot b_g \right]^{(1-\frac{1}{x^*})N} \dots\dots\dots(30)$$

where

$$b_s = \frac{1}{(1-e^{-\theta/T})^3} \prod_{i=1}^3 \frac{1}{1-e^{-h\nu_i/kT}}$$

and

$$b_g = \frac{\pi^{1/2}(8\pi^2 kT)^{3/2}}{2h^3} (I_A I_B I_C)^{1/2} \prod_{i=1}^3 \frac{1}{1-e^{-h\nu_i/kT}} \dots\dots\dots(30')$$

TABLE II. Critical Properties of Various Liquids.

Substance,	Critical temperature($^{\circ}$ K),			Critical Pressure(atm),			Critical volume(cc)		
	Calc.	Obs. ¹¹	$\Delta\%$	Calc.	Obs. ¹¹	$\Delta\%$	Calc.	Obs. ¹¹	$\Delta\%$
A	147.0	150.7	-2.46	45.8	48.0	-4.6	86.5	75.3	14.9
C ₆ H ₆	588.5	562.2	4.68	64.1	48.6	31.9	278.6	260.5	6.95
(CH ₃) ₂ CO	557.5	508.7	9.59	80.6	46.6	73.0	219.4	212.8	3.10
CHCl ₃	568.1	¹⁰ 536.1	5.97	72.0	243.6	¹⁰ 231.4	5.27
CS ₂	601.2	552.2	8.87	104.4	78	33.8	178.3	173.1	3.00
Cl ₂	438.1	417.2	5.01	98.5	76.1	29.4	135.1	123.8	9.13
NH ₃	448.2	405.5	10.5	183.7	111.3	65.0	74.6	73.0	2.19
H ₂ O	711.2	647.4	9.85	345.7	218.3	58.4	60.0	56.3	6.57

D. Viscosity of liquid.

The viscous flow in liquid occurs through an activated state. For the viscous flow with relatively small shear force, the viscosity of liquid is expressed as⁽²⁾

$$\eta = \frac{\lambda_1 \hbar}{\lambda_2 \lambda_3 \lambda^2} \frac{1}{K^*} \dots\dots\dots(31)$$

where λ and λ_1 are the distance between two equilibrium positions in the direction of motion and the one between two shear planes, respectively; $\lambda_2 \lambda_3$ is average area per molecule in the shear plane and K^* is an equilibrium constant between the initial state and the activated state.

H. Pak⁽²¹⁾ has given the latter as follows:

$$K^* = \exp \left(-\frac{\Delta G^*}{RT} \right) = \exp \left(\frac{\partial \ln Q}{\partial N} - \frac{\partial \ln Q^*}{\partial N} \right) \dots\dots\dots(32)$$

where Q and Q^* are the partition functions for the initial state and for the activated state, respectively, and in the latter the translational degree of freedom in the direction of the motion is missed. The partition function for the activated state can be expressed as

$$Q^* = \frac{(N_x)!}{\left[N\frac{1}{x}\right]! \left[Nx-N\frac{1}{x}\right]!} \left[\frac{e^{\frac{E_s-E_a}{RT}}}{(1-e^{-\theta/T})^3} \cdot b_s \right]^{\frac{1}{x}N}$$

$$\left[\frac{2\pi mkT}{h^2} \cdot \frac{(V-V_g)}{\lambda_1} \cdot b_g \right]^{(1-\frac{1}{x})N} \frac{1}{\left[N(1-\frac{1}{x})\right]!} \dots\dots\dots(33)$$

where E_a is the molar activation energy, which is assumed to be proportional to the number of the neighboring molecules, i. e.,

$$E_a = \epsilon \cdot \frac{1}{x} \dots\dots\dots(34)$$

ϵ being the proportionality constant. Assuming $\lambda_1 = \lambda_2 = \lambda_3 = (V/N)^{1/3}$ and $\lambda = 2^{1/6}(V/N)^{1/3}$, which is the shortest distance between the molecules in the closest packing, the viscosity of the liquid is given by

$$\eta = \frac{hN}{2^{1/3}V} \left[\frac{e^{\frac{\epsilon}{xRT}}}{1-e^{-\theta/T}} \right]^{\frac{1}{x}} \left[\frac{(2\pi mkT)^{1/2}}{h} V^{1/3} \right]^{(1-\frac{1}{x})} \dots\dots\dots(35)$$

or

$$\ln \eta = -3 \ln 10 + 1.15287 - \frac{2x+1}{3x} (\ln V_s + \ln x) + \frac{1}{x} \left\{ -\ln(1-e^{-\theta/T}) + (x-1)(-2.69086 + \frac{1}{2} \ln M + \frac{1}{2} \ln T) \right\} + \frac{\epsilon}{x^2 RT} \quad (\eta \text{ in poise}) \dots\dots\dots(35-a)$$

where M is the molecular weight.

The viscosities for various liquids are calculated at various temperatures by using equation (35) and compared them with the experimental data in Table 3.

TABLE 3. The Viscosity of Liquid at Various Temperatures.

Temperature, (°K)	Viscosity $\times 10^3$ (poise), Calc.	Obs. ¹⁰	$\Delta\%$
1. Argon. $\epsilon=456.9$ cal			
83.96	2.86	2.86 ²²	0.00
87.49	2.53	2.51	0.80
97.76	1.84	1.82	1.10
2. Benzene. $\epsilon=2402.1$ cal			
278.675	8.157	8.157	0.00
328.15	4.135	4.115	0.49
353.25	3.183	3.167	0.51
423.15	1.851	1.801	2.78
3. Acetone. $\epsilon=1847.4$ cal			
178.35	23.76
273.15	3.950	3.950	0.00
329.35	2.353	2.326	1.16
373.15	1.783	1.656	7.67
4. Chloroform. $\epsilon=1979.6$ cal			
209.65	21.38
273.15	6.985	6.985	0.00
334.35	3.716	3.854	-3.58
373.15	2.817	2.862	-1.57
5. Carbon disulfide. $\epsilon=1556.9$ cal			
223.15	7.482	*6.884	8.69
273.15	4.294	4.294	0.00
319.40	3.083	3.053	0.98
373.15	2.372	*2.210	7.33
6. Chlorine. $\epsilon=1447.7$ cal			
172.12	11.93	*10.05	18.7
193.15	7.58	7.58	0.0
239.05	3.88	*4.81	-19.3
273.15	2.79	*3.92	-28.8

7. Ammonia. $\epsilon=1409.3$ cal

195.45	5.11
213.15	3.75
239.75	2.60	2.60	0.00
253.15	2.24

8. Water. $\epsilon=3113.3$ cal

273.15	17.938	17.938	0.00
293.15	11.467	10.087	13.68
333.15	5.409	4.699	15.11
373.15	2.981	2.839	5.00

* The extrapolated value,

The viscosity of liquid water is calculated by using the following equation:

$$\ln \eta = -3 \ln 10 - 0.23343 - \frac{2x^* + 1}{3x^*} (\ln V_s + \ln x^*) + \frac{1}{x^*} \left\{ -\ln(1 - e^{-\theta/T}) + (x^* - 1)(-2.69086 + \frac{1}{2} \ln M + \frac{1}{2} \ln T) \right\} + \frac{\epsilon}{x^{*2} RT}$$

(η in poise).....(35-b)

In equation (35-b), $\lambda_1 = \lambda_2 = \lambda_3 = (V^*/N)^{1/3}$ and $\lambda = w \cdot 2^{1/6} \cdot (V^*/N)^{1/3}$ are assumed, where w is a parameter which is taken equal to 2.

III. Discussion.

In Eyring's significant liquid structure theory, an ambiguous positional degeneracy factor has been included, which has been debated by many workers^(7,8). The difficult problem is solved in this paper, and the new partition function derived is applicable not only to the thermodynamic property but also to the transport property.

The calculated values of the properties and the experimental data are in excellent agreements at the various temperatures covering the whole liquid range.

W. Ahn *et al.*⁽²³⁾ have applied their liquid theory to binary liquid system correcting the ground state energy of the system. The similar method can also be used to derive the partition function for the binary liquid system by using equation (9).

In general, the partition function for n -component liquid system can be expressed as

$$Q = \frac{[Nx]!}{\prod_{i=1}^n \left[\left(\frac{x_i}{x} \right)! \left(Nx - Nx \frac{1}{x} \right)! \right]}$$

$$\prod_{i=1}^n \left\{ \left[\frac{e^{E_{ii}/RT}}{(1-e^{-E_{ii}/RT})^3} \cdot b_{ii} \right]^{\xi_i \frac{1}{2}N} \cdot \left[\frac{(2\pi m_i kT)^{3/2}}{h^3} \frac{eV}{\xi_i N} \cdot b_{gi} \right]^{\xi_i (1-\frac{1}{2})N} \right\} \dots (36)$$

where ξ_i is the mole fraction of the component i in the solution and $x=V/V_s$, V and V_s being the total molar volume of the solution and the mean molar volume of the solids,

$$V_s = \sum_{i=1}^n \xi_i V_{si} \dots (37),$$

respectively.

θ_i , b_{ii} , and b_{gi} are the same ones as in equation(9) for the component i of the solution.

The ground state energy of the solid-like molecules of the component i in the solution, E_{ii} , can be given as follows;

$$E_{ii} = \xi_i^2 E_{ci} + \sum_{j=1}^n \xi_i \xi_j E_{cij} + \xi_i a_i \cdot \frac{x-1}{x^2} \dots (38)$$

where E_{cij} is the interaction energy between the neighboring molecules of the components i and j , which can be determined by using the equilibrium condition between the liquid solution and the vapor at a chosen temperature,

$$\mu_i(l) = \mu_i(g) \dots (39)$$

where $i=1, 2, \dots, n$.

From equations (1) through (6) and equation (36), the rate constant for the chemical reaction can be determined.

This is not a final research on the chemical kinetics in liquid solution. Further studies on the multi-component liquid system and on the reaction mechanism have to be done.

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