Transient State Theory of Significant Liquid Structure

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액체 구조의 천이상태 이론

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초 록

액체 내에는 분자들 주위에 분자크기의 빈자리가 들어 있게 되어 빈자리로 뛰어들면서 기체와 같은 자유도를 갖는 분자와, 빈자리에서 좀 떨어져서 고체와 같은 자유도를 갖는 분자와, 빈자리 때문에 변형에 너지를 받고서 천이상태에 있는 분자들이 있다고 가정하여 액체에 대한 상태합을 유도하여 알곤, 질소. 벤젠, 클로로포롬 및 이황화탄소의 액체상태에서의 열역학적 성질들을 계산한 결과 실측치와의 좋은 일 치를 얻었다.

Abstract

In formulating the Transient State Theory of Significant Liquid Structure it is assumed that there exist holes of molecular size in liquids and that the liquid state is partitioned in three states, namely, solid-like state, representing the molecules apart from holes; gas-like state, representing the molecules jumping into the holes; and the transient state, representing the molecules in a possible state of jumping into the holes by aquiring the strain energy due to the holes.

It is found that the partition function derived according to the proposed theory can be applied to the liquids of argon, nitrogen, benzene, chloroform, and carbon disulfide with good accuracy.

Introduction

Liquid occupies an intermediate position between solid and gas in the various thermodynamic properties and therefore, it is to be expected that the structure of liquid is either intermediate between that of solid and gas or has both of

them by some fraction.

The X-ray structural analyses of liquid[1],[2], ascertains that liquid is far from structureless. The distribution of particles within a small region about any fixed particle of a liquid is found to be partially ordered. It is also observed by X-ray studies[3] that the intermolecular distances are about the same in both states of solid and liquid.

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Since 1958, H. Eyring et al have proposed a significant structure theory of liquid[4]-[7]. The significant liquid structure theory has been applied to various liquids with success. Applying the theory, not only the various thermodynamic properties but also surface tension and transport properties of liquid can easily be calculated.

However, the significant liquid structure theory, as indicated in the next section, suffers in its theoretical formulations.

Defect of Significant Liquid Structure Theory

In the Significant Liquid Structure Theory, H. Eyring et al have assumed that vacancies of molecular size are introduced when transition from solid to liquid takes place. The introduction of a molecular-sized hole requires an energy equal to the heat of vaporization of a molecule and they assumed when a molecule jumps into the hole it may possess gas-like degree of freedom. Since $\left(\frac{V-V_s}{V_s}\right)N$ holes are distributed at random among N molecules, the gas-like fraction of the molecules becomes

$$\left(\frac{V-V_s}{V_s}\right)\frac{V_s}{V}=\frac{V-V_s}{V}$$

where V is molar volume of liquid and V_s is that of solid at melting point. And they assumed that the remaining fraction, V_s/V, may be thought of as associated with solid-like molecules, and that there exists degeneracy for solid-like molecules due to the availability of the hole in the neighborhood. They have given the positional degeneracy factor of the solid-like molecule as $1+n\frac{V-V_s}{V_s}e^{-\varepsilon/kt}$, where ε is the strain energy which is proportional to E_s and inversely proportional to the number of neighboring vacancies, $n\frac{V-V_s}{V_s}$, and n is the number of the nearest neighboring sites around a molecule in liquid state.

Then, the partition function of a monatomic liquid given by them is as follows;

$$F=\left\{\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3}\left(1+n\frac{V-V_s}{V_s}e^{n\frac{-aE_s}{V-V_s}RT}\right)\right\}^{\frac{V_s}{V}N}$$
$$\left(\frac{(2\pi mkT)^{3/2}}{h^3}\frac{eV}{N}\right)^{\frac{V-V_s}{V}N}\dots\dots\dots\dots\dots\dots\dots(1)$$

Though the maximum number of the nearest neighboring sites of a molecule cannot be greater than 12, the value n in the above equation becomes greater than 12 in some cases, especially for the substances having very low vapor pressure at the melting point, when it is taken as an adjustable parameter.

Recently, S. Chang and co-workers[8] have modified the significant liquid structure theory. In the modified significant liquid structure theory, they have assumed that n is equal to $12(V_s/V_t)$, where V_s is molar volume of solid-like molecules in liquid and V_t is molar volume of liquid at triple point. Since V_s is, in general, less than V_t, n usually does not exceed 12. However, the modified theory cannot also be applicable to the liquid of very low vapor pressure at the triple point.

Therefore, it is debatable to introduce the positional degeneracy factor, which is taken as a time average of the solid-like molecular states.

Proposed transient state theory

In view of the high density of liquid and the strong interactions among the molecules in liquid, one would expect that the transition of the degree of freedom of the molecules from the solid-like to the gas-like does not occur directly.

As the molecular-size holes are introduced into the liquid, some molecules around the holes will gain strain energy due to the structural distortion; and thus, they may have different energy states from those of the solid-like molecules.

Since $\left(\frac{V-V_s}{V_s}\right)N$ vacancies are introduced at random among N molecules, only $\frac{V_s}{V}N$ molecules are bonded each other, and accordingly, the model is expressed quantitatively as follows.

First, the α portion of the bonded molecules

have solid-like degrees of freedom which are restrained to an equilibrium position much as if they were in the solid state.

Second, the remaining $1-\alpha$ portion of the bonded molecules are in transient state, which is a different energy state from solid-like molecules due to the strain energy which is inversely proportional to the number of the vacant sites around the molecule, $n\frac{V-V_s}{V_s}$, where n is given by $12(V_s/V_t)$. The frequrncy of lattice vibration is, in general, less in transient state than in solid-like state, and both of them are less than that in solid state itself.

Third, the molecules, number of which is expressed by $\left(\frac{V-V_s}{V}\right)N$, jumping into the neighboring vacancies have much like gas-like degrees of freedom.

Then, the partition function of liquid can be given as follows:

$$F=\frac{(N_s+N_t)!}{N_s!\ N_t!}f_s^{Ns}f_t^{Nt}f_g^{Ng}\frac{1}{N_g!}$$

$$=\frac{\left(\frac{V_s}{V}N\right)!}{\left(\frac{V_s}{V}\alpha N\right)!\left(\frac{V_s}{V}(1-\alpha)N\right)!}\cdot$$

$$\left(\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^3}b_s\right)^{\frac{V_s}{V}\alpha N}\cdot$$

$$\left(n\frac{V-V_s}{V_s}\frac{e^{(Es-\varepsilon N)/RT}}{(1-e^{-\theta t/T})^3}b_t\right)^{\frac{V_s}{V}(1-\alpha)N}\cdot$$

$$\left(\frac{(2\pi mkT)^{3/2}(V-V_s)}{h^3}\cdot b_g\right)^{\frac{V-V_s}{V}N}\cdot\frac{1}{\left(\frac{V-V_s}{V}N\right)!}$$

$$\cdots\cdots(2)$$

where θ is Einstein characteristic temperature; E_s, the sublimation energy of the solid-like molecules; and b represent the partition function for the degrees of molecular rotation and interatomic vibrations; here, subscripts s, t, and g mean the states of solid-like, transient and gas-like, respectively.

Since we assume the mixing of molecules of solid-like and those of transient is random, the combinatorial factor, $\frac{(N_s+N_t)!}{N_s!\ N_t!}$, is used.

Using Stirling's approximation for the factorial, equation (2) can be rearranged as follows:

$$\ln F=\left(\frac{V_s}{V}N\right)\ln\left(\frac{V_s}{V}N\right)-\left(\frac{V_s}{V}\alpha N\right)\ln\left(\frac{V_s}{V}\alpha N\right)$$

$$-\left(\frac{V_s}{V}(1-\alpha)N\right)\ln\left(\frac{V_s}{V}(1-\alpha)N\right)+\frac{V_s}{V}\alpha N\ln f_s$$

$$+\frac{V_s}{V}(1-\alpha)N\ln f_t+\frac{V-V_s}{V}N\left(\ln f_g\right.$$

$$\left.-\ln\left(\frac{V-V_s}{V}N\right)+1\right)\cdots\cdots\cdots(3)$$

Since Helmholtz free energy, A, is minimum at the thermodynamic equilibrium, the following equation must be satisfied.

$$\left(\frac{\partial A}{\partial\alpha}\right)_{T,\ V,\ N}=-kT\left(\frac{\partial\ln F}{\partial\alpha}\right)_{T,\ V,\ N}=0\cdots\cdots\cdots(4)$$

If we differentiate the equation (3) with respect to α at constant T, V, and N, and let the result equal to zero according to the condition of equation (4), α is given by

$$\alpha=\frac{f_s}{f_s+f_t}\cdots\cdots\cdots\cdots(5)$$

The term, α, in the equation (2) is eliminated by introducing equation (5) into equation (3) and then, the partition function is given as follows.

$$F=[f_s+f_t]^{\frac{V_s}{V}N}\left(f_g\frac{eV}{(V-V_s)N}\right)^{\frac{V-V_s}{V}N}\cdots\cdots\cdots(6)$$

Equation (6) can be rewritten in detail as follows:

$$F=\left(\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^3}b_s\{1+\lambda(x-1)e^{-\frac{\alpha Es}{n(x-1)RT}}\}\right)^{\frac{1}{x}N}$$

$$\left(\frac{(2\pi mkT)^{3/2}}{h^3}\frac{eV}{N}b_g\right)^{(1-\frac{1}{x})N}\cdots\cdots\cdots(7)$$

where $\lambda=n\left(\frac{1-e^{-\theta s/T}}{1-e^{-\theta t/T}}\right)^3\frac{b_t}{b_s}$ and $x=\frac{V}{V_s}$.

The form of the partition function of equation (7) resembles to that of equation (1) except λ.

Calculation of thermodynmic properties

To use the partition function, of course, one must know the partition function for molecular rotation and interatomic vibrations. Which are expressed by the notations b_s, b_t, and b_g. Since the gas-like molecules are treated as an ideal gas, b_g can easily be known from the energy

of rigid rotator and harmonic oscillater. The energies of interatomic vibration in solid-like and in transient states are taken equal to that of harmonic oscillation in gas-like state. The frequencies of the oscillations and the moment of inertia of the rigid rotator can be found in literatures[9]-[12]. If the free rotation of a molecule in solid state is experimentally proved, such as the case of nitrogen whose entropy of fusion is 2.73 $e.u.$, the rigid rotator partition function can be used in solid-like and in transient state for the molecular rotation without appreciable error. However, an unusually high entropies of fusion of liquid; for example, 8.46 $e.u.$ for benzene, 10.87 $e.u.$ for chloroform and 6.51 $e.u.$ for carbon disulfide, may be resulted due to the hindered molecular rotations in the solid state. Therefore, it may be assumed that the molecular rotations of these substances are limited to tortional oscillation in both solid-like and transient states. Accordingly, the frequencies of the tortional oscillation are equated, approximately, to that of the respective lattice vibrations, as shown by the following equations;

$$f_s^{rot}=\frac{1}{(1-e^{-\theta_s/T})^3} \quad \text{and} \quad f_t^{rot}=\frac{1}{(1-e^{-\theta_t/T})^3}\cdots(8)$$

for benzene and chloroform and

$$f_s^{rot}=\frac{1}{(1-e^{-\theta_s/T})^2} \quad \text{and} \quad f_t^{rot}=\frac{1}{(1-e^{-\theta_t/T})^2}\cdots(9)$$

for carbon disulfide.

The parameters in the liquid partition function θ_s, θ_t, E_s and a can be fixed by using experimental values of molar volume, vapor pressure and molar heat capacity at constant volume of liquid and the entropy of vaporization at a given temperature. When the experimental value for molar heat capacity at constant volume of liquid and the precise interatomic vibrational frequencies are not available, the calculation is facilitated as shown by appendix selecting a arbitrary value of a until the best set of parameters are obtained.

Once, the parameters are determined, the various thermodynamic properties can easily be obtained from the statistical thermodynamic relations. First, the Helmholtz free energies, A, for various values of molar volumes, V, of the system are calculated from the equation

$$A=-kT\ln F\cdots\cdots(10)$$

where F is given by equation (7). When the values of A is plotted against V, a minimum appear in liquid region. A common tangential line can be drawn between the minimum region of liquid and the line of gas, whose slope corresponds to the equilibrium vapor pressure of the liquid. The volumes of liquid and gas can be obtained from the tangential points of liquid and gas, respectively.

After obtaining the two points, the vapor pressure is recalculated using the equation(11).

$$P=-\left(\frac{\partial A}{\partial V}\right)_T=kT\left(\frac{\partial\ln F}{\partial V}\right)_T$$
$$=\frac{RT}{V}\left[\frac{\lambda e^{-\omega}(1+\omega)}{1+\lambda(x-1)e^{-\omega}}-\frac{1}{x}\right.$$
$$\left.\{\sigma-\gamma+1+y-\ln x-x\}\right]\cdots\cdots(11)$$

where σ, γ, y and ω are given as follows;

$$\sigma=\frac{E_s}{RT}-3\ln(1-e^{-\theta_s/T})+\ln b_s,$$
$$\gamma=\ln\left\{\frac{(2\pi mkT)^{3/2}}{h^3}\frac{eV_s}{N}\right\}+\ln b_s,$$
$$y=\ln\{1+\lambda(x-1)e^{-\omega}\},$$

and $\omega=\dfrac{aE_s}{n(x-1)RT}$

Results

The calculated parameters and molar liquid volumes, V in cc, vapor pressures, P in atm. and entropies, ΔS_v in $e.u.$ are listed in the following tables for argon, nitrogen, benzene, chloroform and carbon disulfide, respectively.

Discussion

The Significant Liquid Structure Theory by H. Eyring et al can be applied to many liquids with fair accuracy. However, in formulating the liquid partition function according to the theory there are a few debatable points especially in the introduction of positional degeneracy term.

It has been argued against the fact that the

Table I　Argon

T °K	$V_{calc.}$	$V_{obs.}$ [14]	Δ%	$P_{calc.}$	$P_{obs.}$ [14]	Δ%	$ΔS_{v.calc.}$	$ΔS_{v.obs.}$	Δ%
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)	28.47	28.69	−0.77	1.023	1.000	2.30	18.25	18.65	−2.14
97.76	29.97	30.15	−0.60	2.730	2.682	1.79	15.42	—	—
122.39	35.49	35.08	1.17	13.97	13.61	2.65	9.87	—	—

$θ_s$; 47.65 °K　$θ_t$; 47.33 °K　a; 0.006152　E_s; 1771 cal/mole　(V_s;24.98cc[5])　(n; 10.69[5],[8])

Table II　Nitrogen

T °K	$V_{calc.}$	$V_{obs.}$ [5]	Δ%	$P_{calc.}$	$P_{obs.}$ [5]	Δ%	$ΔS_{v.calc}$	$ΔS_{v.obs}$ [5]	Δ%
63.14(T_t)	32.37	31.95	1.31	0.1284	0.1237	3.80	22.59	23.01	−1.83
68.41	33.16	33.09	0.22	0.3078	0.3005	2.43	20.34	—	—
77.34(T_b)	(34.70)	34.70	0.00	(1.000)	1.000	0.00	(17.24)	17.24	0.00
99.52	40.41	40.51	−0.25	7.10	7.37	−3.80	11.05	—	—

$θ_s$; 54.18 °K　$θ_t$; 50.05 °K　a; 0.02066　E_s;1507 cal/mole　(V_s;29.31cc[5])　(n;11.01[5],[8])

Table III　Benzene[11],[12]

T °K	$V_{calc.}$	$V_{obs.}$ [5]	Δ%	$P_{calc.}$	$P_{obs.}$ [13]	Δ%	$ΔS_{v.calc.}$	$ΔS_{v.obs.}$ [13]	Δ%
278.675(T_t)	(87.29)	87.29	0.00	(0.04718)	0.04718	0.00	(29.78)	29.78	0.00
328.15	92.78	92.80	−0.02	0.4214	0.4302	−2.09	23.44	23.40	0.17
353.25(T_b)	95.48	95.92	−0.46	0.9739	1.000	−2.61	21.00	20.83	0.80
423.15	105.0	106.8	−1.69	5.55	5.70	−2.65	15.44	14.88	3.76

$θ_s$; 54.88 °K　$θ_t$; 48.63 °K a; 0.07537　E_s; 10424 cal/mole　(V_s; 77.00cc[5])　(n; 10.56[5],[8])

Table IV　Chloroform[9]

T °K	$V_{calc.}$	$V_{obs.}$ [14]	Δ%	$P_{calc.}$	$P_{obs.}$ [14]	Δ%	$ΔS_{v.calc.}$	$ΔS_{v.obs.}$	Δ%
209.5(T_t)	73.63	72.60	1.41	0.000899	—	—	39.92	—	—
243.15	76.17	75.47	0.93	0.0134	0.0132	1.52	32.89	—	—
273.15	(78.22)	78.22	0.00	(0.0803)	0.0803	0.00	(28.28)	28.28	0.00
303.15	80.46	81.22	−0.49	0.3235	0.3237	−0.06	24.56	24.36	0.82
334.35(T_b)	83.20	84.75	−1.83	1.018	1.000	1.80	21.31	21.07	1.14
373.15	87.45	89.99	−2.13	3.129	3.197	−2.13	17.88	17.66	1.25

$θ_s$; 38.20 °K,　$θ_t$; 31.00 °K,　a; 0.05023　E_s; 10036 cal/mole　(V_s; 67.00cc[14])　(n; 11.07[8],[14])

Table V　Carbondisulfide[10]

T °K	$V_{calc.}$	$V_{obs.}$ [14]	Δ%	$P_{calc.}$	$P_{obs.}$ [14]	Δ%	$ΔS_{v.calc.}$	$ΔS_{v.obs.}$	Δ%
223.15	56.61	55.74	1.56	0.00934	0.00934	0.00	32.00	—	—
273.15	(58.88)	58.88	0.00	(0.1675)	0.1675	0.00	(24.92)	24.92	0.00
319.40(T_b)	61.39	62.27	−1.41	1.004	1.000	0.40	20.27	20.05	1.10
373.15	65.19	67.65	−3.64	4.36	4.42	−1.36	16.07	15.41	4.28
423.15	70.02	—	—	11.9	12.4	−4.03	12.81	11.77	8.84

$θ_s$; 58.94 °K　$θ_t$; 40.58 °K　a; 0.06879　E_s; 8919 cal/mole　(V_s; 49.00cc[14])　(n; 11.23[8],[14])

* (The values in the parentheses of the above tables are the observed values which are used to fix the parametric values, $θ_s$, $θ_t$, E_s and a.)

positional degeneracy term is taken as time average, while the other terms in the partition function are taken as space average.

The term, n, representing the number of nearest neighbor, which cannot exceed 12, is taken as a parameter in the liquid partition function, and the determined parameter, n, often exceed 12 as shown below. In the equation,

$$\frac{ne^{-\omega}(1+\omega)}{1+n(x-1)e^{-\omega}} = \ln\left(\frac{RT}{PV}\right) - 2$$
$$+ \frac{2PV}{RT} + \frac{V_s}{V}$$

which is derived using the equilibrium condition, $G_l=G_g$, the value for the right side can become higher than 12 for the low vapor pressure liquid, which results the value for the parameter, n, higher than 12, since $\dfrac{e^{-\omega}(1+\omega)}{1+n(x-1)e^{-\omega}}$ cannot exceed 1.

Inconsistancy for the expression of the number of holes per molecule has been pointed out. For some liquid an expression for the number of holes, $n_h = n\dfrac{V-V_s}{V_s}$, is used, while another expression, $n_h = n\dfrac{V-V_s}{V}$, is used for some other liquid.

The proposed theory eliminates the theoretical defects indicated above by assuming the existence of molecules in transient state. In this theory, the number of nearest neighbor, n, is taken as $12(V_s/V_t)$, assuming that the molecules are closely packed. Then, the number of holes per molecule, n_h, can be expressed,

$$n_h = \left(12\frac{V_s}{V_t}\right)\frac{V-V_s}{V_s}$$

The liquid partition function formulated according to this theory is applicable to various liquids with good accuracy. It is especially noted that the "*Transient Theory*" can be applied very well to the liquids of low vapor pressure at triple point, which give considerable difficulties for the application of *the Significant Liquid Structure Theory*. The value of the parameter, a, in the partition function is bigger for liquids with higher intermolecular force; and the bigger value,

a, makes the bigger difference between the values of θ_s and θ_t. This is a reasonable tendency, since the liquid molecules with higher interaction energy will have higher strain energy when it approaches a hole.

In this paper the trial and error method is used for the parameter determination; if enough experimental data to ascertain the molecular structure are available, the parameters can be fixed directly from the equilibrium conditions.

The calculated triple point for CS_2 turns out to be higher than observed value. This is probably due to the fact that the solid volume is taken for V_s, the molar volume of the solid-like molecules, in the calculation. As pointed out by S. Chang at al, the molar volume of the solid-like portion of liquid should be different from that of the solid.

Appendix

The parameter determination in the liquid partition function is shown taking monatomic liquid such as argon as an example.

From the partition function of the liquid, the following equations are derived.

$$-\frac{A}{RT}(\equiv \varphi) = -\frac{1}{x}\left[\sigma + y + (x-1)(\gamma + \ln x)\right]$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(13)$$

where $\sigma = \dfrac{E_s}{RT} - 3\ln(1-e^{-\theta_s/T})$ $\cdots\cdots\cdots$(13a)

$y = \ln\{1+\lambda(x-1)e^{-\omega}\}$ $\cdots\cdots\cdots\cdots\cdots\cdots$(13b)

$\omega = \dfrac{aE_s}{n(x-1)RT}$ $\cdots\cdots\cdots\cdots\cdots\cdots\cdots$(13c)

$\gamma = \ln\left\{\dfrac{(2\pi mkT)^{3/2}}{h^3}\dfrac{eV_s}{N}\right\}$ $\cdots\cdots\cdots\cdots\cdots$(13d)

First, the value of φ is obtained assuming the ideal behavior of gas and using the equilibrium condition of the liquid and vapor at a chosen temperature, $G_l=G_g$.

Rearranging equation(11), we can obtain

$$\frac{(e^y-1)(1+\omega)}{e^y} = (x-1)\{\varphi - (\gamma + \ln x) - 1$$
$$+ \frac{1}{x} + \frac{PV}{RT}\}\cdots\cdots\cdots\cdots(14)$$

In equation(14) the value of righthand side can

be calculated from experimental data (φ; molar volume and vapor pressure of the liquid at the temperature).

Assigning the value of ω, y is found from equation(14), and λ is obtained from equation(13b)

Then, entropy of liquid is derived from equation(13).

$$\frac{S}{R} = \frac{1}{x}\left[-3\ln(1-e^{-\theta_s/T}) + \frac{1}{e^y}\frac{3\theta_s/T\,e^{-\theta_s/T}}{(1-e^{-\theta_s/T})^3} \right.$$
$$+ \left(1-\frac{1}{e^y}\right)\frac{3\theta_s/T\,e^{-\theta_l/T}}{(1-e^{-\theta_l/T})^3} + y$$
$$\left. + \left(1-\frac{1}{e^y}\right)\omega + (x-1)(\gamma+1.5+\ln x) \right]$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(15)$$

If liquid entropy data is available, θ_s and θ_l can be found from the equation(15) and the expression

$$\lambda = n\left(\frac{1-e^{-\theta_s/T}}{1-e^{-\theta_l/T}}\right)^3$$

Then, E_s is found from equation(13) and (13a), and a is calculated from(13 c).

Since the ideal behavior of gas is assumed for the assignment of value, φ, whole procedure for the parameter determination is repeated, using the roughly determined parameters, until the value of parameters converge into constant values. This iteration is especially necessary for the liquid of high vapor pressure at the chosen temperature.

And since the value of ω is taken arbitrarily, redetermination of parameters is necessary taking other values of ω until the best parameters are obtained. This redetermination of parameters can be facilitated by using another set of experimental data of liquid at other temperature.

References

1) F. Zernicke and J. Prins, *Z. Phys.*, **41**, 184 (1927).

2) P. Debye and H. Menke, *Ergeb. d. Tech. Röntg.*, **2**, (1931).

3) A. Eisenstein and N. S. Gingrich, *Phys. Rev.*, **62**, 261 (1942).

4) H. Eyring, T. Ree and N. Hirai, *Proc. Natl. Acad. Sc.*, **44**, 683 (1958).

5) E. J. Fuller, T. Ree and H. Eyring, *ibid*, **45** 1594 (1959).

6) H. Eyring and T. Ree, *ibid*, **47**, 526 (1961)

7) Collected works of Taikye Ree, *Korean Chem. Soc.*, 507-596 (1962).

8) S. Chang, H. Pak, W. Paik, S. Park M. John and W. Ahn, *J. Kor. Chem. Soc.*, **8**, 33 (1964).

9) May Jen and David R. Lide Jr., *J. Chem. Phys.*, **36**, 2525 (1962).

10) Oliver L. I. Brown and George G. Marov, *J. Amer. Chem. Soc.*, **59**, 500 (1937).

11) G. Herzberg, *Molecular spectra and molecular structure*, D. Van Nostrand Co. Inc., (1962).

12) Robert D. Mair and Donald F. Honig, *J. Chem. Phys.*, **17**, 1236 (1949).

13) Lange, *Handbook of chemistry*, 9-th ed., McGraw-Hill Co., (1956).

14) International critical tables of numerical data, Physics, Chemistry and Technology.