THE SIGNIFICANT STRUCTURE THEORY APPLIED TO LIQUID OXYGEN

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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 fundamental approach, and the other is the model approach. In this paper, the “significant structure” theory of liquids is applied to liquid oxygen by the use of models. In this theory a liquid is considered as a “solid-like” structure with “fluidized vacancies” of molecular size randomly distributed throughout the solid. The molecules adjacent to such vacancies have “gas-like” degrees of freedom. The significant structure theory of liquid is based on the assumption that a portion of liquid molecules have solid-like degrees of freedom and the other portion of liquid molecules have gas-like degrees of freedom. The detailed description is found in the literature.¹

According to the significant structure theory, the solid-like portion is given by \((V - V_s)/V\), while the gas-like portion is \(V_s/V\), where \(V\) and \(V_s\) are the molar liquid volume at a given temperature and the molar solid volume at the melting point, respectively. As the partition function of the solid-like degrees of freedom, the Einstein function is generally used; and for the gas-like degrees of freedom, the ideal gas partition function is usually employed. Utilizing these ideas, the partition function for a liquid is obtained; consequently the thermodynamic properties of the liquid are calculated. In the past, the significant structure theory has been applied to various liquids, and the thermodynamic properties were calculated with good results.

In this paper, we apply the significant structure theory to liquid oxygen, and discuss the problems associated with the latter.

2. The Partition Function for Liquid Oxygen.—Oxygen is a diatomic molecule with a normal entropy of fusion (1.95 eu). It has two first-order transitions in the solid state: one at 23.660 K (about 30 degrees below the melting point) and the other at 43.760 K (about 10 degrees below the melting point).² This fact suggests that an oxygen molecule rotates in the solid state near the melting point. Actually, in 1952, Crawford et al. found rotational bands in Raman spectra in liquid oxygen.³ Therefore, the rotational term is included in both the gas-like and solid-like parts of the partition function. Accordingly, the partition function for liquid oxygen can be written as follows:

\[
f = \left[ \frac{\exp(E_\text{rot}/RT)}{1 - \exp(-\theta/T)} \right] ^{3} \left\{ 1 + n(X - 1) e^{-\frac{aE_n}{(X-1)RT}} \right\} \times \frac{3(8\pi^2 kT)}{2h} \frac{1}{1 - \exp(-h\nu/kT)} \right]^{N/X} \times \frac{(2\pi mkT)^{1/2}}{h} \frac{3(8\pi^2 kT)}{N} \frac{1}{2h^2} \frac{1}{1 - \exp(-h\nu/kT)} \right]^{N(X-1)/X} (1)
\]

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where \( I \) is the moment of inertia of an oxygen molecule; \( \nu \), the vibrational frequency; \( E_v \), the heat of sublimation; \( \theta \), the Einstein characteristic temperature; \( m \), the molecular mass; \( X = V/V_0 \); \( N \), Avogadro’s number; \( n \) and \( a \), the parameters to be determined; and other symbols are the usual physical constants. The quantity \( 1 + n (X - 1) \exp \left[ -aE_v/(X - 1)RT \right] \) is the positional degeneracy associated with a solid-like molecule. The factor 3 accompanying the rotational partition function comes from the fact that the ground state of an oxygen molecule is a triplet state.

There are many methods\(^4\)\(-7\) for the determination of the parameters appearing in the partition function. In general, one method does not excel another; i.e., a particular technique is especially good only for the liquid under consideration. Accordingly, a special technique was devised for the parameter determination of liquid oxygen.\(^7\) Utilizing this technique in conjunction with the so-called Seoul technique,\(^6\) the parametric values were obtained with the use of the experimental data\(^5\)\(^,9\) at the triple point, \( T = 54.36^\circ \text{K}, \) where the vapor pressure is 1.14 mm Hg, the molar liquid volume is 24.37 cc,\(^10\) and the molar liquid entropy is 16.04 eu.\(^11\) The best parametric values are as follows: \( V_s = 24.14 \text{ cc/mole}, n = 11.89, \theta = 56.02^\circ \text{K}, \) \( E_s = 1808.0 \text{ cal/mole}, \) and \( a = 0.5893 \times 10^{-4}. \) An approximate value of \( E_s \) is also obtained as \( E_s = \Delta H \) (head of fusion at the melting point\(^'\) + \( \Delta H \) (heat of vaporization at the boiling point\(^b\)) = 105.6 + 1630 = 1735.6 cal/mole. This value is lower by 54.7 cal/mole than the value obtained above. For \( \theta, \) an approximate value of \( \theta \) is also obtained from the literature values\(^b\) of Debye’s characteristic temperature 91\(^0\)K by multiplying it by 3/4, i.e., as \( \theta = 68.25, \) which is higher by a factor of 1.21 than our value of \( \theta. \) The experimental value of \( V_s \) found for the solid state is 23.77 cc/mole.\(^12\) Thus, the parametric values of \( E_s, \theta, \) and \( V_s \) seem to be reasonable.

There is experimental evidence for the fact that oxygen molecules dimerize, but this is neglected here, as it will be discussed later.

From the partition function given above, various thermodynamic properties and viscosity of liquid oxygen are calculated through the entire-liquid range, and are compared with the experimental data. In the calculations, the following literature values are used: \(^13\) \( \nu = 4.73754 \times 10^{13} \text{ sec}^{-1}; \) \( I = 1.938 \times 10^{-39} \text{ gm} \cdot \text{cm}^2; \) \( r_s = 1.2074 \text{ Å,} \) the latter being the atomic distance in an oxygen molecule. All the numerical calculations in this paper were made on an IBM 7040 computer.

**TABLE 1**

**PROPERTIES AT TRIPLE, BOILING, AND CRITICAL POINTS**

<table>
<thead>
<tr>
<th>( T (^\circ \text{K}) )</th>
<th>( P ) (atm)</th>
<th>( V ) (cc/mole)</th>
<th>( S ) (eu/mole)</th>
<th>( \Delta S ) (eu/mole)</th>
<th>( \text{Calc.} )</th>
<th>( \text{Obs}^8-\text{10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.36 (( T_1 ))</td>
<td>0.00146</td>
<td>24.37</td>
<td>16.62</td>
<td>2.53*</td>
<td>\text{Calc.}</td>
<td>\text{Obs}^8-\text{10}</td>
</tr>
<tr>
<td>54.36</td>
<td>0.00150</td>
<td>24.37†</td>
<td>16.04†</td>
<td>1.95†</td>
<td>\text{Calc.}</td>
<td>\text{Obs}^8-\text{10}</td>
</tr>
<tr>
<td>0.00</td>
<td>-2.67</td>
<td>0.00</td>
<td>3.63</td>
<td>29.7†</td>
<td>\text{Calc.}</td>
<td>\text{Obs}^8-\text{10}</td>
</tr>
<tr>
<td>(90.21) (( T_b ))</td>
<td>1.081</td>
<td>27.58</td>
<td>23.07</td>
<td>17.38</td>
<td>\text{Calc.}</td>
<td>\text{Obs}^8-\text{10}</td>
</tr>
<tr>
<td>90.21</td>
<td>1.000</td>
<td>28.06</td>
<td>22.50†</td>
<td>18.07†</td>
<td>\text{Calc.}</td>
<td>\text{Obs}^8-\text{10}</td>
</tr>
<tr>
<td>8.10</td>
<td>-1.67</td>
<td>2.53</td>
<td>-3.82</td>
<td></td>
<td>\text{Calc.}</td>
<td>\text{Obs}^8-\text{10}</td>
</tr>
<tr>
<td>162.78 (( T_c ))</td>
<td>60.55</td>
<td>79.71</td>
<td>28.84</td>
<td></td>
<td>\text{Calc.}</td>
<td>\text{Obs}^8-\text{10}</td>
</tr>
<tr>
<td>154.34</td>
<td>49.713</td>
<td>74.44</td>
<td></td>
<td></td>
<td>\text{Calc.}</td>
<td>\text{Obs}^8-\text{10}</td>
</tr>
<tr>
<td>5.47</td>
<td>21.81</td>
<td>7.08</td>
<td></td>
<td></td>
<td>\text{Calc.}</td>
<td>\text{Obs}^8-\text{10}</td>
</tr>
</tbody>
</table>

\(*\) The entropy of the solid at \( T_1 \) was taken as 14.09 eu, the observed value.\(^11\)
\(†\) There is no literature value for \( V_s. \) Thus, we obtained this value by using the empirical equation\(^9\) representing the rectilinear-diameter law.
\(^*\) Reference 11.
3. Results.—Properties at the triple, boiling, and critical points: In a plot of the Helmholtz free energy $A$, which equals $-kT \ln f$, against volume, a tangent common to all three phases, solid, liquid, and gas, is found at the triple point temperature $T_t$. Here the slope of the tangential line yields the vapor pressure at the triple point $P_t$, i.e., $(\partial A/\partial V)_T = -P_t$; the volumes corresponding to the three tangential points give the volumes of the solid, of the liquid, $V_s$, and of the vapor. The triple point properties thus obtained are shown in Table 1, and compared with experiment.

In the calculation of the boiling point properties, $T_b$ is taken as 90.21°K (the observed value), and $P_b$ and $V_b$ are calculated from the plot of $A$ versus $V$. The entropy is calculated from the equation $S = [\partial (kT \ln f)/\partial T]_V$. The molar entropies calculated at the triple and boiling points and the calculated transition entropies are shown in Table 1 with other properties. From Table 1, one sees that the agreement between theory and experiment is satisfactory.

The critical temperature $T_c$, critical volume $V_c$, and critical pressure $P_c$ are calculated in the usual way by using the two conditions: $(\partial P/\partial V)_T = 0$, $(\partial^2 P/\partial V^2) = 0$. The critical properties thus obtained are also given in Table 1, and are compared with experiment. One notes that the deviation in $P_c$ is especially large, whereas the agreement in $T_c$ and $V_c$ is satisfactory. This fact has been noticed also in other cases in the application of significant structure theory. The large deviation in $P_c$ is considered to be due to the use of an ideal gas partition function for the gas-like degrees of freedom. By considering the presence of dimers, trimers, etc., the critical pressure is considerably improved. The results will be reported elsewhere.

The vapor pressures and densities: The vapor pressures $P$ and the densities $\rho$ are calculated through the entire liquid range using the previously mentioned principles. As shown in Figures 1 and 2, the calculated values agree with the observed data very well, except at the temperatures near the critical point.

The calculations of $\alpha$, $\beta$, $C_V$, and $C_P$: The coefficient of thermal expansion $\alpha$, the compressibility of $\beta$, and the heat capacities at constant volume $C_V$ and at constant pressure $C_P$ are calculated by using the following equations:
\[ C_V = T \left( \frac{\partial S}{\partial T} \right)_V \]  \hspace{1cm} (2)

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \left( \frac{\partial P}{\partial T} \right)_V \left/ \left( \frac{\partial P}{\partial V} \right)_T \right. \]  \hspace{1cm} (3)

\[ \beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -1/V \left( \frac{\partial P}{\partial V} \right)_T \]  \hspace{1cm} (4)

\[ C_P = C_V + TV\alpha^2/\beta \]  \hspace{1cm} (5)

The results are shown in Table 2. One sees satisfactory agreement between the calculated values of \( \alpha \) and the observed one\(^{10} \) which is \( 4.0 \cdot 10^{-3} \text{/degree} \) between 63.16\(^\circ\)K and 91.16\(^\circ\)K.

From Table 2 one also finds satisfactory agreement between calculated and observed values\(^{15} \) of \( C_P \). Because of the lack of experimental compressibility data, we cannot directly compare the calculated values of \( \beta \) with those observed. Considering the satisfactory agreement between the theoretical and experimental \( C_P \)’s, however, one may conclude that the theoretical \( \beta \) values are reasonable.

**Surface tension:** The surface tension \( \gamma \) is expressed by\(^{16} \)

\[ \gamma = 0.9165(V_s/N)^{1/2} \sum_i (F_i' - F_i)/V_i, \]  \hspace{1cm} (6)

where \( F_i' \) is the molar Gibbs free energy of the \( i \)th surface layer; \( F_i \) the corresponding quantity of the bulk liquid; and \( V_i \), the molar volume of the \( i \)th layer. For the calculation of the Gibbs free energy \( F_i' \) the sublimation energy of the \( i \)th surface layer \( E_{st} \) is used instead of \( E_i \) in the partition function of oxygen, equation (1). \( E_{st} \) is obtained from the equation

\[ E_{st} = E_s \left( \frac{6}{12} \rho_i + \frac{3}{12} \rho_{i+1} + \frac{3}{12} \rho_{i-1} \right), \]  \hspace{1cm} (7)

where \( \rho_i, \rho_{i+1}, \) and \( \rho_{i-1} \) are the densities for the \( i \)th, \((i + 1)\)th, and \((i - 1)\)th layer, respectively. The top surface molecular layer is called the first layer (i.e., \( i = 1 \)), then \( i \) increases to 2, 3, . . . toward the bulk liquid phase. By using equations (6) and (7) in conjunction with equation (1), the surface tension of liquid oxygen at various temperatures is calculated. For this purpose, the iteration method of Chang et al.\(^{14} \) is very useful. The calculated values are compared with experiment\(^{17, 18} \) in Figure 3, which reveals a good agreement between the two.

T. S. Ree et al.\(^{19} \) and Lu et al.\(^{20} \) also derived the equations of surface tension, which do not require the iteration. These authors calculated the surface tensions of liquid oxygen by using their equations and obtained satisfactory results.

**Table 2**

<table>
<thead>
<tr>
<th>( T ) ((^\circ)K)</th>
<th>( \alpha \times 10^4 ) (calc) (deg.(^{-1}))</th>
<th>( \beta \times 10^4 ) (calc) (atm.(^{-1}))</th>
<th>( C_V ) (calc) (cal/deg. mole)</th>
<th>( C_P ) (calc) (cal/deg. mole)</th>
<th>( C_P ) (obs)(^{19} ) (cal/deg. mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>54.36 (( T_1 ))</td>
<td>2.911</td>
<td>2.184</td>
<td>8.420</td>
<td>13.56</td>
<td>12.71</td>
</tr>
<tr>
<td>62.56</td>
<td>2.951</td>
<td>2.715</td>
<td>8.476</td>
<td>13.48</td>
<td>12.74</td>
</tr>
<tr>
<td>69.06</td>
<td>3.238</td>
<td>3.455</td>
<td>8.489</td>
<td>13.82</td>
<td>12.84</td>
</tr>
<tr>
<td>74.36</td>
<td>3.498</td>
<td>4.197</td>
<td>8.484</td>
<td>14.10</td>
<td>12.84</td>
</tr>
<tr>
<td>90.21 (( T_6 ))</td>
<td>4.448</td>
<td>7.515</td>
<td>8.406</td>
<td>14.96</td>
<td>12.99</td>
</tr>
</tbody>
</table>
Viscosity: According to significant structure theory, viscosity is given by the following expressions:

\[ \eta = \frac{(V_s/V)\eta_s + [(V - V_s)/V]\eta_v}{6} \]  
(8a)

\[ \eta_s = \frac{Nh V}{Z\kappa \sqrt{2}} \left[ \frac{1}{1 - \exp(-\theta/T)} \right] \frac{1}{V - V_s} \exp \frac{aE_s}{(X - 1)RT} \]  
(8b)

\[ \eta_v = \frac{(2/3d^3)(mkT/\pi^4)^{1/3}}{V - V_s} \]  
(8c)

where \( \eta_s \) and \( \eta_v \) are the viscosities in the solid and in the gaseous state, respectively; \( Z \) is the coordination number; \( \kappa \) is the transmission coefficient; \( d \) is the molecular diameter taken as 2.9333 Å which was calculated from the van der Waals' constant \( b \) by using the relation \( b = 2\pi d^3N/3 \). In this paper, \( Z \) and \( \kappa \) are taken as 12 and 0.446, respectively. By using the parametric values of \( V_s, \theta, E_s, \) and \( a \) previously obtained, the viscosity of liquid oxygen was calculated from equation (8). The results are shown as the full curve in Figure 4. Satisfactory agreement between theoretical and experimental values is obtained except at the melting point.

According to the significant structure theory of viscosity of hard spheres, \( \eta \) is represented by the following equation:

\[ \eta = \frac{(\pi mkT)^{1/3}}{V - V_s} \left[ \left( \frac{\sqrt{2}}{V} \right)^{1/3} - d \right] + \frac{V - V_s}{V} \frac{5}{16d^3} \left( \frac{mkT}{\pi} \right)^{1/3}. \]  
(9)

Equation (9) does not include any arbitrary parameter except \( V_s \), for which we choose \( V_s = 23.77 \text{ cc/mole} \) found for the solid state. The calculated results are
shown by a broken curve in Figure 4. It is interesting to note that equation (9) agrees with experiment better than equation (8).

4. Discussion.—Although an oxygen molecule has an even number of electrons, it is paramagnetic, which means that it has a triplet ground state; i.e., it has two unpaired electrons. Perrier and Onnes found that pure liquid oxygen shows considerably less susceptibility than that predicted by Curie’s law. They concluded that this is due to the dimerization of oxygen molecules, and experimentally proved that there is an equilibrium of the form $O_2 \rightleftharpoons 2O$, with the equilibrium constant $K_e = c_2^2/c_4$, where $c_2$ and $c_4$ are the concentrations of the monomer and the dimer, respectively. $c_2$ and $c_4$ can be determined under the assumption that the monomer is alone responsible for the paramagnetism and that the additivity of volumes holds. They further evaluated $K_e$ at 64.2°, 70.9°, and 77.4°K, and obtained 0.92, 1.01, and 1.10 at the respective temperatures. And from the linear relationship between $\ln K_e$ and $1/T$, they obtained the heat of dissociation of 128 cal/mole for $O_2$.

From the above data, the mole fractions of monomer, $x$, and the equilibrium constants in terms of mole fractions, $K_x$, were obtained. At 64.2°, 70.9°, and 77.4°K, the $K_x$ values are 0.081, 0.631, and 0.6875, respectively, and the mole fractions of monomers are 0.995, 0.944, and 0.948.

$\Delta S$ and $\Delta H$ in the expression $K_e = \Delta S/R - \Delta H/RT$ are obtainable from the above data. Thus $K_e$ for the entire liquid range can be calculated. The calculation reveals that the mole fraction of $O_4$ does not exceed 0.07 at the largest (at the melting point).

Besides Perrier and Onnes’s work, there are other reports that support the existence of $O_4$ molecules. However, some experiments performed by other investigators appear to be inconsistent with the existence of the dimers. Moreover, in case of oxygen the term “dimer” has long been debated. According to Lewis a link between the two monomers is less than 10 per cent as strong as even the weakest chemical bond. For this reason, many investigators prefer to define $O_2$ as two molecules which interact over a period of time that is long compared to the time between the intermolecular collisions.

In this paper the dimer term has been ignored in the partition function of liquid oxygen. This is because the dimer concentration is very small and the existence of $O_4$ is controversial, as stated above. Since our partition function for liquid oxygen is satisfactory, it may be concluded that the small amount of dimers can be ignored.

Summary.—The significant structure theory of liquids was applied to liquid oxygen. The thermodynamic properties calculated from the theory agree with the experimental data within the permissible error. The viscosity of liquid oxygen was also calculated with satisfactory results. In this paper, the presence of the dimeric molecule $O_4$ was neglected because of its small concentration. A brief discussion of $O_4$ is given.

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