Modified Theory of Significant Liquid Structure

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H. Eyring 의 액체구조 이론에 대한 새로운 고찰

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요 약

최근에 H. Eyring 과 그의 공동연구자들은 "Significant liquid structure theory"를 제안하여 여러가지 액체에 대하여 잘 적용됨을 보여오고 있다 [3]-[12]. 그들은 고체와 액체 내부의 고체상분자는 하나의 연속된 상을 이룬다고 보고 고체의 몰부피와 후자의 몰부피 V, 는 같다고 보았으나 Einstein 특성온도 θ 나 승화열 E, 등은 서로 다른 값을 취하지 않으면 않되었을 뿐더러 가장 안정한 분자 주위에 모여 올 수 있는 자리수 n 가 12 보다 크게 되는 등의 실제적으로 생각하기 어려운 결과를 내놓았다.

그러나 우리는 고체상의 분자와 액체내부의 고체상분자와는 일반적으로 서로 다른 상태를 이루고 있으리라는 생각을 히여 액체가 존재하는 가장 낮은 온도 즉 삼중점을 액체의 기저상태로 보고 이점에서 parameter 들을 정하였다. 이와같이 하여 정한 V, 는 고체의 경우보다 약간 크고 θ 나 E, 는 약간 작은 값이 나타나게 되었고 n 도 12 보다 작은 값이 나왔다. 이것은 실제적으로 매우 타당한 결과이며 또 이들을 써서 여러가지 열역학적인 양을 계산한 결과는 우리가 취급한 모든 물질들에 대하여 실측치와 좋은 일치를 보여주고 있다.

It is well known that the liquid density is intermediate in a temperature range between that of solid and vapor except the substances such as water.

X-ray analysis shows that the distance between the nearest neighboring molecules in liquid state is about, but not exactly, the same within the solid state [1] [2].

The significant liquid structure, which was proposed by H. Eyring and co-workers, is very helpful to illustrate the various properties of liquids [3]-[12]. They assumed that the liquid may possess movable vacancies of molecular size, which confer gas-like properties on a neighboring molecule jumping into them, and that a solid-like molecule obtains a positional degeneracy equal to the number of neighboring vacancies. Assuming the random distribution of vacancies, they have obtained the two fractions of gas-like and solid-like molecules as $(V-V_s)/V$ and V_s/V, respectively. And the average number of vacancies next to a molecule is

$Z(V-V_s)/V = (ZV_s/V) \cdot (V-V_s)/V_s \equiv n(V-V_s)/V_s$,
where V and V_s are respectively the molar volumes in liquid and in solid state and Z is the number of nearest neighbors[8].

The value Z cannot be greater than 12. But previous papers on this subject[3]-[14] have assumed it as an adjustable parameter, and the values for some liquids had to be greater than 12.

The authors have assumed that in a melting process not only vacancies are introduced in the lattice as other workers previously assumed, but also the solid structure undergoes slight changes.

Thus, we take the triple point as the ground state of a liquid, so that the molar volume of solid-like structure V_s, Einstein characteristic temperature θ, the ground state energy E_s in the liquid state, which can be determined easily (see Appendix), may be different from those of solid state.

Assuming the molecules are close-packed in liquid, for the most stable position of a molecule the number of accessible sites n is $n = 12 \cdot V_s/V_t$, where V_s is the molar volume of solid-like molecule in liquid state and V_t is that of liquid at triple point. And if we assume a vacancy to be about the same with the molecular size in liquid state, the number of vacancies in a mole of liquid are $N \cdot (V-V_s)/V_s$, where V is the molar volume of liquid at various temperatures and N

is Avogadro number. Therefore, the number of vacancies accessible to the most stable position of a molecule is given by $n_k = n \cdot (V-V_s)V_s$.

Than, the liquid partition function can be written straightforwardly as follows;

$$f = \left[\frac{e^{Es/RT}}{(1-e^{-\theta/T})^3} \cdot f_{rot}{}^s \cdot f_{vib} \left\{ 1 + n_k e^{\frac{-\alpha Es}{RT n_k}} \right\} \right]^{\frac{V_s}{V}N} \cdot$$

$$\left[\frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \cdot f_{rot}{}^g \cdot f_{vib} \right]^{\frac{V-V_s}{V}N} \quad \cdots\cdots (1)$$

In the above, f_{vib} is the intramolecular vibrational partition function and, without appreciable error, can be assumed to have the same value for solid, liquid and gas state. And $f_{rot}{}^s$ and $f_{rot}{}^g$ are respectively the rotational partition function for solid-like and gas-like molecules in liquid. The rotational partition function for a rigid rotator could be used for gas-like molecule if the molecules are non-polar. The rotational partition function for solid-like molecules could be taken equal to $f_{rot}{}^g$ in a few simple liquids which have relatively high sticking coefficients like argon[3], methane[4], nitrogen[4] and carbon tetrachloride[15]. But for liquids like chlorine[6], bromine[14], iodine[14] and benzene[4] which have far less sticking coefficients, $f_{rot}{}^s$ can be approximated as f_{vib} for a harmonic oscillator, frequency of which is equal to that of the lattice.

Parameters and some thermodynamic properties for various liquids are listed in the following tables.

Table 1. Argon.

n; 10.325　　　 a; 0.11548　　　 θ; 51.384 °K　　　 Es; 1871.68 cal/mole　　　 Vs; 24.116 c.c.

Molar volume and vapor pressure.

T　°K	$V_{calc.}$ cc	$V_{obs.}$ cc (20)	% error,	P_{calc} atm	P_{obs} atm (20)	% error
83.96(Tt)	(28.03)	28.03		(0.6739)	0.6739	
87.49(Tb)	28.72	28.69	0.10	1.0218	1.0000	2.18
97.76	30.47	30.15	1.06	2.6998	2.6818	0.67
122.39	35.92	35.08	2.38	13.653	13.612	0.30

Entropy of vaporization and critical point properties

	ΔS_v at T_t e.u.	ΔS_v at T_b e.u.	T_c °K	P_c atm	V_c c.c.
calc.	(19.331)	18.111	157.82	56.895	82.00
obs. [19,20]	19.431	18.647	150.71	47.996	75.26
% error		2.87	4.72	18.5	8.96

Table 2. Nitrogen.

a; 10.938   a; 0.05017 θ; 53.740   Es; 1538.29 cal/mole   Vs; 29.154 c.c.

Molar volume and vapor pressure.

T° K	$V_{calc.}$ cc	$V_{obs.}$ cc (4)	% error,	$P_{calc.}$ atm	$P_{obs.}$ atm (3, 20)	% error
63.30(Tt)	(31.935)	31.985		(0.1268)	0.1268	
68.41	32.96	33.09	−0.39	0.3015	0.3005	0.33
77.34(Tb)	34.60	34.70	−0.29	0.9895	1.0000	−1.05
99.52	40.41	40.51	−0.25	7.251	7.37	−1.61

Entropy of vaporization and critical point properties.

	ΔS_v at Tt e.u.	ΔS_v at Tb e.u.	T_c °K	P_c atm	V_c c.c.
calc.	(23.008)	17.321	133.82	40.709	97.30
obs. [19]	23.008	17.24	126.0	33.49	90.1
% error		0.47	6.21	21.6	7.99

Table 3. Methane.

n; 11.048 a; 0.040238 θ; 71.340   °K Es; 2200.7 cal/mole   Vs; 31.060 c.c.

Molar volume and vapor pressure

T °K	$V_{calc.}$ cc	$V_{obs.}$ cc (4)	% error,	$P_{calc.}$ atm	$P_{obs.}$ atm (19)	% error
90.65(Tt)	(33.63)	33.63		(0.1154)	0.1154	
99.67	34.73	...	...	0.3303	0.3284	0.56
111.67(Tb)	36.12	37.79	−4.4	0.9954	1.0000	−0.46
123.15	37.64	39.37	−4.4	2.298	2.35	−2.24

Entropy of vaporization and critical point properties.

	ΔSv at T_t e.u.	ΔSv at T_b e.u.	T_c °K	P_c atm	V_v c.c.
calc.	(23.198)	17.514	211.29	60.59	103.83
obs. [19]	23.198	17.51	191.05	45.8	99.34
% error		0.00	10.6	32.3	4.52

Table 4. Benzene

n; 11.386 a; 0.014389 θ; 44.354   °K Es; 9636.1 cal/mole   Vs; 82.826 c.c.

Molar volume and vapor pressure.

T °K	$V_{calc.}$ cc	$V_{obs.}$ cc (4)	% error,	$P_{calc.}$ atm	$P_{obs.}$ atm (19)	% error
278.675(Tt)	(87.29)	87.29		(0.047179)	0.047179	
298.15	89.15	89.36	−0.24	0.1244	0.1252	−0.64
328.15	91.98	92.80	−0.88	0.4246	0.4302	−1.30
353.25(Tb)	94.63	95.92	−1.34	0.9834	1.0000	−1.66
373.15	97.00	98.46	−1.48	1.739	1.757	−1.02
423.15	104.44	106.8	−2.21	5.503	5.70	−3.46

Entropy of vaporization and critical point properties.

	ΔS_v at T_t e. u.	ΔS_v at T_b e. u.	T_c °K	P_c atm	V_c c. c.
calc.	(29.79)	21.05	609.11	65.80	274.2
obs. [19]	29.79	20.83	562.15	48.6	260.5
% error		1.06	8.35	35.4	5.26

Table 5. Chlorine

n; 11.676 a; 0.004675 θ; 38.479 °K   Es; 5940.3 cal/mole   Vs; 40.455 c.c.

Molar volume and vapor pressure.

T °K	$V_{calc.}$ cc	$V_{obs.}$ cc (20)	% error,	$P_{calc.}$ atm	$P_{obs.}$ atm (18)	% error
172.12 (Tt)	(41.571)	41.571		(0.01374)	0.01374	
193.15	42.624	42.584	0.093	0.07597	0.07606	−0.12
213.15	43.687	43.713	−0.059	0.2710	0.2730	−0.73
239.05 (Tb)	45.270	45.447	−0.39	0.9820	1.0000	−1.80
273.15	47.826	48.308	−1.00	3.488	3.644	−4.28

Entropy of vaporization and critical point properties.

	ΔS_v at T_t e. u.	ΔS_v at Tb e. u.	T_c °K	P_c atm	V_c c. c.
calc.	(32.676)	20.326	466.35	103.5	133.1
obs. [18,19]	32.676	20.406	417.15	76.1	123.8
% error		−0.39	11.8	36.0	7.51

Table 6. Bromine

n; 11.446 a; 0.01296 θ; 27.699 °K   Es; 8567.6 cal/mole   Vs; 47.457 c.c.

Molar volume and vapor pressure.

T °K	$V_{calc.}$ cc	$V_{obs.}$ cc (20)	% error,	$P_{calc.}$ atm	$P_{obs.}$ atm (20)	% error
265.85 (Tt)	(49.755)	49.755		(0.061053)	0.061053	
273.15	50.135	50.143	−0.016	0.08941	0.08671	3.11
293.15	51.088	51.240	−0.297	0.2256	0.2276	−0.879
303.15	51.564	51.813	−0.480	0.3402	0.3474	−2.07
323.15	52.556	52.998	−0.834	0.7112	0.7421	−4.16
331.93 (Tb)	53.012	53.536	−0.979	0.9504	1.0000	−4.96

Entropy of Vaporization and critical point properties.

	ΔS_v at Tt e. u.	ΔS_v at T_b e. u.	T_c °K	P_c atm	V_c c. c.
calc.	(28.275)	20.854	665.53	125.16	157.08
obs. [19,20]	28.275	20.784	584.15	102	135.17
% error		0.377	13.9	22.7	16.2

Table 7. Iodine

n; 11. 333   *a*; 0. 016764   *θ*; 31. 236 °K   E*s*; 13241 cal/mole   V*s*; 60. 259 c. c.

Molar volume and vapor pressure

T °K	$V_{calc.}$ cc	$V_{obs.}$ cc (16)	% error,	$P_{calc.}$ atm	$P_{obs.}$ atm (19)	% error
287. 30(T*t*)	(63. 804)	63. 804		(0. 11105)	0. 11105	
393. 15	64. 143	64. 096	0. 073	0. 13924	0. 13864	0. 433
413. 15	65. 201	65. 115	0. 132	0. 28090	0. 27961	0. 461
433. 15	66. 243	66. 341	−0. 148	0. 52650	0. 52209	0. 845
457. 50	67. 579	68. 489	−1. 33	1. 0389	1. 0238	1. 47

Entropy of vaporization and critical point properties

	ΔS_v at T$_t$ e. u.	ΔS_v at T$_b$ e. u.	T$_c$ °K	P$_c$ atm	V$_c$ c. c.
calc.	(29. 711)	23. 44	796. 45	117. 35	200. 66
obs. [19, 20]	29. 711	22. 73	785. 15	...	...
% error		3. 17	1. 44	...	...

Summary

As expected, the molar volume of solid-like molecules in the liquid state is slightly larger than in the solid state and values of E*s* and *θ* in the liquid state are less than those in the solid state. For all liquids, the calculated values of n are less than 12. This is in good agreement with what is ought to be expected from the liquid model.

For chlorine, iodine and benzene, changing in values of V*s* during a melting process are much greater than for other liquides. The change is believed too great to have resulted from a simple lattice expansion. Rather, it could be better explained by assuming that phase transition of solid state takes place during the melting process.

X-ray analysis[17] show that there are about 3 to 5% of lattice expansions in melting processes, which the results by the authers also conform. More experimental analysis of liquid structure using X-ray or other new techniques will be needed to further substantiate the lattice expension in melting process.

Appendix

The parameters E*s*, *θ*, *a*, and V*s* in the equation (1) can be obtained as following manner.

If we substitute the equation (1) into the statistical thermodynamic relation $A=-kT \cdot lnf$ and $P=\left(\frac{\partial A}{\partial V}\right)_{T, N}$,

the following equations are obtained.

$$\varphi \equiv -\frac{A}{RT}=\frac{1}{x}(\sigma+y)+\left(1-\frac{1}{x}\right)(\gamma+lnx)\cdots\cdots(2)$$

where $\sigma=\frac{Es}{RT}-3ln1-e^{-\theta/T}+lnf_{rot}{}'+lnf_{vib}$ (2a)

$$y=ln\{1+n(x-1)e^{-\omega}\}\cdots\cdots(2b)$$

$$\omega=\frac{aEs}{n(x-1)RT}\cdots\cdots(2c)$$

$$\gamma=ln\left\{\frac{(2\pi mkT)^{3/2}}{h^3}\cdot\frac{eV_s}{N}\right\}+ln\ f_{rot}{}^r$$
$$+lnf_{vib}\cdots\cdots(2d)$$

$$\text{and } x=\frac{V}{V_s}\cdots\cdots(2e)$$

$$\text{and } qx\equiv\frac{PVs}{RT}\cdot x=-\varphi+\frac{ne^{-\omega}(1+\omega)}{1+n(x-1)e^{-\omega}}+\gamma$$
$$+lnx+1-\frac{1}{x}\cdots\cdots(3)$$

Equation (3) is rearranged to

$$Q\equiv\frac{ne^{-\omega}(1+\omega)}{1+n(x-1)e^{-\omega}}-\frac{1}{x}=\varphi-(\gamma+lnx)-1+qx(4)$$

The right hand side of the equation (4), which is independent on V*s* and *a*, has a definite value at a given temperature and the value can be calculated from the experimental values of the liquid and of vapor pressure. On the other hand, the left hand side is a function of V*s* and *a*. Therefore, the condition of $\left(\frac{\partial Q}{\partial \omega}\right)_{V_s}=0$ must be satisfied at a given temperature, then

$$\omega=n(x-1)e^{-\omega}\cdots\cdots(5)$$

Introducing the equation n=12·(Vs/Vt) and the equation (5) into the equation (4), we can obtain

$$Q=(12e^{-\omega}-1)\left(1-\frac{\omega}{12e^{-\omega}}\right)\cdots\cdots(6)$$

at the triple point. From the equation (6), *ω* is solved

and then from the equtionas (5) and (2e) Vs can be calculated.

Knowing the entropy value of the liquid at the triple point, θ can be obtained from following equation which does not involve Es.

$$S=-\left(\frac{\partial A}{\partial T}\right)_{V\cdot N}=kT\frac{\partial lnf}{\partial T}+klnf\cdots\cdots\cdots(7)$$

Finally, Es is obtained from the equations (2) and (2a), and a from the equation (2c).

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Refferences

1) A Eisenstein and N. S. Gingrich, *Phys. Rev.*, **58** 307 (1940); **62** 261 (1942).

2) Clusiut K., *Z. Phys. Chem.*, **B 31**, 459(1936)

3) H. Eyring, T. Ree and Nishio Hirai, Procredings of the national academy of sciences, **44**, (7) 683 (1958).

4) E. Jack Fuller, T. Ree and H. Eyring, *ibid* **45** (11), 1594(1959).

5) Charles M. Carlson, H. Eyring and T. Ree, *ibid.*, **46**(3), 333(1960).

6) Tom R. Thnmson, H. Eyring, and T. Ree, *ibid.*, **46**(3), 336 (1960).

7) Charles M. Carlson, H. Eyring and T. Ree, ibid., **46**(5), 649 (1960).

8) H. Eyring and T. Ree, *ibid.*, **47**(4) 526 (1962).

9) Teresa S. Ree, T. Ree and H. F ring, *ibid.*, **48** (4), 501(1962).

10) Seihun Chang, T. Ree, H. Eyring and Ingrid Matzner, Progress in international research on thermodynamic and transport properties, The American Society of Mechanical Engineers. Academic press., New York, (1962).

11) H. Eyring, Douglass Henderson and T. Ree, *ibid.*, (1962)

12) H. Eyring, T. Ree, David M. Grant and Robert C. Hirst, *Z. Elek. Ber. Bunsen Phys. Chem.*, **B 64**(1), 146 (1960).

13) Hyungsuk Pak, and Seihun Chang, *J. Kor. Chem Soc.*, **7**(2), 174 (1963).

14) Hyungsuk Pak, and Seihun Chang, *ibid.*, **7**(2), 179 (1963).

15) Woon-Kie Paik and Seihun Chang, *ibid.*, in this volume.

16) J. W. Mellor, Compreh. treat. inorg. and theor. chem., Vol **I**, Longmans Green and Co., (1937).

17) See for example, D. Van Nostrand S. Glasstone, Textbook of physical chemistry (1946) p. 504-507; and Walter J. Moore; Physical chemistry, Prentice'Hall (1960), p. 415.

18) W. F. Giaque and T. M. Powell, *J. Am. Chem. Soc.*, **61**, 1970 (1939).

19) Lange's Handbook of Chemistry, 9th ed., McGrawHill, (1956).

20) International Critical Tables.