A Partition Function for Liquid Metals

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液體金屬의 狀態和

金 完 奎

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要 約

筆者는 週間表 1 族에 属している 液體金屬의 狀態으로서 輔助inan 液體金屬은 2 原子分子의 振動子로 構成

하여 이 振動子는 自分가 占有하는 見方(site)을 따라 두거나 이나가 損耗中 하나를 取除하여 만다고 認識

함으로서 液體狀態를 認識하였다.

이 標識式은 本質의으로는 하나의 物質固有의 常数(s)을 內包하고 있으므로 液體金屬에 對하여 이 標識式

은 常数으로서 彼の在ち 熱力学的 性質 및 液態金屬의 热力学의 構成を 보이다. これ 質を 算出하여 實測値と 比較하여

보았다. その結果는 塊足されている 一致を 보여준다.

The author assumes that pure liquid metal is composed of molecular oscillators whose energy states are classified into two subgroups, i.e., A and B states, each being accessible to either one of the two sorts of lattice sites. The partition function involves constants characteristic of substance, which are obtained from the Debye characteristic temperature assigned to its solid state.

Calculation has been made for the various thermodynamic properties such as the vapor pressure, the entropy, and the heat capacity of liquid metals of Group I elements over the temperature range from the melting points to the boiling points. The theoretical values thus obtained are in good accordance with those observed, within experimental error, although a slight derivation is observed in the atomic heat capacity.

1. Introduction

Eyring and Hirschfelder, and Lennard-Jones and Dovonshire have employed the cell model in the formulation of theories of the liquid state that are quite successful interpreting the properties of simple nonpolar liquids. Kirkwood has shown how the cell model can be explained by means of well-defined approximations to the classical statistical mechanics of the canonical ensemble. Recently, Hirai, Reo and Eyring have set up a partition function for the inert gas based upon their well-known hole theory. For liquid metals, Kincaid and Eyring, and Hirschfelder, Stevenson and Eyring have formulated partition function under the assumption that the constituent particles of liquid mercury are monatomic. In this paper, however, the constituent is assumed to be diatomic according to the following reasons. Herzberg has given the experimental evidence that there exist diatomic molecules in the liquid phase of mercury and in the vapor phase of some metallic elements. Furthermore, Gordon’s calculation indicates a strong tendency for alkali elements to associate. If we extend his argument to the extreme case in which the vapor is confined within a small volume (i.e., such system is equivalent to liquid state), we may conclude that the monatomic species involved in such a system should disappear. Hence the author assumes that the constituents of some metallic liquids are diatomic.

On the other hand, Blackman, Montroll,
Newell[10] and Van Hove[10] theoretically derived that there are two maxima in the frequency distribution of oscillators in solid crystalline state. This fact suggests that we can make an approximation that there exists two discrete frequencies allowed for the oscillator in a crystal. In fact, Lindemann and Nearest assumed for some crystals to have the two kinds of oscillators and assigned one of the frequencies to be the half of the other's, and then, calculated the atomic heat capacity of the crystals according to this modified Einstein model. Their calculation has given better result than those calculated from the Einstein crystalline partition function.

Summarizing these arguments the author assumes that some kinds of metals, i.e., Group I elements, consist of diatomic molecules in the liquid state and the molecules can occupy either one of two sorts of sites, say A and B sites. Then the total accessible energy levels of a given molecule in the liquid may be given by the energy levels in A site plus those calculated from the Einstein crystalline partition function.

1. Derivation of the Partition Function for Liquid Metals

Let $e_{A}$ and $e_{B}$ be the energies of the quantum states accessible to site A and B. Then the partition function $q_{A}$ and $q_{B}$ are defined by

$$q_{A} = \sum e^{-e_{A}/kT} \text{ and } q_{B} = \sum e^{-e_{B}/kT}.$$  

According to the present model, a given molecule can occupy either one of the two sites, i.e., a given molecule has accessible to it the full set of states of site A and site B. Thus the partition function for a molecule is given by

$$q = \sum e^{-q_{A}} + \sum e^{-q_{B}} = q_{A} + q_{B}.$$  

According to Boltzmann's law, the equilibrium fractions of molecules present in the subgroups A and B are given by the following equations, respectively:

$$\frac{N_{A}}{N_{A}+N_{B}} = \frac{q_{A}}{q} \text{ and } \frac{N_{B}}{N_{A}+N_{B}} = \frac{q_{B}}{q},$$

where $N_{A}$ and $N_{B}$ being the mean numbers of molecules in the states A and B, respectively. Therefore the equilibrium ratio, $q(T)$, of the mean numbers of molecules is given by:

$$q(T) = \frac{N_{A}}{N_{A}+N_{B}} = \frac{e^{-\frac{e_{A}}{kT}}}{e^{-\frac{e_{A}}{kT}} + e^{-\frac{e_{B}}{kT}}},$$

The canonical ensemble partition function $Q(N, V, T)$ for the system described above may be given by:

$$Q(N, V, T) = q^{N} = (q_{A} + q_{B})^{N},$$

where we have partially neglected the communal entropy term. Actually the communal entropy is already partially taken care of by the assumption that a given molecule can occupy either one of the site A and B. It is also worthwhile to note that the mean numbers $N_{A}$ and $N_{B}$ may be obtained by the following equations:

$$\frac{N_{A}}{N_{A}+N_{B}} = q_{A} = \frac{\partial \ln q}{\partial q_{A}} \text{ and } \frac{N_{B}}{N_{A}+N_{B}} = q_{B} = \frac{\partial \ln q}{\partial q_{B}}.$$  

Now, the explicit formula for the partition functions $q_{A}$ and $q_{B}$ may be easily given by the three-dimensional isotropic Hook's law assumption for the force field of the site. We shall also assume that the internuclear vibration of the diatomic molecule is harmonic and that the rotational degree of freedom is classical. These assumptions suffice to write down for the partition functions $q_{A}$ and $q_{B}$ as follows:

$$q_{A} = \left(1 - e^{-\frac{e_{A}}{kT}}\right)^{N_{A}} \text{ and } q_{B} = \left(1 - e^{-\frac{e_{B}}{kT}}\right)^{N_{B}},$$

where

$$\theta_{A} = \hbar \omega_{A} / k, \theta_{B} = \hbar \omega_{B} / k, \theta = \hbar \omega / k$$

and

$$\theta_{e} = \hbar^{2}/6 \pi^{2} \theta \omega^{2},$$

where $\omega_{A}$ and $\omega_{B}$ are the vibrational frequencies of the molecules in the three-dimensional Hook's law field in the sites A and B, $\omega_{A}$ and $\omega_{B}$ are the energies of the lowest quantum states of the molecules in sites A and B, $\nu$ is the natural frequency of internuclear vibration of the diatomic molecule and $I$ is the moment of inertia. We have also assumed that the lowest energy level of the molecule is non-degenerate. The symmetry number equals two, because we are considering symmetric diatomic molecules.

The complete expression of $q(T)$ then can be put in the form:
\( g(T) = q_s \left( 1 + \frac{q_n}{q_h} \right) \)
\[
= \left( \frac{T}{\omega} \right)^3 g(T) \left[ 1 + g(T) \right] e^{\alpha T} \quad (5),
\]
where
\[
5 \ln \delta = \ln(2\theta \theta^2) = -2jT \quad \ldots \quad (6. a).
\]
\[
g(T) = \left( \frac{T}{1 - e^{\alpha T}} \right) \left( \frac{T}{1 - e^{\alpha T}} \right) \quad (6. b).
\]
\[
g(T) = \left( \frac{T}{1 - e^{\alpha T}} \right) \left( \frac{T}{1 - e^{\alpha T}} \right) \quad (6. c).
\]
\[
\text{to} = z_e - z_4 \quad \ldots \quad (6. d).
\]
When the temperature becomes high \( g(T) \) becomes unity, i.e., the quantum correction becomes negligible. The expression for \( g(T) \) is the explicit form of the equilibrium ratio given by Eq. 2. It will be shown later that the equilibrium ratio becomes also negligible as compared to unity at high temperature. Thus at high temperature the liquid is represented by the single characteristic temperature \( \Theta \) defined in Eq. 6.a.

Now it is a simple matter to derive thermodynamic properties from Eq. 5. If \( A \) and \( \mu \) represent the Helmholtz free energy and the molecular chemical potential of the system, it follows that
\[
\frac{A}{2NT} = -lnq = -\frac{\delta A}{\delta T} = 2j^2 - 2\delta T \ln T \quad \ldots \quad (7).
\]
\[
\mu = \frac{A}{2NT} = -\frac{\delta A}{\delta T} = 2j^2 - 2\delta T \ln T \quad \ldots \quad (8),
\]
where \( z_e = z_A = PV / N \) and \( j^2 \) is defined by Eq. 6.a. The internal energy \( E \) and enthalpy \( H \) of the system are given by,
\[
\frac{E}{2NT} = T \left( \frac{\partial \ln g(T)}{\partial T} \right) \quad \ldots \quad (9).
\]
\[
\frac{H}{2NT} = E + PV \quad \ldots \quad (10),
\]
where
\[
d(T) = 4 - 3 \frac{\delta A}{\delta T} - 2 \frac{\delta A}{\delta T} + 2 \left( \frac{\delta A}{\delta T} - 1 \right) \quad (11).
\]
We see that term \( d(T) \) can be ignored when \( \Theta / T < 1 \). Since entropy \( S \) is defined thermodynamically as \( S = (E - A) / T \), the combination of Eqs. 7 and 9 yields
\[
\frac{S}{2NT} = 2j^2 - 5\delta T \ln T \quad \ldots \quad (12).
\]

f. Evaluation of Characteristic Constants

Rotational Characteristic Temperature \( \theta_r \).
Introducing the numerical values of the universal constants in Eq. 4.e we obtain
\[
\log \theta_r = 1.598 - \log(10^9 \cdot 1)
\]
with \( H(g \cdot cm^2) = Me^2 / 2N_0 \),
where \( M \) is the atomic weight of the lithium element considered, \( N_0 \) is avogadro's number and \( r_1 \) is the equilibrium distance in \( \AA \) unit between two nuclei of the molecule in the liquid state. In this paper, the numerical values of \( r_1 \) for lithium, sodium, and potassium are taken from the data for diatomic molecules in vapor phase (Hersberg). For the other elements we have taken from the atomic (or covalent) diameter given in Moeller's book.\(^1\) The values of \( r_1 \) chosen are given in Table 1.

![Table 1](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_1 )</td>
<td>2.6723(H)</td>
<td>3.079(H)</td>
<td>3.922(H)</td>
<td>4.438(M)</td>
<td>4.70(M)</td>
<td>2.346(M)</td>
<td>2.678(M)</td>
<td>2.672(M)</td>
</tr>
<tr>
<td>(-\log \theta_r )</td>
<td>0.0162</td>
<td>0.6954</td>
<td>1.1004</td>
<td>1.5240</td>
<td>1.7889</td>
<td>0.8684</td>
<td>1.20920</td>
<td>1.4698</td>
</tr>
<tr>
<td>( \theta_r \times 10^8 )</td>
<td>96.33</td>
<td>21.90</td>
<td>7.936</td>
<td>2.992</td>
<td>1.628</td>
<td>13.65</td>
<td>6.170</td>
<td>2.390</td>
</tr>
</tbody>
</table>

\(^1\) Hersberg: Moeller: Moeller
Vibrational Characteristic Temperatures: $\theta_D$ and $\theta_B$. We see from Table I that the following relationship holds for the alkali vapor molecules:

$$\theta_D = \frac{5}{7} \frac{h\nu}{k},$$

where $h\nu/k$ is the fundamental characteristic temperature assigned to the internuclear vibration of metallic diatomic gas in the ground state and $\theta_D$ is the Debye temperature given to its solid state. Eyring and Hirschfelder suggested that the best value of the characteristic temperature $\theta_B$ for the liquid metals is given by $\theta_B = 1.1 \theta_D$. Hence following the Lindemann's and Eyring's suggestions the author assumes that

$$\theta = \frac{h\nu}{k} = \frac{7}{5} \theta_B \quad \text{................................................}(13.a),$$

$$\theta_B = \frac{10}{9} \theta_B \quad \text{................................................}(13.b),$$

and $\theta_A = \frac{1}{2} \theta_B \quad \text{................................................}(13.c).$

<table>
<thead>
<tr>
<th>Element</th>
<th>$h\nu/k$ (obs.)</th>
<th>$5/7 \frac{h\nu}{k}$</th>
<th>$\theta_D$ (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>506(H)</td>
<td>229(H)</td>
<td>133(H)</td>
</tr>
<tr>
<td>Na</td>
<td>164</td>
<td>95</td>
<td>58.9</td>
</tr>
<tr>
<td>K</td>
<td>100(A)</td>
<td>59(A)</td>
<td>43.1</td>
</tr>
<tr>
<td>Rb</td>
<td>160(A)</td>
<td>100(A)</td>
<td>59(A)</td>
</tr>
<tr>
<td>Cs</td>
<td>360(F)</td>
<td>160(A)</td>
<td>60.4(H)</td>
</tr>
</tbody>
</table>

(H) : Herzberg. (A) : AIP (American Institute of Physics Handbook),
(F) : Fowler-Guggenheim.

These coefficients are expected to depend upon the crystal structure. Fortunately all of the elements of Group I have the same type of crystal structure in liquid state so that these coefficients can be treated as being common in Group I elements.

Calculation. We shall assume that in the fusion process of the metals the states A and B occur at equal probabilities. Thus we assign $g(Tm)=1$ where $Tm$ is the melting point of the metals. Thus, we obtain from Eq. 6. c

$$\frac{\nu}{kTm} = 3\ln(1 - e^{-\frac{\nu}{kTm}}) = 3 \ln(1 - e^{-\frac{\nu}{kTm}}).$$

From Eqs. 13 and 14 we can calculate the numerical value of $\nu/kTm$. The values calculated for Group I elements are given in Table I.

$\chi$ Calculation. If we assume that the system of vapor under consideration consists of ideal, monatomic vapor—this is empirically true for metallic vapor near its melting point—the change in enthalpy $\Delta H$ per gram-atom on vaporization may be given by the following equation using Eq. 10:

$$\Delta H = \frac{NkT}{2} \left\{ \frac{\nu}{kT^2} + \frac{\nu}{g(T)T^2} \right\} \frac{g(T)}{1 + g(T)} + d(T).$$

For the computation of $\chi$, the author has used the values of $\Delta H$ at melting point calculated from Kelley's empirical equation (16) (see Table II).

V. Calculation of Thermodynamic Properties

A. Vapor Pressure and Boiling Temperature.

According to Gordon's indication for the alkali vapor, let us consider a dissociation process in vapor phase, i.e., $M_2 \rightarrow 2M$. For such a system we define $G_1$ as a molar thermodynamic property given for the system of monatomic vapor at a partial pressure $P_1$ and at a mole fraction $x_1$, $G_2$ as the corresponding property for diatomic vapor and $G$ as that for vapor mixture at pressure $P$ and temperature $T$. Assuming ideal vapor mixture we deduce then

$$G(P, T) = G(P_1, T) - x_1G(P_2, T) \times \frac{x_1}{1 + x_2} \quad \text{................................................}(16).$$

If we denote the chemical potentials of monatomic and diatomic molecules and of the system as a whole by $\mu_1$, $\mu_2$ and $\mu$, respectively,
### Table II
Characteristic Constants for the Liquid Partition Function

<table>
<thead>
<tr>
<th>Element</th>
<th>$\theta_A$</th>
<th>$\theta_B$</th>
<th>$\theta$</th>
<th>$\frac{\partial g}{\partial T}$</th>
<th>$\frac{N_0g^2}{\theta}$</th>
<th>$\theta_D$</th>
<th>$\Delta H(H)_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>130</td>
<td>400</td>
<td>505(H)</td>
<td>1.75</td>
<td>34.28</td>
<td>360(F)</td>
<td>35.26</td>
</tr>
<tr>
<td>Na</td>
<td>80</td>
<td>78</td>
<td>220(H)</td>
<td>2.02</td>
<td>24.52</td>
<td>160(A)</td>
<td>25.18</td>
</tr>
<tr>
<td>K</td>
<td>50</td>
<td>111</td>
<td>133(H)</td>
<td>2.11</td>
<td>20.34</td>
<td>100(A)</td>
<td>20.87</td>
</tr>
<tr>
<td>Rb</td>
<td>36</td>
<td>80</td>
<td>82.5(H)</td>
<td>2.20</td>
<td>19.49</td>
<td>72(*)</td>
<td>19.95</td>
</tr>
<tr>
<td>Cs</td>
<td>21.5</td>
<td>47.8</td>
<td>60.4(H)</td>
<td>2.26</td>
<td>17.91</td>
<td>43(A)</td>
<td>18.33</td>
</tr>
<tr>
<td>Cu</td>
<td>158</td>
<td>350</td>
<td>441</td>
<td>2.18</td>
<td>74.64</td>
<td>315(A)</td>
<td>76.64</td>
</tr>
<tr>
<td>Ag</td>
<td>114</td>
<td>270</td>
<td>321</td>
<td>2.33</td>
<td>62.56</td>
<td>229(C)</td>
<td>64.75</td>
</tr>
<tr>
<td>Au</td>
<td>87.5</td>
<td>194</td>
<td>245</td>
<td>2.27</td>
<td>83.66</td>
<td>175(C)</td>
<td>85.61</td>
</tr>
</tbody>
</table>

$\theta_A = \frac{1}{2} \theta_D$, $\theta_B = \frac{10}{9} \theta_D$, $\theta(H) = \frac{h^2}{k}$ and $\theta = \frac{7}{8} \theta_D$.


K: Kelly's empirical formula. (*) Average value of $\theta_D$'s in AlPH and CEH.

The vapor system at dissociation equilibrium has thus been thermodynamically simplified to be handled. We now consider a system where a liquid and its vapor exist in the state of equilibrium. From the phase equilibrium law we obtain then

$$\frac{1}{2} \mu^2(P, T) = \mu^2(P_0, T) = \mu^2(P_0, T) \quad (19).$$

where factor of 1/2 is inserted due to counting each atom twice for a liquid molecule. $\mu^2$ and $\mu^2$ may be expressed in the following statistical-mechanical languages from Eq. 8 and from the ordinary discussion about monatomic, ideal vapor, respectively.

$$\frac{1}{2} \mu^2(P, T) = \frac{T^2}{2k} - \frac{T^2}{2} \ln T - \frac{5}{2} \ln g(T) \times \{1 + g(T)\} \quad (20).$$

$$\mu^2(P_0, T) = \ln P_0(\text{atm}) - j^2 - \frac{5}{2} \ln T \quad (21).$$

where

$$j^2 = \ln \left[ \frac{T}{2m(1-\gamma)/h^2} \right] \quad (22).$$

and $P^*$ represents one atmosphere in this paper and $j^2$ and $w^2$ are so-called chemical constant and electronic weight, respectively, given for a monatomic vapor. The values of $j^2$ and $j^2$ for the Group I elements are given in Table II. Eqs. 19, 20 and 21 give saturated vapor equation for liquid metal as follows:

$$\log P_0(\text{atm}) = \left( \frac{A'}{T} + j' - \frac{1}{2} \log y(T) \right) \times \{1 + g(T)\} \quad (23),$$

with

$$A' = \chi_0/2\mu 10$$

and

$$j' = (j^2 - j^2)/\mu 10 \quad (24).$$

The third term included in Eq. 23 is so insensitive to the variation in temperature that we may use, instead of second and third terms, the constant value averaged over a range of temperature from the melting point to the boiling point.

We thus rewrite Eq. 23 as follows:

$$\log P = -\frac{A'}{T} + B' \quad \text{with} \quad z_1 = 1 \quad (25,a).$$

where

$$B' = j' - \frac{1}{2} \log y(T) \{1 + g(T)\} \quad (25,b)$$

The constants $A'$ and $B'$ for the Group I elements are given in Table II.
TABLE II

Vapor Constants Involved in Eqs. 20, 21, and 25.

<table>
<thead>
<tr>
<th>Element</th>
<th>A'</th>
<th>A'</th>
<th>B'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>7.49</td>
<td>4.92</td>
<td>4.55</td>
</tr>
<tr>
<td>Na</td>
<td>5.39</td>
<td>7.56</td>
<td>4.55</td>
</tr>
<tr>
<td>K</td>
<td>1.46</td>
<td>1.00</td>
<td>4.71</td>
</tr>
<tr>
<td>Rb</td>
<td>4.25</td>
<td>1.01</td>
<td>4.71</td>
</tr>
<tr>
<td>Cs</td>
<td>3.91</td>
<td>1.09</td>
<td>4.55</td>
</tr>
<tr>
<td>Cu</td>
<td>16.32</td>
<td>4.31</td>
<td>4.55</td>
</tr>
<tr>
<td>Ag</td>
<td>13.74</td>
<td>1.77</td>
<td>4.55</td>
</tr>
<tr>
<td>Au</td>
<td>18.30</td>
<td>2.16</td>
<td>4.55</td>
</tr>
</tbody>
</table>

According to Eqs. 23 and 25, we can calculate the vapor pressures at melting points and normal boiling temperatures, assuming \( z_1 = 1 \). The results shown in Table II are all in good accordance with the Quill's empirical values given for a system containing only monatomic vapor.

The boiling temperatures at different pressures have been calculated by Eq. 25 and compared with the Quill's data again. Inspite of its simple form the results shown in Table II are satisfactory.

TABLE III

Vapor Pressure at Melting Point and Normal Boiling Temperature, Assuming \( z_1 = 1 \).

<table>
<thead>
<tr>
<th>Element</th>
<th>Calculated from</th>
<th>Observed</th>
<th>Calculated from</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>8.99×10^{-13}</td>
<td>1.00×10^{-13}</td>
<td>10.6×10^{-13}</td>
<td>1.45×10^{-13}</td>
</tr>
<tr>
<td>Na</td>
<td>7.40×10^{-13}</td>
<td>1.00×10^{-13}</td>
<td>7.94×10^{-13}</td>
<td>1.18×10^{-13}</td>
</tr>
<tr>
<td>K</td>
<td>6.58×10^{-13}</td>
<td>1.00×10^{-13}</td>
<td>14.1×10^{-13}</td>
<td>1.05×10^{-13}</td>
</tr>
<tr>
<td>Rb</td>
<td>2.61×10^{-13}</td>
<td>1.00×10^{-13}</td>
<td>7.08×10^{-13}</td>
<td>1.05×10^{-13}</td>
</tr>
<tr>
<td>Cs</td>
<td>8.23×10^{-13}</td>
<td>1.00×10^{-13}</td>
<td>15.9×10^{-13}</td>
<td>1.05×10^{-13}</td>
</tr>
<tr>
<td>Cu</td>
<td>4.21×10^{-13}</td>
<td>1.00×10^{-13}</td>
<td>15.9×10^{-13}</td>
<td>1.05×10^{-13}</td>
</tr>
<tr>
<td>Ag</td>
<td>2.08×10^{-4}</td>
<td>1.95×10^{-4}</td>
<td>2.94×10^{-4}</td>
<td>2.94×10^{-4}</td>
</tr>
</tbody>
</table>

Q : obtained by means of extrapolation method from Quill's data \(^{41} \) A: taken from AlPH.

E1: Van Looz Equation, \( \log P(\text{mm Hg}) = -\frac{9.030}{T} + 1.2\log T + 12 \).

E2: van Looz Equation, \( \log P(\text{atm}) = -\frac{20.760}{T} + 7.20 \).

B. Entropy

From Eq. 10 and Eq. 12 the enthalpy and entropy of a liquid metal per gram atom are given by

\[
H/T = -\frac{Nk}{2} \left[ \frac{z_f}{kT} + 5 - \frac{z_g}{kT} - \frac{g(T)}{1 + g(T)} d(T) \right] \tag{26}
\]

and

\[
S = -\frac{Nk}{2} \left[ z_f + 5\ln T + 5\ln(1 + g(T)) + 5 \frac{z_f}{kT} \frac{g(T)}{1 + g(T)} d(T) \right] \tag{27}
\]

From these equations it is possible to calculate the entropy of vaporization and fusion.

Entropy of Vaporization. The enthalpy \( H_1(P, T) \) and entropy \( S_1(P, T) \), and \( H_2(P, g) \) and \( S_2 \) (Pa, T) are the partial molar quantities given for the system of monatomic and diatomic vapor, respectively. Then, according to the ordinary statistical treatment we may express them in the following forms:

\[
H_1/T = 5R/2 \tag{28}
\]

\[
H_2/T = R(5/2 + \frac{\hbar^2}{kT} - D/RT) \tag{29}
\]

and

\[
S_1 = R(n_f) + \frac{5}{2} + \frac{5}{2} \ln T - \ln P_1(\text{atm}) \tag{30}
\]

where \( \hbar^2/k \) and \( D \) are the fundamental characteristic temperature and molar heat of dissociation assigned to the diatomic molecule in the
ground state, respectively, and their values have been given by Herzberg.\(^7\)

Let us denote the enthalpy and entropy of vaporization for the hypothetical system consisting of ideal, monatomic vapor only, and those for the real system containing diatomic vapor by \(H_v\) and \(S_v\)\(^1\) and by \(H_e\) and \(S_e\) respectively. Then we will obtain the following expressions by the application of Eqs. 26 to 30:

\[
\frac{\Delta H_v}{T} = \frac{N_x k}{2T} + \frac{N_x k}{2} \left[ \frac{\varepsilon_x}{kT} \frac{g(T)}{[1 + g(T)]} + d(T) \right]
\]

\[
\frac{\Delta H_e}{T} = \frac{\Delta H_v}{T} - \left( \frac{D}{N_x kT} \frac{3}{2} \frac{hT}{e^{\frac{hT}{kT}} - 1} \right) \times \frac{x^2}{1 + x^2} \quad \ldots \ldots \ldots (31).
\]

\[
\Delta S_v = \Delta S_v = - \frac{N_x k}{2} \left[ \frac{\varepsilon_x}{kT} \frac{g(T)}{[1 + g(T)]} + d(T) \right]
\]

\[
\Delta S_e = \Delta S_v = - N_x k \left( \frac{D}{N_x kT} + \frac{3}{2} \frac{hT}{e^{\frac{hT}{kT}} - 1} \right) \times \frac{x^2}{1 + x^2} \quad \ldots \ldots \ldots (32).
\]

where \(j = j - j\). The results calculated from these equations, as shown in Tables VI and VII, are in good accordance with those observed. We notice, however, that the entropies of vaporization calculated at normal boiling point are somewhat larger than those observed but do not exceed the commumal entropy \(R\). This discrepancy perhaps comes from the fact that we have treated the total number of lattice sites and the minimum potential energies \(x\)'s as constant though we consider them as the functions of temperature and volume.

### Table VI

The Boiling Temperature at Different Pressures, Assuming \(x = 1\)

<table>
<thead>
<tr>
<th>Element</th>
<th>10(^{-4})</th>
<th>10(^{-5})</th>
<th>Pressure in atm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>710</td>
<td>743</td>
<td>875</td>
</tr>
<tr>
<td>Na</td>
<td>507</td>
<td>561</td>
<td>775</td>
</tr>
<tr>
<td>K</td>
<td>434</td>
<td>481</td>
<td>629</td>
</tr>
<tr>
<td>Rh</td>
<td>466</td>
<td>500</td>
<td>621</td>
</tr>
<tr>
<td>Cs</td>
<td>339</td>
<td>423</td>
<td>496</td>
</tr>
<tr>
<td>Cu</td>
<td>1398</td>
<td>1530</td>
<td>1440</td>
</tr>
<tr>
<td>Ag</td>
<td>1194</td>
<td>1305</td>
<td>1440</td>
</tr>
<tr>
<td>Au</td>
<td>1570</td>
<td>1720</td>
<td>1440</td>
</tr>
</tbody>
</table>

Observed: taken from the Quill's data.

### Table VII

Entropy of Vaporization at Melting Point—
Calculated From Eqs. 31 and 33

<table>
<thead>
<tr>
<th>Element</th>
<th>(\Delta H_v/Tm)</th>
<th>(\Delta S_e)</th>
<th>(\Delta S_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>72.7</td>
<td>77.5</td>
<td>77.7 (K)</td>
</tr>
<tr>
<td>Na</td>
<td>67.9</td>
<td>67.9</td>
<td>67.9 (K)</td>
</tr>
<tr>
<td>K</td>
<td>62.0</td>
<td>62.0</td>
<td>62.0 (K)</td>
</tr>
<tr>
<td>Rh</td>
<td>64.0</td>
<td>64.0</td>
<td>63.9 (A)</td>
</tr>
<tr>
<td>Cs</td>
<td>60.8</td>
<td>60.8</td>
<td>60.7 (A)</td>
</tr>
<tr>
<td>Cu</td>
<td>56.5</td>
<td>56.5</td>
<td>56.5 (K)</td>
</tr>
<tr>
<td>Ag</td>
<td>52.5</td>
<td>52.5</td>
<td>52.5 (K)</td>
</tr>
<tr>
<td>Au</td>
<td>64.1</td>
<td>64.1</td>
<td>64.1 (K)</td>
</tr>
</tbody>
</table>

On computation of \(\Delta H_v/Tm\) the melting points used are given in AIPH. \(K\) : Calculated from the Kelly's empirical equation. \(A\) : AIPH.
A Partition Function for Liquid Metals

**Table III**

<table>
<thead>
<tr>
<th>Element</th>
<th>Assuming $z_1=1$</th>
<th>Using the Values of $z_i$ given below</th>
<th>Observed (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated (e.u.)</td>
<td>Calculated (e.u.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta H_v^{(1)}/TB$</td>
<td>$\Delta S_v^{(1)}$</td>
<td>$\Delta H_v^{(2)}/TB$</td>
</tr>
<tr>
<td>Li</td>
<td>21.81(A)</td>
<td>22.13</td>
<td>19.77(Q)</td>
</tr>
<tr>
<td>Na</td>
<td>21.42(A)</td>
<td>21.07</td>
<td>19.51(A)</td>
</tr>
<tr>
<td>K</td>
<td>19.99(A)</td>
<td>19.43</td>
<td>19.28(A)</td>
</tr>
<tr>
<td>Rb</td>
<td>20.80(A, Q)</td>
<td>19.66</td>
<td>19.35(A)</td>
</tr>
<tr>
<td>Cs</td>
<td>18.83(A, Q)</td>
<td>18.65</td>
<td>18.95(Q)</td>
</tr>
<tr>
<td>Cu</td>
<td>24.41(A)</td>
<td>26.19</td>
<td>19.02(A)</td>
</tr>
<tr>
<td>Ag</td>
<td>23.87(A)</td>
<td>25.88</td>
<td>18.01(Q)</td>
</tr>
<tr>
<td>A</td>
<td>23.93(A)</td>
<td>26.93</td>
<td>16.96(A)</td>
</tr>
</tbody>
</table>

a) A and Q in the second, fourth and last columns denote that the boiling temperatures and entropies taken from the data of AIPH (A) and from Quill's data (Q), respectively.

b) The values of $z_i$ at normal boiling point have been calculated by the usual statistical methods, using the data given by Herzberg's book. The numerical values of $z_i$ for alkali metals are: Li(0.845), Na(0.866), K(0.950), Rb(0.95), and Cs(0.942).

**Entropy of Fusion.** Before discussing the entropy of fusion, it is necessary to consider the state of solid for alkalis and to set up a crystalline partition function of their solid states. As pointed out by several authors, solid alkalis are composed of the two allotropic modifications, i.e., $\alpha$ and $\beta$-forms. For example, E. Cohen and G. de Bruin argue that under ordinary conditions solid sodium consists of two allotropic modifications, i.e., $\alpha$-sodium and $\beta$-sodium, the portions of which are dependent upon their previous thermal treatments. The transition point yet undetermined lies between 273 and 283° K, possibly near 280° K. Moreover, it is seen in the literature that there exist the two allotropic modifications for lithium, potassium and copper in their solid states. Then the solid crystalline partition function $K(T)$ of the system can be written by

$$K(T) = (q_\alpha(T) + q_\beta(T))^N,$$

where $q_\alpha$ and $q_\beta$ are the molecular partition functions for the two forms of modification. At the melting point, we assume that $q_\alpha = q_\beta$ in accordance with the previous assumption in the case of liquid state. The above equation thus reduces to $K(T_m) = (2q_\alpha)^N = (2q_\beta)^N$. Hence combining this equation with the usual Einstein model $K(T)$ will be given by

$$K(T) = \left[\frac{\theta_E^2}{1 - e^{-\theta_E/T}}\right]^N,$$

where $\theta_E$ is the so-called Einstein characteristic temperature and $\epsilon$ is the energy required for the separation of one of the oscillators in the normal state from the other to the infinite distance.

We may assume further that the Einstein oscillators are reduced to the classical form at the melting point so that we have in the following final form:

$$K(T_m) = \left[\frac{\theta_E^2}{1 - e^{-\theta_E/T}}\right]^N(\text{at melting point})$$

At the melting point, the entropy of the solid crystalline will be thus given by

$$S^K(T_m) = NK(\chi t + 3 + 3 \ln T_m)$$

where $\chi t = \ln(2/\theta_E^2)$

Let us then check the entropy equation, Eq. 36 by comparing the values of entropy of sublimation calculated with those observed. From the combina-
function of Eqs. 30 and 38, the entropy of sublimation 
\( \Delta S_f \) will be given by

\[
\Delta S_f(T_s) = N_c k \left( j^2 - j^F - \frac{1}{2} \ln T_s - \frac{1}{2} \frac{e_v}{kT_s} \right) - \frac{1}{2} d(T_s) + \frac{1}{2} \ln 2 g(T_s)
\] (37).

Eq. 37, together with Fowler's rule, i.e., \( \theta_d = \frac{5}{7} \theta_e \) make it possible to calculate the entropy of sublimation or the Debye characteristic temperature by reversed calculation.

On the computation the data given in AIPH are used and the values calculated are shown in Table II. The results are satisfactory compared with those observed. This means that the solid crystalline partition function and Fowler's rule about the Einstein characteristic temperature work correctly to give the Debye temperature.

**Table II**  
Einstein and Debye Temperatures. Calculated from the Entropy of Sublimation.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ca</th>
<th>Bc</th>
<th>Cd</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>35.2</td>
<td>667</td>
<td>118</td>
<td>70.3</td>
</tr>
<tr>
<td>( \theta_d )</td>
<td>49.3</td>
<td>994</td>
<td>165</td>
<td>98.5</td>
</tr>
<tr>
<td>Eq. 37</td>
<td>43</td>
<td>1160</td>
<td>165</td>
<td>75</td>
</tr>
<tr>
<td>Eq. 38</td>
<td>68</td>
<td>900</td>
<td>168</td>
<td>97</td>
</tr>
<tr>
<td>AIPH CEH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Since the crystalline partition function given by Eq. 35, together with Fowler's rule have been confirmed to work correctly, we may use them to derive the equation of the entropy of fusion. By means of Eqs. 27 and 35 the entropy of fusion will be expressed in the following form, introducing the limiting value of \( g(T) \) at melting point, i.e. \( g(T_m) = 1 \)

\[
\Delta S_j = N_c k \left( j^2 - j^F - \frac{1}{2} \ln T_m - \frac{1}{2} \frac{e_v}{kT_m} \right) - \frac{1}{2} d(T_m) + \frac{1}{2} \ln 2 g(T_m)
\] (38).

On computation we have used the data in AIPH and the results obtained (shown in Table I) are successful to give the correct values of the Debye temperature. From this fact we may conclude that the liquid partition function retains its correct feature to describe the state of the liquid at melting point.

**Table I**  
Einstein and Debye Temperatures. Calculated from Entropy of Fusion

<table>
<thead>
<tr>
<th>Element</th>
<th>Ca</th>
<th>Bc</th>
<th>Cd</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp.</td>
<td>35.2</td>
<td>667</td>
<td>118</td>
<td>70.3</td>
</tr>
<tr>
<td>( \theta_d = \frac{7}{5} \theta_e )</td>
<td>49.3</td>
<td>994</td>
<td>165</td>
<td>98.5</td>
</tr>
<tr>
<td>Eq. 38</td>
<td>43</td>
<td>1160</td>
<td>165</td>
<td>75</td>
</tr>
<tr>
<td>Eq. 38</td>
<td>68</td>
<td>900</td>
<td>168</td>
<td>97</td>
</tr>
<tr>
<td>AIPH CEH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Furthermore, if we neglect the contribution due to the quantum effect and put \( e_v/kT_m = 2 \) as the average value for the various elements, Eq. 38 becomes

\[
\Delta S_j = R \left( j^2 - j^F - \frac{1}{2} \ln T_m - 1 + \frac{1}{2} \ln 2 \right) \] (39).

Substituting the following relations into Eq. 39:

\[
j^2 = \frac{5}{2} \ln \Theta = - \frac{1}{2} \ln (2 \Theta \theta_e^3),
\]

\[
\theta_e = k^2 \theta_e \theta_e = k^2 N_c \frac{4 \pi^2 k M_r \theta_e^4}{2} \text{ and } j^F = \ln (2 \Theta \theta_e^3).
\]

We obtain

\[
\Delta S_j = R \ln \left( \frac{7}{2} \right) + R \ln \left( \frac{5}{7} \theta_e^3 \theta_e \right)
\]

or

\[
\theta_e = \left( \frac{h}{T_m} \right)^{\frac{1}{2}} \left( \frac{N_c}{k} \right)^{\frac{1}{2}} \frac{\alpha e_v^4}{R T_m^{\frac{1}{2}}} \] (40).

where \( \gamma \equiv \theta_e \theta_e \theta_e \theta_e \).

We see that Debye temperature \( \theta_d \) is proportional to \( (T_m/M_r)^{1/2} \), which has been derived also by Lindemann.10

**C. Atomic Heat Capacity**

Atomic heat capacity at constant volume \( C_V \) and that at constant pressure \( C_P \) are thermodynamically expressed in the formulas:

\[
C_V = \left( \frac{\partial E}{\partial T} \right)_V
\]

and

\[
C_P = C_V + \frac{\alpha^2}{\beta} VT
\]

respectively, where \( \alpha \) and \( \beta \) represent the coefficients of the cubical thermal expansion and of the compressibility, respectively. Therefore the application of Eq. 9 gives
A Partition Function for Liquid Metals

\[ C_v = \frac{5}{2} R + \frac{R}{2} \left[ \frac{\theta_i}{kT} + \frac{1}{2} \log \frac{y(T)}{1+y(T)} \right] \]

\[ -3 \left( \frac{\theta_i}{kT} \right)^2 \frac{g(T)}{1+g(T)} \left[ \frac{g(T)}{1+g(T)} \right] \]

with \( \theta_i = \frac{\theta_i}{kT} \cos \phi_i \).

The atomic heat capacities of the several elements at melting point have been calculated from Eq. 41 and compared with empirical values, as given in Table XI. We see some discrepancies between the values calculated and those observed, but the results may be satisfactory, because there are wide discrepancies even among the observed values themselves as shown in Meller’s book. If we neglect quantum effect Eq. 41 then becomes

\[ C_v = \frac{5}{2} R + \frac{R}{2} \left( \frac{\theta_i}{kT} \right)^2 \frac{g(T)}{1+g(T)} \left[ \frac{g(T)}{1+g(T)} \right] \]

This equation gives the following limiting values:

\[ C_v(T) = 2R - 2.5R \text{ as } T_v = -T_s. \]

Since \( \epsilon/kT\rightarrow 0 \), \( g(T_v) = 1 \) and

\[ g(T_b)/(1+g(T))^2 \rightarrow 0. \]

This tendency for the limiting values is consistent with the empirical facts found in mercury, argon and neon etc.

### Table XI

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_v \text{ (calc.)} )</td>
<td>6.11</td>
<td>6.30</td>
<td>6.39</td>
<td>6.35</td>
<td>6.42</td>
<td>6.27</td>
<td>6.40</td>
<td>6.40</td>
</tr>
<tr>
<td>( C_v \text{ (obs.)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_p \text{ (calc.)} )</td>
<td>6.46</td>
<td>6.46</td>
<td>6.81</td>
<td>6.66</td>
<td>6.66</td>
<td>6.91</td>
<td>6.91</td>
<td>6.91</td>
</tr>
<tr>
<td>( C_p \text{ (obs.)} )</td>
<td>7.48</td>
<td>7.43</td>
<td>7.09</td>
<td>7.40</td>
<td>7.67</td>
<td>7.40</td>
<td>7.40</td>
<td>7.40</td>
</tr>
</tbody>
</table>

a) \( C_v \text{ (calc.)} \): calculated from Eq. 41. b) \( C_v \text{ (obs.)} \) and \( C_p \text{ (calc.)} \): calculated from the formula \( C_v = C_i + a_i + VT^2 \). With the numerical values of \( a_i \) and \( \beta \), taken from Landolt’s Physicalische Chemische Tabellen and Washburn’s International Critical Table. c) \( C_p \text{ (obs.)} \): taken from Lyon’s book.

### Conclusions

1. Using the present liquid model the following results have been obtained.

   1.1. The pressure of saturated vapor is given by

   \[ \log P_1(\text{atm}) = \frac{A'}{T} + B' \]

   This equation is reduced to the ordinary thermodynamic expression

   \[ \log P_1(\text{atm}) = \frac{A'}{T} + B' \]

   \( A' \) and \( B' \) are characteristic constants involved in the above two equations have been evaluated by the statistical mechanical method.

2. The entropy of vaporization at the normal boiling point becomes

   \[ dS_v(T_b) = R(e^{y} - 1) \]

3. From the consideration of rates of fusion and sublimation at melting point it is confirmed that Fowler’s rule, i.e., \( \theta_v = \frac{5}{2} \theta_b \), is applicable to the calculation of the Debye characteristic temperature from the liquid partition function.

4. The atomic heat capacity has the following limiting values:

   \[ C_v(T) = 3R - 2.5R \text{ as } T_v = -T_s. \]

This result is also in accordance with the ex-
pectation from the solid crystal theory and empirical results about liquids.

5. Ignoring the quantum effect we may rewrite the liquid partition function Eq. 5 as follows:

\[ q(T) = \left( \frac{T}{\theta} \right)^n \left[ 1 + \left( \frac{\theta}{2} \right)^n \right]^{\frac{1}{\theta}} \]

Applying the relation of \( g(Tm) = 1 \) to the above equation we may obtain the following equation:

\[ q(T) = \left( \frac{T}{\theta} \right)^n \left[ 1 + \left( \frac{\theta}{2} \right)^n \left( \frac{Tm}{T} \right) \right] \]

We therefore conclude that equation (b) is probably the simplest possible one that retains the correct qualitative features, especially for a liquid metal with \( \frac{\theta}{T}(1) \).

II. Acknowledgement

The author wishes to express his sincere gratitude to Dean Henry Eyring, Professor Taikyue Rhee and Professor Shoon Kyung Kim, whose encouragement and guidance have made this work possible.

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