

## LIQUID OXYGEN

Treated by "The transient state theory of significant liquid structure"

by

**Moon-Bin Yim, Kak-Choong Kim,\* and Seihun Chang**

Seoul National University, Seoul, Korea

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액체구조에 관한 천이상태 이론의 산소에 대한 적용

서울 대학교

임문빈·김각중\*\*·장세훈

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要 約

천이상태 이론을 액체 산소에 적용하여 열역학적량을 구하였다. 그 결과는 실험치와 근사하게 일치함.

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### Abstract

The thermodynamic properties of the liquid oxygen are calculated by applying "The Transient State Theory of Significant Liquid Structure". The results show good agreement with experimental observations.

### 1. Introduction

Since the middle of the nineteen thirties when statistical mechanics began to play an important role in science, two different approaches to liquid theory have been made. The one is the formal or fundamentalist approach pioneered by Mayer<sup>1</sup>, Kirkwood<sup>2</sup>, and others; the other is by the use of models, such as "The cell theory" developed by Lennard-Jones<sup>3</sup>, Devenshire, and others.

Eyring and al<sup>4</sup> developed "The Significant Structure Theory of Liquids", a model approach, and applied

it to many liquids successfully.

Chang and al<sup>5</sup> have worked out "The Transient State Theory of Significant Liquid Structure" with the basic idea of "The Significant Structure Theory of Liquids", which is also applied to many liquids successfully.

In 1964, Kim<sup>6</sup>, one of the authors, has done a theoretical work on liquid oxygen applying "The Significant Structure Theory of Liquids". This research is a further study on liquid oxygen in view of "The Transient State Theory of Significant Liquid Structure".

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\* Korea University, Seoul, Korea

\*\* 고려 대학교

## 2. Formulation of the Partition Function

### A. Theoretical Considerations

In "The Significant Structure Theory of Liquids", it is assumed that holes of molecular size are introduced when a solid is transformed to a liquid. In one mole of liquid there are  $N(V-V_s)/V_s$  holes, since the volume increase during the phase transition is  $(V-V_s)$ , where  $V$  is the molar volume of the liquid and  $V_s$  is the molar volume of the solid. This volume increase leads to an important idea that there exist two kinds of molecules in a liquid: the one which possess solid-like degrees of freedom and the other which possess gas-like degrees of freedom. This is the basic idea in formulating a partition function for liquids. Accordingly, "The significant structure theory of liquids" gives the molar partition function for a monatomic liquid as follows:

$$F = \left[ \frac{\exp(E_s/RT)}{\{1 - \exp(-\theta/T)\}^3} \{1 + n_h \exp(-\epsilon/RT)\} \right]^{N(V_s/V)} \left[ \frac{(2\pi mkT)^{3/2}}{h^3} (V - V_s)^{N(V-V_s)/V} \left[ \frac{N(V-V_s)}{V} \right]! \right]^{-1} \dots \dots \dots (1)$$

or using stirling's approximation

$$F = \left[ \frac{\exp(E_s/RT)}{\{1 - \exp(-\theta/T)\}^3} \{1 + n_h \exp(-\epsilon/RT)\} \right]^{N(V_s/V)} \left[ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} \right]^{N(V-V_s)/V} \dots \dots \dots (2)$$

where  $E_s$  and  $\theta$  are sublimation energy at the ground state and Einstein's characteristic temperature, respectively. The quantity  $\{1 + n_h \exp(-\epsilon/RT)\}$  is the geometrical degeneracy factor, where  $n_h$ , the number of holes around a molecule, is expressed by  $n_h = n(V - V_s)/V_s$ ; here,  $n$  is the number of the nearest neighbor, and  $\epsilon$  is the strain energy which is inversely proportional to the number of holes around a molecule and directly proportional to the energy of sublimation of the solid, i.e.,  $\epsilon = aE_s V_s / \{n(V - V_s)\}$ , where "a" is a proportionality constant. Other symbols in the partition function have their usual physical significance. In the partition function for a non-localized independent system, the number of complexions is overcounted due to the indistinguishability of particles; therefore, it must be divided by  $\{N(V - V_s)/V\}!$ , the number of gas-like particles factorial.

Here, the solid-like molecules are represented by the Einstein oscillator, and the gas-like molecules are assumed to behave like those in an ideal gas.

"The Transient State Theory of Significant Liquid Structure" assumes that the transition of the degree of freedom of molecules from the solid-like to the gas-like does not occur directly, but only through a transient state such transition takes place. Here, the 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.

Accordingly, there are three kinds of degree of freedom in liquids; namely, gas-like, transient and solid-like degrees of freedom. Then, there arise a problem as to how these degrees of freedom are partitioned. Since  $N(V - V_s)/V_s$  vacancies are introduced at random among  $N$  molecules, only  $N(V_s/V)$  molecules are bonded each other. of  $N(V_s/V)$ , only  $\alpha N(V_s/V)$  molecules keep equilibrium position as if they were in the solid state; and accordingly,  $\alpha N(V_s/V)$  molecules possess solid-like degrees of freedom, where,  $\alpha$  is a fractional number. The remaining  $(1 - \alpha)N(V_s/V)$  molecules are in the transient state. Here, the transient state differ from the solid-like state by the amount of strain energy which is proportional to the sublimation energy and inversely proportional to the number of vacant sites around the molecule,  $n(V - V_s)/V_s$ , where  $n$  is given by  $n = 12(V_s/V_s)$ ; here,  $V_t$  refers to the molar volume of liquid at the triple point. Then,  $N(V - V_s)/V$  molecules will possess the gas-like degree of freedom.

Accordingly, the partition function for liquids can be written as

$$F = \frac{(N_s + N_t)^{N_s} N_t^{N_t}}{N_s! N_t!} f_s^{N_s} f_t^{N_t} f_g^{N_g} \frac{1}{N_g!} = \frac{[(V_s/V)N]!}{(\alpha N V_s/V)! [(1 - \alpha)N V_s/V]!} \left[ \frac{\exp(E_s/RT)}{\{1 - \exp(-\theta_s/T)\}^3} b_s \right]^{\alpha N V_s/V} \left[ \frac{\{n(V - V_s)/V_s\} \exp\{(E_s - \epsilon)/RT\} b_t}{\{1 - \exp(-\theta_t/T)\}^3} \right]^{(1 - \alpha)N V_s/V} \left[ \frac{(2\pi mkT)^{3/2} (V - V_s)}{h^3} b_g \right]^{N(V - V_s)/V} \cdot \frac{1}{\left( \frac{V - V_s}{V} N \right)!}$$

$$\dots\dots\dots(3)$$

where  $b$  is the partition function for the degrees of molecular rotation and vibrations; here, subscripts  $s$ ,  $t$ , and  $g$  designate the states of solid-like, transient, and gas-like, respectively.  $n(V-V_s)/V_s$  refers to the number of positional degeneracy, and " $\varepsilon$ " is the molar energy difference between solid-like and transient states; and it can be expressed as  $\varepsilon = aE_s/[n(X-1)]$ , where  $X = V/V_s$  and " $a$ " is a proportionality constant. 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.

At the thermodynamic equilibrium, the following expression can be used.

$$(dA/d\alpha)_{T, V, N} = -kT(d \ln F/d\alpha)_{T, V, N} = 0 \dots\dots(4)$$

By rearranging the equation (3) and differentiating it with respect to  $\alpha$  at constant  $T, V, N$ , " $\alpha$ " is given by

$$\alpha = f_s/(f_s + f_t) \dots\dots\dots(5)$$

When equation (5) is introduced into equation (3), the partition function becomes

$$F = \left[ \frac{\exp(E_s/RT)}{\{1 - \exp(-\theta_s/T)\}^2} b_s \left\{ 1 + \lambda(X-1) \exp \left( \frac{-aE_s}{n(X-1)RT} \right) \right\} \right]^{\frac{N}{X}} \left[ \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} b_g \right]^{N(1-\frac{1}{X})} \dots\dots\dots(6)$$

$$\text{where } \lambda = n \left( \frac{1 - \exp(-\theta_s/T)}{1 - \exp(-\theta_t/T)} \right)^2 \frac{b_t}{b_s}$$

### B. The Partition Function for Liquid Oxygen

Oxygen is a diatomic molecule with normal entropy of fusion (1.95 e. u.). It has two first-order transitions in the solid state: one at 23.66°K (about 30 degrees below the melting point) and the other at 43.75°K (about 10 degrees below the melting point). In 1952, Crawford<sup>9</sup> found rotational bands in infra-red spectra of liquid oxygen. These facts suggest that oxygen molecules rotate in the solid state near the melting point. Therefore, the rotational term is included in both and gas-like and the solid-like parts of the partition function. Accordingly, the partition function for liquid oxygen can be written as follows:

$$F = \left[ g_e \frac{e^{E_s/RT}}{(1 - e^{-\theta_s/T})^2} b \left\{ 1 + \lambda \exp \left( \frac{-aE_s}{n(X-1)RT} \right) \right\} \right]^{\frac{N}{X}}$$

$$\left[ g_e \frac{(2\pi mkT)^{3/2}}{h^3} \frac{eV}{N} b \right]^{N(1-\frac{1}{X})} \dots\dots\dots(7)$$

For oxygen  $b_s$ ,  $b_t$ , and  $b_g$  are equal and taken as

$$b = \frac{(8\pi^2 I k T)}{2 h^2} \frac{1}{\left( 1 - \exp \frac{-h\nu}{kT} \right)}$$

where  $I$ ,  $\nu$ , and  $g_e$  are moment of inertia, vibrational frequency and electronic degeneracy of oxygen molecule, respectively.

### 3. Determination of Parameters

There are various ways to determine the parameters appearing in the partition function. Here, the parameters are determined at triple point using the method developed by Chang and al.<sup>7</sup>

The literature values used for the parameter determination are:

Moment of Inertia <sup>10</sup>	1.933 × 10 <sup>-39</sup> gr-cm <sup>2</sup>
Vibrational frequency between oxygen atoms in a molecule <sup>12</sup>	4.73754 × 10 <sup>13</sup> sec <sup>-1</sup>
Molar volume of liquid at triple point <sup>11</sup>	24.66 cm <sup>3</sup>
Molar volume of solid at triple point <sup>12</sup>	24.0 cm <sup>3</sup>
Triple point <sup>11</sup>	56.36°K
Pressure at triple point <sup>11</sup>	0.0015 atm.

$\Delta S_v$  at triple point is not available in literature; therefore, the value,  $\Delta S_v$  (at triple point) = 33.52 e. u., is obtained from  $\Delta S_v$  values<sup>13</sup> at higher temperatures by extrapolation.

The parameters thus obtained are:

$$E_s = 1818 \text{ cal/mole}$$

$$\theta_s = 58.62^\circ \text{K}$$

$$\theta_t = 52.06^\circ \text{K}$$

$$a = 0.00567$$

### 4. Results

#### A. Vapor Pressures and Densities

The vapor pressure can be expressed as

$$P = -(dA/dV)_T \dots\dots\dots(8)$$

The plot for helmholtz free energy vs volume can be drawn at constant temperature as shown in Figure 1.

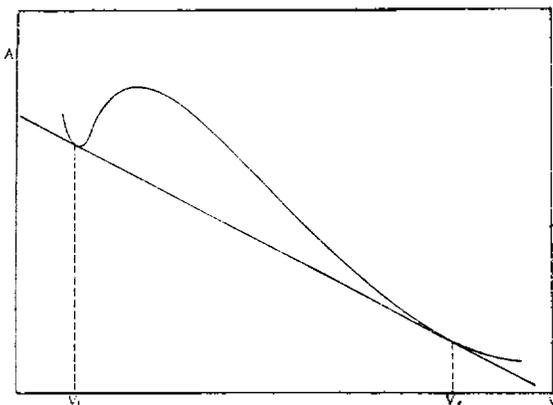


Figure 1. A Plot for Helmholtz Free Energy vs Volume

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, hence density, of liquid at the temperature. Both the vapor pressures and the densities are calculated at various temperatures from triple point to boiling point. Good agreements between calculated values and literature values<sup>11</sup> are observed as shown in Figures 2 and 3.

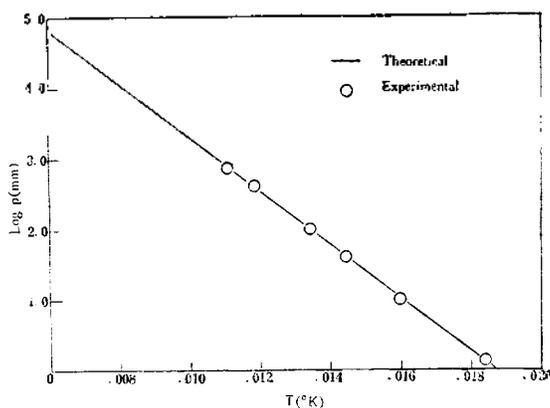


Figure 2. Vapor Pressure of Liquid Oxygen

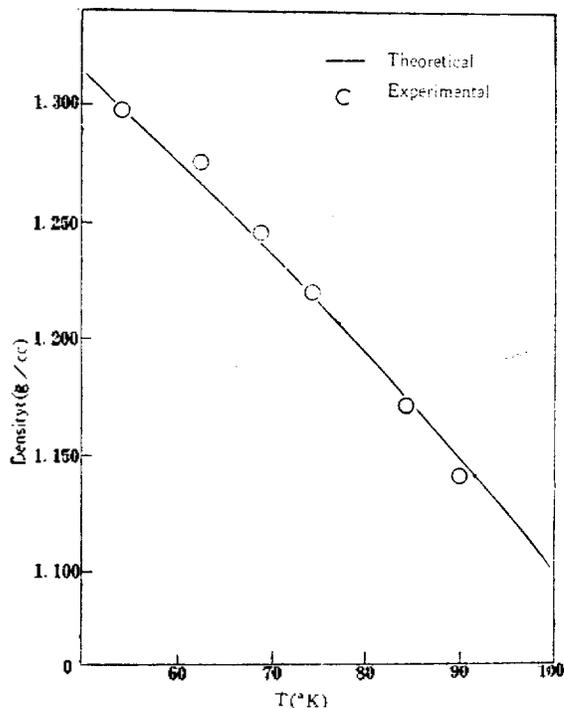


Figure 3. Density of Liquid Oxygen

**B. Entropies of Vaporization and Compressibilities**

The entropy expression is given by

$$S = k \ln F + kT (\ln F / dT)_v \dots\dots\dots(9)$$

From the above expression,  $S_g$  and  $S_l$  can be calculated; then, from them entropy of vaporization can be obtained.

The iscompressibility,  $\beta$ , can be calculated by using the following expression.

$$\beta = -\frac{1}{V} \left( \frac{dV}{dP} \right)_T = -\frac{1}{V} \left( \frac{d^2 A}{dV^2} \right)_T \dots\dots\dots(10)$$

The entropies of vaporization and the compressibilities are calculated at various temperatures and tabulated in Table 1. Good agreements between the calculated values and the literature values<sup>12,14</sup> are observed.

**Table 1. Entropy of Vaporization and Compressibility**

Temp. (°K)	$\Delta S_v$ (calc) (e. u.)	$\Delta S_v$ (obs) (e. u.)	%	$\beta$ (calc) $\times 10^5$ (atm <sup>-1</sup> )	$\beta$ (obs) $\times 10^6$ (atm <sup>-1</sup> )
54.36	33.52	33.52		62.53	
62.56	28.83			67.89	
65.00					106
69.06	24.30			84.20	
70.00					119

74.36	23.28	23.45	+0.73	100.9	
80.00					149
84.36	19.74	19.80	+0.30	143.3	
90.00					179
90.21	17.97	18.07	-0.55	175.9	

### 5. Discussion

Although an oxygen molecule has an even number of electrons, it shows paramagnetic property, which means that it has a triplet ground states; i. e., it has two unpaired electrons. Parrier and Onnes found that pure liquid oxygen shows considerably less susceptibility than that predicted by Curie's law<sup>6</sup>. They performed a series of measurements, diluting liquid oxygen with liquid nitrogen, and found that the susceptibility increases with dilution, reaching a value at infinite dilution which corresponds approximately to that calculated for a free molecule<sup>15</sup>. The experimental results obtained by them are in accord with Lewis' hypothesis on the existence of O<sub>4</sub><sup>8</sup>.

Vereshchagin and Prebrazhenskii<sup>17,18</sup> have reported that they found O<sub>4</sub> concentration increased rapidly with increasing pressure over the range of 600-1300 atm. From this they have concluded that above 3000 atm. oxygen will consist entirely of O<sub>4</sub> molecules.

Considering the above cases, the dimer term should be included in the partition function for liquid oxygen.

However, some experiments performed by other investigators<sup>9,19,20</sup> appear to be inconsistent with the existence of dimers. Moreover, in the case of oxygen the term "dimer" has long been debated.

According to Lewis, a link between the two monomer is less than 10 per cent as strong as even the weakest chemical bond<sup>16</sup>. For this reason, many investigators prefer to define O<sub>4</sub> as two molecules which interact over a period of time that is long compared to the time between intermolecular collisions<sup>15</sup>.

For this work the dimer term in the partition function of liquid oxygen is ignored. Introducing the dimer terms in the partition function only gives considerable complications; and, yet, does not give any better results. Our partition function for liquid oxygen is satisfactory in predicting the thermodynamic properties, and it can be concluded that the effect of dimers is negligible.

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