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Transient State Theory of Significant Liquid Structure Applied to Nitrogen Oxides

by

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액체 구조의 천이상태이론의 질소산화물들에 대한 적용

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요 약

액체구조의 천이상태이론을 아산화질소(N_2O)와 사산화질소(N_2O_4)에 적용하여 이 액체들의 상태합을 유도하였다. 이상태합들을 써서 각 액체의 몰부피, 증기압, 증발엔트로피, 임계점에서의 성질 등, 여러 가지 열역학적 양들을 계산한 결과 모두 실험치와 좋은 일치를 얻었다.

Abstract

The transient state theory of significant liquid structure is applied to nitrous oxide and nitrogen tetroxide. The partition functions for the two liquids are derived according to the transient state theory. The various thermodynamic properties; such as, molar volumes, vapor pressures, entropies of vaporization, and critical point properties agree well with the experimental values.

Introduction

The transient state theory of significant liquid structure developed by S. Chang et al has been applied to various liquids including binary mixtures successfully[1]-[3]. This work is the further application of the theory to nitrogen oxides, N_2O and N_2O_4.

Both N_2O and N_2O_4 have anomalous physical properties in the liquid state. N_2O has a very short liquid range, an unusually high vapor pressure at the triple point, and an enormous entropy of fusion[4]. Although X-ray diffraction studies[5], and other experimental works[6]-[8] reveal that N_2O_4 molecules do not dissociate in the solid state, they dissociate to NO_2 in both gaseous and liquid states. It is also found that the degree of dissociation of N_2O_4 is far less in the liquid state than in the gaseous state. N_2O_4 molecules form symmetrical planer structures[5].

Formulation of the Partition Function

A. Theoretical Considerations

According to the transient state theory of significant liquid structure[1], the liquid possesses three kinds of degree of freedom, i.e. the solid-like, the transient, and the gas-like degrees of freedom. The proposed theory assumes that the transition of the degrees of freedom from the solid-like to gas-like takes place only through a transient state. Here, the

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transient state is such a state that molecules are in different energy state from solid-like molecules by acquiring strain energy due to the structural distortion. According to the theory, the number of holes introduced in a random fashion among N molecules, is assumed to be $N(V-V_s)/V_s$, where N, V, and V_s are Avogadro's number, the molar volume of liquid, and the molar volume of solid-like molecules, respectively; then, only $N(V_s/V)$molecules must be bonded to each other.

Therefore, among N molecules, $N(V-V_s)/V$ molecules have gas-like degree of freedom, and the remaining $N(V_s/V)$ molecules are partitioned among the solid-like and the transient degrees of freedom in such a manner that $\alpha N(V_s/V)$ and $(1-\alpha)N(V_s/V)$ are the numbers of molecules possessing solidlike and transient degrees of freedom, respectively. Here, α is a fractional number.

The strain energy, "ϵ", which is the energy difference between solid-like and transient states, is proportional to the heat of sublimation, E_s, and inversely proportional to the number of vacant sites around a molecule (in other words, the number of positional-degeneracy, $n(V-V_s)/V_s$; here, $n=12V_s/V_t$, where V_t is the molar volume of liquid at the triple point. Therefore, $\epsilon=aE_s/n(X-1)$, where $X=V/V_s$ and "a" is a proportionality constant. Accordingly, the partition function for the liquid can be written as

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

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

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

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

where "θ" is the Einstein's characteristic temperature; E_s, the sublimation energy of solid-like molecules. "b" is the partition function for molecular rotational and vibrational degrees of freedom; here, subscripts s, t, and g designate the states of solid-like, transient, and gas-like, respectively. A combinatorial factor, $(N_s+N_t)!/(N_s!N_t!)$, is used, because it is assumed that molecules of solid-like and transient are mixed in a random fashion.

Einstein's oscillator model is applied to both the solid-like and the transient states, and the gas-like molecules are assumed to behave like an ideal gas.

B. The Partition Function for N_2O

There are experimental evidences that a N_2O molecule has a linear structure and that the linear molecules of N_2O do not rotate freely in the solid state near the melting point[4],[9]. Therefore, it can be assumed that a N_2O molecule in the solid-like state or in the transient state has four vibrational degrees of freedom and its Einstein's oscillator has five degrees of freedom.

Accordingly, the partition function for liquid N_2O can be written as

$$F_{N2O}=\frac{\left[\frac{V_s}{V}N\right]!}{\left[\frac{V_s}{V}\alpha N\right]!\left[\frac{V_s}{V}(1-\alpha)N\right]!}$$

$$\left[\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^3}\prod_{i=1}^{4}\frac{1}{1-e^{-h\nu i/kT}}\right]^{\frac{Vs}{V}\alpha N}$$

$$\left(n\frac{V-V_s}{V_s}\frac{e^{(Es-\epsilon N)/RT}}{(1-e^{-\theta t/T})^3}\prod_{i=1}^{4}\frac{1}{1-e^{-h\nu i/kT}}\right)^{\frac{Vs}{V}(1-\alpha)N}$$

$$\left(\frac{(2\pi mkT)^{3/2}(V-V_s)}{h^3}\frac{8\pi^2/kT}{h^2}\right.$$

$$\left.\prod_{i=1}^{4}\frac{1}{1-e^{-h\nu i/kT}}\right]^{\frac{V-Vs}{V}N}\frac{1}{\left[\frac{V-V_s}{V}N\right]!} \quad (2)$$

C. The Partition Function for N_2O_4

N_2O_4 molecules do not dissociate in the solid state. In the liquid state, they dissociate somewhat; however, the degree of dissociation for liquid N_2O_4 is negligibly small compared with gaseous N_2O_4. Therefore, in formulating the partition function for N_2O_4 liquid, the dissociation of gas-like molecules is considered only. In consideration of the dissociation of gas-like molecules, the following equilibrium can be assumed.

$$N_2O_4 \rightleftharpoons 2NO_2$$
$$1-z \qquad 2z$$

where z is the degree of dissociation. Therefore, the gas-like degrees of freedom is partitioned by $(1-z)\cdot(V-V_s)/V$ for N_2O_4 and $2z(V-V_s)/V$ for NO_2.

The nitrogen dioxide molecule has two electronic degeneracies and two symmetry numbers, while N_2O_4

molecule has four symmetry numbers only[5]. In the solid like and the transient states, the N_2O_4 molecule has 12 vibrational degrees of freedom and its Einstein's oscillator has 6 degrees of freedom.[11),(12)]

Accordingly, the partition function for N_2O_4 can be written as

$$F_{N2O4}=\frac{\left[\frac{V_s}{V}N\right]!}{\left[\frac{V_s}{V}\alpha N\right]!\left[\frac{V_s}{V}(1-\alpha)N\right]!}\left(\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^6}\prod_{i=1}^{12}\frac{1}{1-e^{-h\nu i/kT}}\right)^{\frac{V_s}{V}\alpha N}\left(\frac{V-V_s}{n\frac{V_s}{V}}e^{(Es-\varepsilon N)/RT}\frac{}{(1-e^{-\theta t/T})^6}\prod_{i=1}^{12}\frac{1}{1-e^{-h\nu i/kT}}\right)^{\frac{V_s}{V}(1-\alpha)N}\left[\frac{(2\pi mkT)^{3/2}(V-V_s)}{h^3}\frac{\pi^{1/2}(8\pi^2kT)^{3/2}(IAI_BI_C)^{1/2}}{4h^3}\prod_{i=1}^{12}\frac{1}{1-e^{-h\nu i/kT}}\right)^{\frac{V-V}{V}(1-z)N}\frac{1}{\left[\frac{V-V_s}{V}(1-z)N\right]!}\left[g\frac{(2\pi m'kT)^{3/2}(V-V_s)}{h^3}\frac{\pi^{1/2}(8\pi^2kT)^{3/2}(IA'I_B'I_C')^{1/2}}{2h^3}e^{-D/RT}\prod_{i=1}^{3}\frac{1}{1-e^{-h\nu i'/kT}}\right)^{\frac{V-V_s}{V}2zN}\frac{1}{\left[\frac{V-V_s}{V}2zN\right]!} \tag{3}$$

where D is dissociation energy at the ground state; g, the electronic degeneracy of NO_2 m', IA', I_B', I_C', and ν_i' are molecular mass, three moments of inertia and vibrational frequencies for NO_2 molecules, respectively.

Determination of Parameters

Since the free energy of a system becomes minimum at equilibrium, the following relationship can be obtained.

$$\alpha=\frac{f_s}{f_s+f_t} \tag{4}$$

Substituting equation (4) into equations (2) and (3), the following equations can be obtained.

$$F_{N2O}=\left[\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^5}\{1+\lambda(x-1)e^{-aEs/n(x-)RT}\}\prod_{i=1}^{4}\frac{1}{1-e^{-h\nu i/kT}}\right]^{\frac{1}{x}N}\left[\frac{(2\pi mkT)^{3/2}}{h^3}\frac{eV}{N}\frac{8\pi^2/kT}{h^2}\prod_{i=1}^{4}\frac{1}{1-e^{-h\nu i/kT}}\right]^{\left(1-\frac{1}{x}\right)N} \tag{5}$$

where $\lambda=n\left(\frac{1-e^{-\theta s/T}}{1-e^{-\theta t/T}}\right)^5$

$$F_{N2O4}=\left[\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^6}\left\{1+\lambda(x-1)\ e^{\frac{-aEs}{n(x-1)RT}}\right\}\prod_{i=1}^{12}\frac{1}{1-e^{-h\nu i/kT}}\right]^{\frac{1}{x}N}\left[\frac{f_g\cdot e}{(1-z)N}\right]^{\left(1-\frac{1}{x}\right)(1-z)N}\left[\frac{f_g'e}{2zN}\right]^{\left(1-\frac{1}{x}\right)2zN} \tag{6}$$

where $\lambda=n\left(\frac{1-e^{-\theta s/T}}{1-e^{-\theta t/T}}\right)^6$

$$f_g=\frac{(2\pi mkT)^{3/2}V}{h^3}\frac{\pi^{1/2}(8\pi^2kT)^{3/2}(IAI_BI_C)^{1/2}}{4h^3}\prod_{i=1}^{12}\frac{1}{1-e^{-h\nu i/kT}}$$

$$f_g'=g\frac{(2\pi m'kT)^{3/2}V}{h^3}\frac{\pi^{1/2}(8\pi^2kT)^{3/2}(IA'I_B'I_C')^{1/2}}{2h^3}\prod_{i=1}^{3}\frac{1}{1-e^{-h\nu i'/kT}}e^{-D/RT}$$

From equation (5), the parameters for N_2O are determined at the triple point according to the method developed by S. Chang et al[1].

From thermodynamic equilibrium condition,

$$\left(\frac{\partial A}{\partial z}\right)_{N\cdot V\cdot T}=-kT\left(\frac{\partial \ln F_{N2O4}}{\partial z}\right)_{N\cdot V\cdot T}=0 \tag{7}$$

the following expression is obtained.

$$\frac{f_g'^2}{f_g}=\frac{(2z)^2}{1-z}N \quad \text{or} \quad \left(\frac{f_g'}{2z}\right)^2\frac{1}{N}=\frac{f_g}{1-z} \tag{8}$$

Rewritting equation (8),

$$\ln\frac{(2z)^2}{1-z}=-\frac{2D}{RT}+3\ln T+\ln V+\sum_{i=1}^{12}\ln(1-e^{-h\nu i/kT})-2\sum_{i=1}^{3}\ln(1-e^{-h\nu i/kT})+K \tag{9}$$

where

$$K=\ln\left\{g^2\frac{(2\pi k)^{3/2}}{h^4N^{5/2}}\left(\frac{M'}{2}\right)^{3/2}\frac{\pi^{1/2}\ (8\pi^2k)^{3/2}}{h^3}\frac{IA'I_B'I_C'}{(IAI_BI_C)^{1/2}}\right\}$$

Since, equation (9) holds for the vaper phase, the dissociation energy for gaseous N_2O_4 can be calculated by the use of equation (9), substitution V_g and z_g for V and z, respectively. The value for V_g is calculated from the expression, $V_g=(1+z_g)RT/P$ (the ideal gas equation); and the literature value[13] for z_g, 0.08737, is used for the calculation. The dissociation energy thus obtained is 6593 cal./mole.

Introducing equation (8) into equation (6), we obtain

$$F_{N2O_4}\left[\frac{e^{Es/RT}}{(1-e^{-\theta s/T})^6}\left\{1+\lambda(x-1)e^{-\frac{aEs}{n(x-1)RT}}\right\}\right.$$

$$\left[\prod_{i=1}^{12}\frac{1}{1-e^{-h\nu i/kT}}\right]^{\frac{1}{x}N}\left[f_g\frac{e^z}{1-z}\right]^{(1-\frac{1}{x})N} \qquad (10)$$

Assigning appropriate value for E_s in equation (10), the parameters for N_2O_4 are obtained according to the method developed by S. Chang and et al[1].

The literature values used for parameter determinations are:

For N_2O:

T_b, Boiling point 183.65° K[14]

V_s, Molar volume of solid-like molecules 28.18 cc/mole[15]

V, Molar volume of liquid at b. p. 35.90 cc/mole[14]

$\Delta H_{vap.}$, Heat of vaporization 90.1 cal/gram[16]

I, Moment of Inertia[17] 66.0×10^{-40} gr.$-$cm^2

For N_2O_4:

V_s, Molar volume of solid-like molecules 47.09 cc/mole[5]

V_t, Molar volume of liquid at triple pt. 60.82 cc/mole[18]

P_t, Vapor pressure at triple pt. 0.1839 atm.[11]

T_t, Triple point temp. 261.95° K[11]

$I_A'I_B'I_C'^{11} = 1.44\times10^{-116}$ gr^3.$-$cm^6

$I_AI_BI_C^* = 8.798\times10^{-114}$ gr^3.$-$cm^6

*This is calculated from the molecular structure[5].

The parameters thus obtained are

For N_2O	For N_2O_4
$\theta_s = 64.83$°K	$\theta_s = 60.92$°K
$\theta_t = 54.70$°K	$\theta_t = 45.80$°K
$E_s = 5478$ cal/mole	$E_s = 1.060\times10^4$cal/mole
$a = 0.1725$	$a = 0.2531$

Calculation of Thermodynamic Properties

A. Vapor Pressures and Molar Volumes

Using the expression,

$$A = -kT\ln F \qquad (11)$$

the curve for Helmholtz free energy vs volume is plotted at a constant temperature as shown in Figure 1. The values for z appeared in the partition function for N_2O_4, equation (3), at constant temperature are calculated from equation (9) at various values of V.

Then, the negative slope of the common tangential line between the liquid region (at the vicinity of liquid minimum) and the gaseous region will give the vapor pressure at the given temperature. And the tangential point at the liquid region will give the molar volume at the temperature. Good agreements between calculated values and literature values are observed as shown in Tables 1 and 2.

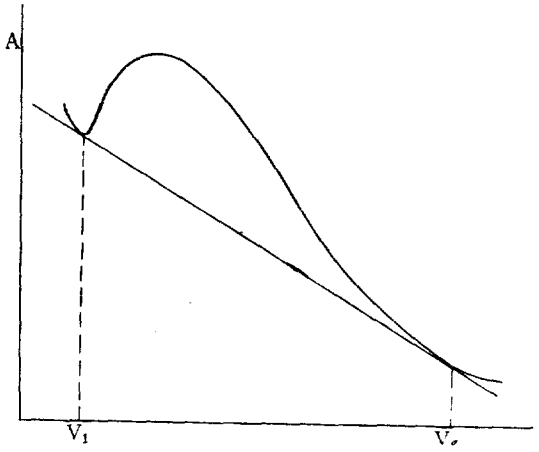

Figure 1. Plot for Helmholtz Free Energy vs Volume

Table 1. Molar Volume and Vapor Pressure for N_2O

T°K	V c. c. /mole			P atm.		
	Calc.	Obsd[14]	Δ%	Calc.	Obsd[14]	Δ%
182.25(T. P.)	35.71	(35.79)	−0.22	0.919	0.920	0.11
183.65(B. P.)	35.90	35.90	0.00	1.000	1.000	0.00
203.15	37.86	37.62	0.64	2.83	2.81	0.71
223.15	40.03	39.73	0.76	6.65	6.60	0.76
243.15	42.68	42.33	0.83	13.4	13.3	0.75
263.15	46.15	45.96	0.41	23.9	24.0	0.42

Table 2. Molar Volume and Vapor Pressure for N_2O_4

T°K	V c. c. /mole			P atm.		
	Calc.	Obsd[18]	Δ%	Calc.	Obsd[11]	Δ%
261.95(T. P.)	60.82	(60.82)	0.00	0.1845	0.1839	0.38
273.15	62.44	61.76	1.10	0.3413	0.3453	−1.12
283.15	63.62	62.64	1.56	0.5676	0.5822	−2.51
294.30(B. P.)	64.80	63.63	1.84	0.9660	1.000	−3.40
303.15	65.74	—	—	1.436	1.488[19]	3.49
313.15	66.77	—	—	2.201	2.273[19]	−3.17

B. Entropies of Vaperization

The entropy is expressed as

$$S = k\ln F + kT(d\ln F/dT)_v \qquad (12)$$

From the euqation (12), S_q, the entropy at the gaseous state, and S_l, the entropy at the liquid state, can be calculated. Then, the entropy of vaperization can be obtained from the expression

$$\Delta S_{vap} = S_g - S_l \quad (13)$$

The calculated values are tabulated in Table 3.

Table 3. Entropies of Vaperization, ΔS_{vap}, cal/deg.

For N_2O

T°K	Calc.	Obsd.[16]	Δ%
182.25(T. P.)	21.8	(21.9)	−0.46
183.65(B. P.)	21.6	(21.6)	0.00
203.15	18.3	(18.1)	1.1
223.15	15.6	(15.2)	2.6
243.15	13.2	(12.7)	3.9
263.15	10.8	(10.6)	1.9

These values are obtained from the plot based on literature values.

For N_2O_4 at boiling point, 294.30°K

Calc.	Obsd.[12]	Δ%
31.01	30.96	0.16

C. Critical Point Properties

As shown in Figure 2, when values for $(dP/dV)_T$ is plotted against X values; a maximum of the curve is found at $(dP/dV)_T=0$ if $T=T_c$, whereas a maximum appears in the region of $(dP/dV)_T>0$ if $T<T_c$, and in the region of $(dP/dV)_t<0$ if $T>T_c$. Accordingly, the critical temperature is determined by plotting the calculated value of $(dP/dV)_T$ against X at various temperatures to find the temperature at which the maximum appears at $(dP/dV)_T=0$. At this temperature the critical conditions, $(dP/dV)_T=0$ and $(d^2P/dV^2)_T=0$, are automatically satisfied. The crit-i cal volume is determined from X_c at which $(dP/dV)_T=0$, V_c being equal to X_cV_s. The crtical pres sure is calculated from equation (6) by using T_c and V_c obtained above. The calculated values for the critical point properties are shown in Table 4.

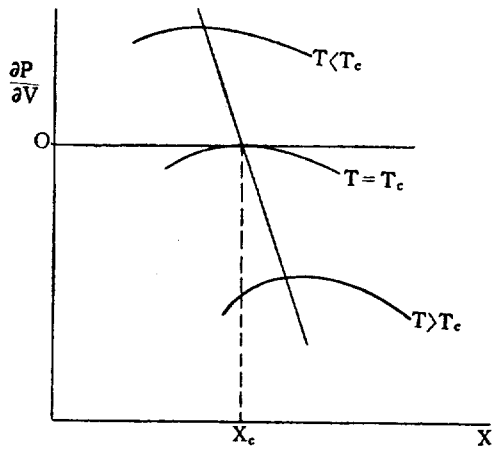

Figure 2. Isotherms of $(dP/dV)_T$ Near the Critical Point

Table 4. Critical Point Properties

For N_2O_4

	T_c°K	V_c c.c./mole	P_c atm.
Calc.	326.20	104.3	93.2
Obsd.[15]	309.65	96.32	71.7
Δ%	5.3	8.3	30.0

For N_2O_4

	T_c°K	V_c c.c./mole	P_c atm.
Calc.	447.0	161.0	152.3
Obsd.[20]	431.4	165.3	99.96
Δ%	3.62	−2.60	52.4

D. Degree of Dissociation

As explained in the previous section, $N-A$, the degree of dissociation of N_2O_4 in gaseous state, z_g, can be calculated from equation (9), introducing the values of V_g for V in the expression at the given temperature. The degree of dissociation of N_2O_4 in liquid state can be obtained by multiplying the value for z, the value calculated from equation (9) using the liquid volume for V in the expression, by $(V-V_s)/V$, the fraction of gas-like molecules in the liquid. The degrees of dissociation in gaseous and liquid states, thus calculated, are shown in Tables 5 and 6, respectively.

Table 5. Degree of Dissociation in Gaseous Phase

T°K	Calculated ($Z_g\times10^2$)	Observed[13] ($Z_g\times10^2$)
291.95(T. P.)	8.698	8.737
273.15	11.201	11.000
283.15	13.771	13.179
294.30(B. P.)	16.998	15.888
303.15	19.673	—
313.15	23.101	—

Discussion

As mentioned above, the difference between the boiling point and the triple point of N_2O is extremely

Table 6. Degree of Dissociation in Liquid Phase

T°K	Calculated ($Z_1 \times 10^3$)	Observed[13] ($Z_1 \times 10^3$)
261.95(T. P.)	0.50	0.18
273.15	0.87	0.36
283.15	1.42	0.66
294.30(B. P.)	2.39	1.19
303.15	3.54	—
313.15	5.29	—

small, 1.4 degree centigrade, and the vapor pressure of N_2O at the melting point is extremely high, 0.92 atm.. When N_2O solid melts, the expansion of volume is unusually high, about 27% increase, and the entropy of fusion of N_2O is very high, 8.6 e.u. These unusual qualities of liquid N_2O are successfully varified by the theoretical calculations of liquid N_2O according to the transient state theory of the significant liquid structure. Besides having the similar unusual qualities to N_2O, N_2O_4 molecules dissociate in gaseous and liquid phases. However, the degree of dissociation in liquid phase is in the range of several hundredth of that in gaseous phase. It is experimentally proved that N_2O_4 molecules do not dissociate in solid state. And from the fact that the energy difference between solid state and transient state is very small, about 1,000cal./mole, compared with the dissociation energy of N_2O_4 molecules, 13,186 cal./mole, it can be stated that the molecules in the transient state do not dissociate either. Accordingly, as it is done in this work, it is reasonable assumption that the molecules of N_2O_4 do not dissociate in either transient or solid state.

As shown in the theoretical calculations, the abnormal liquid properties of N_2O_4 are also successfully treated by the transient state theory of the significant liquid structure.

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