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A Theory of Liquid

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요 약. 액체분자는 고체와 같은 그리고 기체와 같은 자유도를 가진다는 가정하에 액체의 상태합을 유도하였다. 이 상태합을 아르곤, 염소, 암모니아, 벤젠 등의 액체에 적용하여 이들 액체의 열역학적 성질들을 계산한 결과가 실험치와 잘 일치하였다.

ABSTRACT. A theory of liquid is proposed by assuming that the molecules in the liquid state have the solid-like and the gas-like degrees of freedom. The calculated values of the thermodynamic properties of argon, chlorine, ammonia and benzene are in good agreements with those of the observed values.

INTRODUCTION

The liquid state has long been regarded as presenting the least tractable of all problems in the field of statistical mechanics. For the description of the liquid state, various theories have been proposed. The radial distribution function theory¹ is the formal one, but because of the mathematical complications it is difficult to apply the theory to the actual problems of the liquid state. As the model approach to the liquid state, there are free volume theory², quasi-lattice theory³, and the significant structure theory⁴. Among the above theories the last one developed by Eyring, Ree and Hirai has been proved to be very useful in calculation of the various physical properties of the liquids, though it has some theoretical defects. The theory has been

improved by Chang *et al.*^{5,6}, and Pak⁷ improved it further by assuming that the solid-like and the gas-like molecules exist in the liquid. In the present paper, Pak's theory of liquid is modified and a new theory of liquid is presented.

THEORY

The experimental data of X-ray diffraction⁸ indicates that the arrangement of the molecules in the liquid keeps short range order with about the same intermolecular distance in the solid. However, about ten percent volume increment is observed when the solid melts to form the liquid. From the above and some other experimental facts, it is assumed that $N(V - V_s)/V_s$ of molecular size holes are introduced at random in one mole of the liquid, where N is the Avogadro's number; V , the molar volume of the

liquid at the temperature under consideration; and V_s , the molar volume of the solid-like molecule which is assumed to vibrate at the equilibrium position as if they were in the solid state.

However, the value of V_s is not necessarily equal to the molar volume of the solid. As the holes are introduced during the melting process, some structural change occurs, i.e., some molecular rearrangement should occur keeping the intermolecular distance about the same with that in the solid. If $N(V-V_s)/V_s$ holes are distributed at random, there are $N(V-V_s)/V_s + N = N(V/V_s) = N_s$ sites in a mole of the liquid. Since the intermolecular force in the liquid is the short range one, the $N(V/V_s)$ sites should have the closest packing structure, that is, each of the site is coordinated by twelve nearest neighbors. Therefore, the site is surrounded by $12N/N(V/V_s) = 12(V_s/V)$ molecules and $12(V-V_s)/V$ holes in average to the nearest neighbor of the site.

Since the molecules have constant thermal motion, the molecule may jump into one of the neighboring holes. The jumping molecules have the gas-like degrees of freedom, and they can move around in the volume $(V-V_s)$ under the potential energy E_g . This potential energy is assumed to be proportional to $(V_s/V)^2$, e.i., $E_g = \epsilon(V_s/V)^2$, where ϵ is the proportionality constant. The total number of the gas-like molecules is equal to $N(V-V_s)/V \approx N_g$. And the remaining molecules $N(V_s/V) = N_s$ vibrate just like the Einstein oscillators, having solid-like degrees of freedom. Since the N_s solid-like molecules are distributed at the N_s sites, there are $N_s C_{N_s}$ ways of distributions.

The partition function of the liquid is then given as follows.

$$Q = N_s C_{N_s} \left[\frac{b_s e^{E_s/RT}}{(1 - e^{-\theta/T})^3} \right]^{N_s} \left[\frac{b_g (2\pi m k T)^{3/2}}{h^3} \right]^{N_g} \frac{1}{N_g!} \quad (1)$$

where E_s and θ are the ground state energy of the solid-like molecule and the Einstein characteristic temperature, respectively. And b is the product of the molecular rotational and the internal partition functions; here, the subscripts s and g stand for the solid-like and the gas-like molecules, respectively⁷.

CALCULATION of the THERMODYNAMIC PROPERTIES

Various thermodynamic properties are obtainable from the following equation.

$$A = -kT \ln Q \quad (2)$$

The parametric values E_s , θ and ϵ can be found at the triple point by the use of the following equations.

$$p = - \left(\frac{\partial A}{\partial V} \right)_{T, N} \quad (3)$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V, N} \quad (4)$$

$$A + pV = A_g + pV_g \quad (5)$$

where A_g and V_g are the Helmholtz free energy and the molar volume of the vapor which is in thermal equilibrium with the liquid, and the values may be found from the partition function of the ideal gas.

As the liquid has a high fluidity compared with that of the solid it can be assumed that, at the least one neighboring site of the molecule is occupied by a hole, and therefore the number of the gas-like molecules should not be less than $N(1/12)$. At the triple point, the lowest temperature that liquid can exist, $N_g = N(V-V_s)/V \approx N(1/12)$ is assumed, accordingly $V_s = V(11/12)$ is obtained. Here, V is the molar volume of the liquid at the triple point.

By using all of the above equations the molar volume of the liquid, the vapor pressure and the entropy of vaporization can be calculated. The

critical point properties are found from the following relations.

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N}, \quad \left(\frac{\partial P}{\partial V}\right)_{T,N} = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T,N} = 0 \quad (6)$$

RESULTS and DISCUSSIONS

The triple point properties, the normal boiling point properties, and the critical point properties of argon, chlorine, ammonia and benzene are calculated. The results are compared with the observed values^{9,10} in the *Table 1*, where the subscripts *t*, *b* and *c* stand for the triple point, the normal point and the critical point, respectively. In the *Table 1*, the numerical values in the parentheses are the observed values. The calculated parametric values are also given in

the *Table 1*.

The calculated values of the thermodynamic properties are in good agreements with those of the observed values. In calculating the properties, the vapor which is in equilibrium with the liquid is assumed to behave ideal. However, if the theory of liquid is extended to the vapor, the more excellent results could be expected.

The value of *V*, calculated is slightly greater than the molar volume of the solid as shown in the *Table 2*. This fact indicates a slight lattice expansion during the melting process besides the introduction of holes.

In calculating the thermodynamic properties, the rotational partition functions of the solid-like molecules of chlorine, ammonia and benzene

Table 1. Thermodynamic properties.

	Argon	Chlorine	Ammonia	Bbenzene
T_t (°K)	(83.96)	(172.12)	(195.45)	(278.675)
p_t (atm)	(0.6739)	(0.01374)	(0.0605)	(0.04718)
V_t (cm ³)	(28.03)	(41.57)	(23.20)	(87.29)
$\Delta S_{v,t}$ (eu)	(19.43)	(31.69)	(30.94)	(29.78)
T_b (°K)	(87.49)	(239.05)	(239.75)	(353.25)
p_b (atm)	0.9982	0.9848	0.9810	0.9724
V_b (cm ³)	28.51 (28.69)	46.66 (45.45)	25.00 (24.98)	96.78 (95.92)
$\Delta S_{v,b}$ (eu)	18.36 (18.65)	20.52 (20.41)	23.45 (23.24)	21.16 (20.83)
T_c (°K)	144.9 (150.7)	436.9 (417.2)	445.5 (405.5)	583.5 (562.2)
p_c (atm)	43.24 (48.0)	94.68 (76.1)	172.0 (111.3)	59.35 (48.6)
V_c (cm ³)	87.53 (75.3)	137.0 (123.8)	77.33 (73.0)	285.6 (260.5)
E_t (cal/mole)	1,721	6,038	6,355	9,627
ϵ (cal/mole)	195	2,457	2,362	2,797
θ (°K)	40.94	43.41	155.0	46.57

Table 2. Comparison of the molar volume of the solid-like molecule with that of the solid.

	Argon	Chlorine	ammonia	benzene
V_s of the solid-like	25.69	38.11	21.27	80.02
V_s of the solid	24.98	37.32	20.57	77.00

are approximated to those of the oscillators, and the vibrational frequencies are taken as the same values of the lattice vibrations of the respective solid-like molecules. The rotational partition function of the gas-like molecules are taken as those of the rigid free rotators.

REFERENCES

1. J. G. Kirkwood, *J. Chem. Phys.*, **3**, 300 (1935).
2. I. Prigogine, "The molecular theory of solutions," North Holland Pub. Co., Amsterdam, 1957.
3. T. L. Hill, "Statistical Mechanics," McGraw-Hill Book Co. Inc., New York, 1956.
4. H. Eyring, T. Ree and N. Hirai, *Proc. Nat. Acad. Sci.*, **44**, 683 (1958).
5. S. Chang, H. Pak, W. Paik, S. Park, M. Jhon and W. Ahn, *J. Korean Chem. Soc.*, **8**, 33 (1964).
6. H. Pak, W. Ahn and S. Chang, *ibid.*, **10**, 18 (1966).
7. H. Pak, *ibid.*, **132**, 63 (1969).
8. A. Eisenstein and N. S. Gingrich, *Phys. Rev.*, **62**, 261 (1942); N. S. Gingrich, *Rev. Mod. Phys.*, **15**, 90 (1943).
9. International Critical Tables of Numerical Data, Physics, Chemistry and Technology, National Research Council, U.S.A., McGraw-Hill Book Co. Inc., 1933.
10. N. A. Lange, "Handbook of Chemistry," 9th Ed., Handbook Pub. Inc., Sandusky, Ohio, 1965.