

A Partition Function for Liquid Metals

By Wan Kyuc Kim

Department of Chemistry, Ewha Womans University

液體金屬의 狀態和

金 完 奎*

(1962. 2. 20 受理)

要 約

筆者는 週期表 1 族에 適用되는 液體金屬의 模型으로서 純粹한 液體金屬은 2 原子分子의 單振動子로 構成되며 이 振動子는 自己가 占有하는 싸이트(site)種에 따라 두가지 에너지狀態中 하나를 取하게 된다고 假想함으로써 液體狀態和를 誘導하였다.

이 狀態和式은 本質의 으로는 하나의 物質固有의 常數(Θ)를 內包하고 있으며 液體金屬에 對하여 이 特性值를 用으로써 여러가지 熱力學的 性質 즉 蒸氣壓, 液體의 엔트로피, 比熱 등을 算出하여 實測值와 比較하여 보았다. 그 結果는 滿足스러운 一致를 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 accesible to either one of the two sorts of lattice sites. The partition function involves constants characteristic of substance, which are obtainable 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 accordances with those observed, within experimental error, although a slight derivation is observed in the atomic heat capacity.

1. Introduction

Eyring and Hirschfelder,¹⁾ and Lennard-Jones and Devonshire²⁾ 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. Kirkwood³⁾ 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, Ree and Eyring⁴⁾ have set up a partition function for the inert gas based upon their well-known hole theory. For liquid metals, Kincaid and Eyring,⁵⁾ and Hirschfelder, Stevenson and Eyring⁶⁾ 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. Herzberg⁷⁾ 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,⁸⁾ Gorden'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.

*梨花女子大學校 化學科

On the other hand, Blackmann,⁹⁾ Montroll,¹⁰⁾

Newell⁽¹⁾ and Van Hove⁽²⁾ 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 Nernst 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 in B sites.

1. Derivation of the Partition Function for Liquid Metals

Let $\epsilon_{A,i}$ and $\epsilon_{B,j}$ 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

$$q_A = \sum_i e^{-\epsilon_{A,i}/kT} \text{ and } q_B = \sum_j e^{-\epsilon_{B,j}/kT}.$$

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

$$q = \sum_i e^{-\epsilon_{A,i}/kT} + \sum_j e^{-\epsilon_{B,j}/kT} = q_A + q_B \dots (1).$$

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, $g(T)$, of the

mean numbers of molecules is given by.

$$g(T) = \frac{N_B}{N_A} = \frac{q_B}{q_A} \dots (2).$$

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

$$Q(N, V, T) = q^N = (q_A + q_B)^N \dots (3),$$

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 forces 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:

$$q_A = (1 - e^{-\theta_A/T})^{-3} (1 - e^{-\theta/T})^{-1} \frac{T}{2\theta_r} e^{x_A/kT} \dots (4. a),$$

$$q_B = (1 - e^{-\theta_B/T})^{-3} (1 - e^{-\theta/T})^{-1} \frac{T}{2\theta_r} e^{x_B/kT} \dots (4. b),$$

where

$$\theta_A = h\nu_A/k, \theta_B = h\nu_B/k, \theta = h\nu/k \text{ and}$$

$$\theta_r = h^2/8\pi^2 I k \dots (4. c),$$

where ν_A and ν_B are the vibrational frequencies of the molecules in the three-dimensional Hook's law field in the sites A and B, x_A and x_B are the energies of the lowest quantum states of the molecules in sites A and B, ν 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:

$$q(T) = q_A(1 + q_B/q_A) \\ = \left(\frac{T}{\Theta}\right)^5 y(T) \{1 + g(T)\} e^{\chi_A/kT} \dots (5),$$

where

$$5 \ln \Theta = \ln(2\theta_r \theta_A^3) = -2j^L \dots (6. a),$$

$$y(T) = \left(\frac{\theta_A/T}{1 - e^{-\theta_A/T}}\right)^3 \left(\frac{\theta/T}{1 - e^{-\theta/T}}\right) \dots (6. b),$$

$$g(T) = \left(\frac{1 - e^{-\theta_A/T}}{1 - e^{-\theta_B/T}}\right)^3 e^{\epsilon_0/kT} \dots (6. c),$$

$$\epsilon_0 = \chi_B - \chi_A \dots (6. d).$$

When the temperature becomes high $y(T)$ 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 Θ defined in Eq. 6. a.

Now it is a simple matter to derive thermodynamic properties from Eq. 5. If A and μ represent the Helmholtz free energy and the molecular chemical potential of the system, it follows that

$$\frac{A}{NkT} = -\ln q = -\frac{\chi_A}{kT} - 2j^L - 5\ln T - \ln y(T) \times \\ \{1 + g(T)\} \dots (7)$$

$$\frac{\mu}{kT} = \frac{A + PV}{NkT} = -\frac{\chi_0}{kT} - 2j^L - 5\ln T - \ln y(T) \times \\ \{1 + g(T)\} \dots (8),$$

where $\chi_0 = \chi_A - PV/N$ and j^L is defined by Eq. 6. a. The internal energy E and enthalpy H of the system are given by,

$$\frac{E}{NkT} = T \left(\frac{\partial \ln q}{\partial T} \right)_{V,N} = -\frac{\chi_A}{kT} + 5 - \frac{\epsilon_0}{kT} \times \\ \frac{g(T)}{1 + g(T)} - d(T) \dots (9),$$

$$\frac{H}{NkT} = \frac{E + PV}{NkT} = -\frac{\chi_0}{kT} + 5 - \frac{\epsilon_0}{kT} \frac{g(T)}{1 + g(T)} \\ - d(T) \dots (10),$$

where

$$d(T) = 4 - 3 \frac{\theta_A/T}{e^{\theta_A/T} - 1} - \frac{\theta/T}{e^{\theta/T} - 1} + 3 \left(\frac{\theta_A/T}{e^{\theta_A/T} - 1} \right. \\ \left. - \frac{\theta_B/T}{e^{\theta_B/T} - 1} \right) \frac{g(T)}{1 + g(T)} \dots (11).$$

We see that term $d(T)$ can be ignored when $\theta/T \ll 1$. Since entropy S is defined thermodynamically as $S = (E - A)/T$, the combination of Eqs. 7 and 9 yields

$$\frac{S}{NkT} = 2j^L + 5\ln T + \ln y(T) \{1 + g(T)\} + 5 \\ - \frac{\epsilon_0}{kT} \frac{g(T)}{1 + g(T)} - d(T) \dots (12).$$

II. Evaluation of Characteristic Constants

Rotational Characteristic Temperature θ_r .

Introducing the numerical values of the universal constants in Eq. 4. c we obtain

$$\log \theta_r = 1.598 - \log(10^{10} \cdot I)$$

$$\text{with } I(\text{g}\cdot\text{cm}^2) = Mr_e^2/2No,$$

where M is the atomic weight of the liquid element considered, No is avogadro's number and r_e is the equilibrium distance in Å unit between two nuclei of the molecule in the liquid state. In this paper, the numerical values of r_e for lithium, sodium, and potassium are taken from the data for diatomic molecules in vapor phase (Herzberg). For the other elements we have taken from the atomic (or covalent) diameter given in Moeller's book.¹³⁾ The values of r_e chosen are given in Table I.

TABLE I
Rotational Characteristic Constants

Element	Li	Na	K	Rb	Cs	Cu	Ag	Au
r_e	2.6723(H)	3.079(H)	3.923(H)	4.43(M)	4.70(M)	2.346(M)	2.678(M)	2.672(M)
$-\log \theta_r$	0.01623	0.65954	1.1004	1.5240	1.7889	0.86484	1.20970	1.4698
$\theta_r \times 10^2$	96.33	21.90	7.936	2.992	1.626	13.65	6.170	3.390

H: Herzberg⁷⁾ M: Moeller¹³⁾

Vibrational Characteristic Temperatures: θ, θ_A and θ_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 θ_D is the Debye temperature given to its solid state. Eyring and Hirschfelder suggested that the

best value of the characteristic temperature θ_i for the liquid metals is given by $\theta_i = 1.1 \theta_D$. Hence following the Lindermann's and Eyring's suggestions the author assumes that

$$\theta = \frac{h\nu}{k} = \frac{7}{5} \theta_D \dots\dots\dots (13. a),$$

$$\theta_B = \theta_i = \frac{10}{9} \theta_D \dots\dots\dots (13. b),$$

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

TABLE I
Rule of $\theta_D = \frac{5}{7} \frac{h\nu}{k}$ for the Alkali Metals

Element	Li	Na	K	Rb	Cs
$\frac{h\nu}{k}$ (obs.)	505(H)	229(H)	133(H)	82.5(H)	60.4(H)
$\frac{5}{7} \frac{h\nu}{k}$	361	164	95	58.9	43.1
θ_D (obs.)	360(F)	160(A)	100(A)	59(A)	43(A)

(H): Herzberg,⁷⁾ (A): AIPH (American Institute of Physics Handbook),

(F): Fowler-Guggenheim.¹⁴⁾

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.

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

$$\frac{\epsilon_0}{kT_m} = 3 \ln(1 - e^{-\theta_B/T_m}) - 3 \ln(1 - e^{-\theta_A/T_m}) \dots (14).$$

From Eqs. 13 and 14 we can calculate the numerical value of ϵ_0/kT_m . The values calculated for Group I elements are given in Table II.

χ_0 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 ΔH_v per gram-atom on vaporization may be given by the following equation using Eq. 10:

$$\Delta H_v = -\frac{N_0 k T}{2} \left\{ \frac{\chi_0}{kT} + \frac{\epsilon_0}{kT} \frac{g(T)}{1+g(T)} + d(T) \right\} \dots (15),$$

For the computation of χ_0 the author has used the values of ΔH_v at melting point calculated from Kelley's empirical equation¹⁵⁾ (see Table III).

IV. Calculation of Thermodynamic Properties

A. Vapor Pressure and Boiling Temperature.

According to Gorden's indication⁸⁾ for the alkali vapor, let us consider a dissociation process in vapor phase, i.e., $M_2 \rightleftharpoons 2M$. 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

$$G(P, T) = G_1(P_1, T) - \{2G_1(P_1, T) - G_2(P_2, T)\} \times \frac{x_2}{1+x_2} \dots\dots\dots (16).$$

If we denote the chemical potentials of monatomic and diatomic molecules and of the system as a whole by μ_1 , μ_2 and μ^c , respectively, equil-

TABLE II
Characteristic Constants for the Liquid Partition Function

Element	θ_A	θ_B	θ	$\frac{\epsilon_0}{kT_m}$	$\frac{N_0\chi_0}{2}$ kcal/g-atom	θ_D obs	$\Delta H_v(T_m)^K$ kcal/g-atom
Li	180	400	505(H)	1.75	34.28	360(F)	35.26
Na	80	178	229(H)	2.02	24.52	160(A)	25.18
K	50	111	133(H)	2.11	20.34	100(A)	20.87
Rb	36	80	82.5(H)	2.20	19.49	72(*)	19.95
Cs	21.5	47.8	60.4(H)	2.26	17.91	43(A)	18.33
Cu	158	350	441	2.18	74.64	315(A)	76.64
Ag	114	270	321	2.39	62.86	229(C)	64.75
Au	87.5	194	245	2.27	83.66	175(C)	85.61

$$\theta_A = \frac{1}{2}\theta_D, \quad \theta_B = \frac{10}{9}\theta_D, \quad \theta(H) = \frac{h\nu}{k} \quad \text{and} \quad \theta = \frac{7}{5}\theta_D.$$

F: Fowler-Guggenheim, A: AIPH, C: CEH (J.H. Perry's Chemical Engineer's Handbook).

K: Kelly's empirical formula.¹⁵⁾ (*) Average value of θ_D 's in AIPH and CEH.

ibrium law gives

$$\mu_2(P_2, T) = 2\mu_1(P_1, T) \quad (17).$$

Introducing Eq. 17 into Eq. 16, we obtain

$$\mu^G(P, T) = \mu_1(P_1, T) \quad (18).$$

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

$$\frac{1}{2}\mu^L(P, T) = \mu^G(P, T) = \mu_1(P_1, T) \quad (19),$$

where factor of 1/2 is inserted due to counting each atom twice for a liquid molecule. μ^L and μ_1 may be expressed in the following statistical-mechanical languages from Eq. 8 and from the ordinary discussion about monatomic, ideal vapor, respectively.

$$\frac{1}{2} \frac{\mu^L}{kT} = -\frac{\chi_0}{2kT} - j^L - \frac{5}{2} \ln T - \frac{1}{2} \ln y(T) \times \{1+g(T)\} \quad (20),$$

$$\mu_1(P_1, T) = \ln P_1(\text{atm}) - j_1^G - \frac{5}{2} \ln T \quad (21),$$

where

$$j_1^G = \ln \left\{ \frac{(2\pi m_1 k)^{3/2}}{h^3} \frac{k}{P_0} \omega_1^G \right\} \quad (22),$$

and P_0 represents one atmosphere in this paper and j_1^G and ω_1^G are so-called chemical constant and electronic weight, respectively, given for a monatomic vapor. The values of j^L and j_1^G for the Group I elements are given in Table IV. Eqs. 19, 20 and 21 give saturated vapor equation for liquid metal as follows:

$$\log P_1(\text{atm}) = -\frac{A'}{T} + j' - \frac{1}{2} \log y(T) \times \{1+g(T)\} \quad (23),$$

with

$$A' = \chi_0/2k \ln 10 \quad \text{and} \quad j' = (j^G - j^L)/\ln 10 \quad (24).$$

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:

$$\log P = -\frac{A'}{T} + B' \quad \text{with} \quad x_1 = 1 \quad (25.a),$$

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 IV.

TABLE IV

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

Element	A'	$j_1'G$	$-j_1'L$	j'	B'
Li	7,492	-0.0239	4.8769	4.5530	4.55
Na	5,359	0.7566	3.8603	4.6169	4.55
K	4,446	1.1002	3.1714	4.2736	4.25
Rb	4,261	1.6118	2.6762	4.2880	4.50
Cs	3,914	1.8994	2.1898	4.0892	4.05
Cu	16,320	1.4186	4.3383	5.7579	5.70
Ag	13,740	1.7734	3.8838	5.6572	5.60
Au	18,300	2.1584	3.5232	5.6816	5.65

$$-j_1'G = j_1'G/\ln 10 \quad \text{and} \quad j_1'L = j_1'L/\ln 10.$$

According to Eqs. 23 and 25, we can calculate the vapor pressures at melting points and normal boiling temperatures, assuming $x_1=1$. The results shown in table V are all in good accordance with the Quill's¹⁶⁾ 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. In spite of its simple form the results shown in Table V are satisfactory.

TABLE V

Vapor Pressure at Melting Point and Normal Boiling Temperature, Assuming $x_1=1$.

Element	Vapor Press. at M.P. (atm)			Normal Boiling Temp. (°K)			
	Calculated from		Observed	Calculated from		Observed	
	Eq. 23	Eq. 25		Eq. 23	Eq. 25	Quill	AIPH
Li	8.99×10^{-13}	10.9×10^{-13}	10.6×10^{-13} (El)	1580	1645	1680	1599
Na	7.40×10^{-11}	10.20×10^{-11}	7.94×10^{-11} (Q)	1182	1180	1187	1162
K	6.58×10^{-10}	10.82×10^{-10}	14.1×10^{-10} (Q)	1059	1058	1052	1030
Rb	2.61×10^{-10}	6.98×10^{-10}	7.08×10^{-10} (Q)	1009	950	952	952
Cs	8.28×10^{-10}	11.91×10^{-10}	15.9×10^{-10} (A)	968	965	963	963
Cu	3.21×10^{-7}	4.667×10^{-7}	3.98×10^{-7} (Q)	2878	2864	2878	2855
Ag	2.08×10^{-6}	2.931×10^{-6}	1.95×10^{-6} (Q)	2464	2478	2485	2466
Au	6.17×10	8.912×10	4.23×10 (E2)	3265	3240	3239	2933

Q: obtained by means of extrapolation method from Quill's data.¹⁶⁾ A: taken from AIPH.

El: Van Loar Equation, $\log P(\text{mm Hg}) = -\frac{9,030}{T} - 1.2 \log T + 12$.

E2: van Lient 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

$$H/T = \frac{N_0 k}{2} \left\{ -\frac{\chi_0}{kT} + 5 - \frac{\epsilon_0}{kT} \frac{g(T)}{1+g(T)} - d(T) \right\} \quad (26),$$

and

$$S = \frac{N_0 k}{2} \left\{ 2jL + 5 \ln T + \ln y(T) \{1+g(T)\} + 5 - \frac{\epsilon_0}{kT} \frac{g(T)}{1+g(T)} - d(T) \right\} \quad (27).$$

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

Entropy of Vaporization. The enthalpy $H_1(P_1, T)$ and entropy $S_1(P_1, T)$, and $H_2(P_2, y)$ and S_2

(P_2, 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:

$$H_1/T = 5R/2 \quad (28),$$

$$H_2/T = R(5/2 + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - D/RT) \quad (29),$$

and

$$S_1 = R \left\{ j_1'G + \frac{5}{2} + \frac{5}{2} \ln T - \ln P_1(\text{atm}) \right\} \quad (30),$$

where $h\nu/k$ and D are the fundamental characteristic temperature and molar heat of dissociation assigned to the diatomic molecule in the

TABLE VI
The Boiling Temperature at Different Pressures, Assuming $x_1=1$

Element		Pressure in atm.					
		10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	1
Li	calc.	710	743	875	990	1142	1645
	obs.	705(L)	775	865	980	1130	1640
Na	calc.	507	561	629	711	820	1180
	obs.	510(L)	558	623	705	813	1187
K	calc.	434	481	539	614	710	1047
	obs.	429(L)	475	534	605	702	1052
Rb	calc.	406	450	502	569	657	950
	obs.	403(L)	445	496	561	650	952
Cs	calc.	339	432	496	555	647	965
	obs.	383(L)	425	476	544	634	963
Cu	calc.	1398	1530	1686	1879	2121	2864
	obs.	1400(L)	1530	1685	1875	2117	2868
Ag	calc.	1194	1305	1440	1610	1820	2478
	obs.	1200(S)	1305(L)	1442	1607	1816	2485
Au	calc.	1570	1720	1889	2118	2395	3240
	obs.	1570(L)	1720	1896	2182	2388	3239

Observed: taken from the Quill's data.

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 $Hv^{(1)}$ and $Sv^{(1)}$ and by Hv and Sv , respectively. Then we will obtain the following expressions by the application of Eqs. 26 to 30.

$$\frac{\Delta H_v}{T} = \frac{N_o \chi_o}{2T} + \frac{N_o \chi_o}{2} \left\{ \frac{\epsilon_o}{kT} \frac{g(T)}{1+g(T)} + d(T) \right\} \quad (31),$$

$$\frac{\Delta H_v}{T} = \frac{\Delta H_v^{(1)}}{T} - \left(\frac{D}{N_o k T} + \frac{3}{2} - \frac{h\nu/kT}{e^{h\nu/kT} - 1} \right) \times \frac{x_2}{1+x_2} \quad (32),$$

$$\Delta Sv^{(1)} = -\frac{N_o k}{2} [2j - 2 \ln P_1 - \ln y(T) \{1+g(T)\}] + \frac{N_o k}{2} \left\{ \frac{\epsilon_o}{kT} \frac{g(T)}{1+g(T)} + d(T) \right\} \quad (33),$$

and

$$\Delta Sv = \Delta Sv^{(1)} - N_o k \left(\frac{D}{N_o k T} + \frac{3}{2} - \frac{h\nu/kT}{e^{h\nu/kT} - 1} \right) \times \frac{x_2}{1+x_2} \quad (34),$$

where $j = j_1^G - j_1^L$. The results calculated from these equation, 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 commual 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 VII
Entropy of Vaporization at Melting Point—
Calculated From Eqs.31 and 33.

Element	Calculated(e. u.)		Observed(e. u.)
	$\Delta H_v^{(1)}/T_m$	ΔSv	ΔSv
Li	77.7	77.5	77.7(K)
Na	67.9	67.9	67.9(K)
K	62.0	62.0	62.0(K)
Rb	64.0	64.0	63.9(A)
Cs	60.8	60.8	60.7(A)
Cu	56.5	56.5	56.5(K)
Ag	52.5	52.5	52.5(K)
Au	64.1	64.1	64.1(K)

On computation of $\Delta H_v/T_m$ the melting points used are given in AIPH. K: Calculated from the Kelly's empirical equation, A: AIPH.

TABLE VIII
Entropy of Vaporization at Boiling Point—Calculated From Eqs. 31, 32, 33 and 34.

Enthalpy of Vaporization at Boiling Point—Calculated From Eqs. 31, 32, 33 and 34.

	Assuming $x_1=1$		Using the Values of $x_1^{b)}$ given below		
Element	Calculated (e.u.)		Calculated (e.u.)		Observed(e.u.)
	$\Delta H_v^{(1)}/T_b$	$\Delta S_v^{(1)}$	$\Delta H_v/T_b$	ΔS_v	
Li	21.91(A) 20.83(Q)	22.13	19.57(A) 18.49(Q)	19.79	19.8(Q)
Na	21.42(A) 20.99(Q)	21.07	19.51(A) 19.08(Q)	19.16	19.48(Q)
K	19.99(A) 19.59(Q)	19.43	19.35(A) 18.95(Q)	18.79	17.93(Q)
Rb	20.80(A, Q)	19.64	20.22(A, Q)	19.02	19.02(A)
Cs	18.83(A, Q)	18.65	18.19(A, Q)	18.01	16.95(A)
Cu	24.41(A)	26.19	—	—	25.4(A)
Ag	25.87(A)	25.88	—	—	24.62(A)
A	28.93(A) 26.31(Q)	26.93	—	—	25.30(A)

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 x_1 at normal boiling point have been calculated by the usual statistical methods, using the data given in Herzberg's book. The numerical values of x_1 for alkali metals are: Li(0.845), Na(0.865) K(0.950), Rb(0.95), and Cs(0.942).

Entropy of Fusion. Before discussing the entropy of fusion, it should be 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 authors¹⁷⁾ solid alkalis are composed of the two allotropic modifications, i.e., α and β -forms. For example E. Cohen and G. de Bruin argue that under ordinary conditions solid sodium consists of two allotropic modifications, i.e., α -sodium and β -sodium, the portions of which are dependent upon their previous thermal treatments. The transition point yet undetermined lies between 273 and 263° K, possibly near 348° K. Moreover, it is seen in the literature¹⁷⁾ 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_α and q_β 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

$$K(T) = \left\{ 2 \frac{e^{-\epsilon_s/T}}{(1 - e^{-\theta_E/kT})^3} \right\}^N$$

where θ_E is the so-called Einstein characteristic temperature and ϵ_s 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:

$$K(T_m) = \left\{ 2 \left(\frac{T_m}{\theta_E} \right)^3 e^{-\epsilon_s/kT_m} \right\}^N \quad (\text{at melting point}) \quad \dots\dots\dots(35).$$

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

$$S^K(T_m) = Nk(j^K + 3 + 3 \ln T_m) \quad \dots\dots\dots(36).$$

where $j^K = \ln(2/\theta_E^3)$

Let us then check the entropy equation, Eq. 36 by comparing the values of entropy of sublimation calculated with those observed. From the combina-

tion of Eqs. 30 and 36, the entropy of sublimation ΔS_s will be given by

$$\Delta S_s(T_m) = N_0 k \left(j_1 G - j^K - \frac{1}{2} \ln T_m - \frac{1}{2} - \ln P_1 \right) \dots \dots \dots (37).$$

Eq. 37, together with Fowler's rule, i.e., $\theta_E = \frac{5}{7} \theta_D$ 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 X. 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 X

Einstein and Debye Temperatures, Calculated from the Entropy of Sublimation.

Element	Einstein Temp.	Debye Temperature, θ_D		
	Calcd. from Eq. 37	Calcd. from $\theta_D = \frac{7}{5} \theta_E$	Obsd. AIPH	CEH
Cs	35.2	49.3	43	68
Be	667	934	1160	900
Cd	118	165	165	168
Hg	70.3	98.5	75	97

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. $g(T_m) = 1$

$$\Delta S_f = N_0 k \left\{ j^L - j^K - \frac{1}{2} \ln T_m - \frac{1}{2} - \frac{1}{4} - \frac{\epsilon_0}{k T_m} - \frac{1}{2} d(T_m) + \frac{1}{2} \ln 2y(T_m) \right\} \dots \dots \dots (38).$$

On computation we have used the data in AIPH and the results obtained (shown in Table X) are successful to give the correct values of the Debye temperature. From this fact we may co-

nclude that the liquid partition function retains its correct feature to describe the state of the liquid at melting point.

TABLE Y

Einstein and Debye Temperatures, Calculated from Entropy of Fusion

Element	Einstein Temp.	Debye Temperature		
	Calcd. from Eq. 38	Calcd. from $\theta_D = \frac{7}{5} \theta_E$	Observed AIPH	CEH
Li	288	403	430	510
Na	111	156	160	202
K	65.5	92	100	120
Rb	43.6	61	59	85
Cs	30.0	42	43	68
Cu	215	301	343	315
Ag	156	218	229	218
Au	117	164	164	175

Furthermore, if we neglect the contribution due to the quantum effect and put $\epsilon_0/kT_m = 2$ as the average value for the various elements, Eq. 38 becomes

$$\Delta S_f = R \left(j^L - j^K - \frac{1}{2} \ln T_m - 1 + \frac{1}{2} \ln 2 \right) \dots (39).$$

Substituting the following relations into Eq. 39:

$$j^L = -\frac{5}{2} \ln \Theta = -\frac{1}{2} \ln (2\theta_D \theta_E A^3),$$

$$\theta_E = h^2/8\pi^2 I k = k^2 N_0/4\pi^2 k M r_e^2 \text{ and } j^K = \ln(2/\theta_E^3).$$

$$\text{We obtain } \Delta S_f = R \ln \frac{\gamma}{2e} + R \ln \frac{\theta_D/T_m}{(\theta_E/T_m)^{1/2}}$$

$$\text{or, } \theta_D = \left(\frac{h}{\gamma \pi} \right) \left(\frac{N_0}{k} \right)^{1/2} e^{\Delta S_f/R} \left(\frac{T_m}{M r_e^2} \right)^{1/2} \dots (40),$$

$$\text{where } \gamma^2 \equiv \theta_E^6 / \theta_D A^3 \theta_D^2.$$

We see that Debye temperature θ_D is proportional to $(T_m/M r_e^2)^{1/2}$, which has been derived also by Lindemann.¹⁹⁾

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 $C_p = C_v + \frac{\alpha^2}{\beta} V T$, respectively, where α and β represent the coefficients of the cubical thermal expansion and of the compressibility, respectively. Therefore the application of Eq. 9 gives

$$C_v = \frac{5}{2}R + \frac{R}{2} \left\{ \frac{\epsilon_0}{kT} + 3 \left(\frac{\theta_A/T}{\beta A/T - 1} \right) - 3 \left(\frac{\theta_B/T}{\beta B/T - 1} \right) \right\}^2 \frac{g(T)}{[1+g(T)]^2} - C' \dots (41.a),$$

$$C' = \frac{R}{2} \left\{ 4 - u^2 - 3u_A^2 + 3(u_A^2 - u_B^2) \times \frac{g(T)}{1+g(T)} \right\} \dots (41.b),$$

$$\text{with } u_i = \frac{\theta_i}{2T} \operatorname{csch} \frac{\theta_i}{2T}.$$

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.¹⁰⁾ If we neglect quantum effect Eq. 41 then becomes

$$C_v = \frac{5}{2}R + \frac{R}{2} \left(\frac{\epsilon_0}{kT} \right)^2 \frac{g(T)}{[1+g(T)]^2} \dots (42):$$

This equation gives the following limiting values:

$$C_v(T) \approx 3R \rightarrow 2.5R \text{ as } T_m \rightarrow T_b.$$

Since $\epsilon_0/kT_m \sim 2$, $g(T_m) = 1$ and

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

This tendency for the limiting values is consistent with the empirical facts²⁰⁾ found in mercury, argon and neon etc.

TABLE XI
Atomic Heat Capacity

	Li	Na	K	Rb	Cs	Cu	Ag	Au
C_v calc. a)	6.11	6.30	6.39	6.35	6.42	6.27	6.60	6.40
obs. b)		6.46	6.91	6.81	6.66	—	—	—
C_p calc. b)	—	7.27	7.09	7.40	7.67	—	—	—
obs. c)	6.94	7.43	7.65	7.82	7.91	—	7.46	7.00

a) C_v (Calc.): calculated from Eq. 41. b) C_v (obs.) and C_p (calc.): calculated from the formula $C_p = C_v + \frac{\alpha^2}{\beta} VT$ with the numerical values of α and β taken from Landort's *Physikalische Chemische Tabellen* and Washbirn's *International Critical Table*. c) C_p (obs.): taken from Lyon's book.²¹⁾

V. Conclusions

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

1. The pressure of saturated vapor is given by

$$\log P_1(\text{atm}) = -\frac{A'}{T} + j' + \frac{1}{2} \log y(T) \times [1+g(T)].$$

This equation reduce to the ordinary thermodynamic expression

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

The 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

$$\Delta S_v(T_b) \approx R(j_1^G - j_1^L),$$

$$\text{and } R(j_1^G - j_1^L) = \left\{ \text{constant} + \ln \left(\frac{M}{r_s} \omega_1 g_D \right) \right\} + \ln \theta_D \dots (a.).$$

It has been found by the author that the first term of equation (a) is constant, characteristic of the subgroup in the periodic table and hence that the greater the value of θ_D the larger the value of $\Delta S_v(T_b)$ in accordance with empirical fact.

3. From the consideration of entropies of fusion and sublimation at melting point it is confirmed that Fowler's rule, i.e., $\theta_E = \frac{5}{7} \theta_D$, 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:

$$C_v(T) = 3R \rightarrow 2.5R \text{ as } T_m \rightarrow T_b.$$

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:

$$q(T) = \left(\frac{T}{\Theta}\right)^3 \left\{ 1 + \left(\frac{\Theta_A}{\Theta_B}\right)^3 e^{\epsilon_0/kT} \right\}^{1/2} e^{\epsilon_A/kT}$$

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

$$q(T) = \left(\frac{T}{\Theta}\right)^3 \left\{ 1 + e^{-\frac{\epsilon_0}{kT_m} \left(\frac{T-T_m}{T} \right)} \right\} e^{\epsilon_A/kT} \quad (b).$$

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

VI. Acknowledgement

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

VII. References

1. Eyring, H., and Hirschfelder. *J.O.J. Phys. Chem.*, 41, 184 (1937)
2. Lennard-Jones, J.E., and Devonshire, A.F. *Proc. Roy. Soc. London*, A 163, 53(1937) A 165, 1(1938)
3. Kirkwood, J.G., *J. Chem. Phys.*, 18, 380(1950)
4. Hirai, Rhee, and Eyring. The Proceedings of the National Academy of Sciences Vol. 44, 7, pp.683-688, July, 1958.
5. J.F. Kincaid and H. Eyring, *J. Chem. Phys.*, 5, 505(1937)
6. J. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.* 5, 896(1937)
7. G. Herzberg, *Spectra of Diatomic Molecules*.
8. Gordon, *J. Chem. Phys.*, 4, 100(1936)
9. M. Blackman, *Proc. Roy. Soc.*, A, 159, 416 (1937)
10. Montroll, *J. Chem. Phys.* 15, 575 (1947)
11. G.F. Newell, *J. Chem. Phys.* 21, 1877 (1953)
12. L. Van Hove, *Phys. Rev.* 89, 1189 (1953)
13. T. Moeler, *Inorganic Chemistry, An Advanced Textbook*, New York. John Wiley & Sons, Inc.
14. Fowler and Guggenheim, *Statistical Thermodynamics*, Cambridge University Press.
15. K.K. Kelly, *U.S. Bur. Mines Bull.*, 383(1935) 393 (1936), 434 (1940)
16. L.L. Quill, *The Chem. and Metallurgy of Miscellaneous Materials, Thermodynamics*, McGraw-Hall Book Company.
17. J.W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* Vol. III. pp 343, Vol. IV. pp 434, pp 720
18. E. Cohen and G. de Bruin, *Proc. Acad. Amsterdam*, 17, 926(1914)
19. Lindemann, *Physik-Leitschr.* 11, 609(1910): Dissertation, Berlin, 1911
20. S. Takeuchi, *Structure of Liquid Metal*, Nippon Kinzoku Gakkai (1958)
21. N.R. Lyon, *Liquid Metals Handbook*. The Atomic Energy Commission and The Bureau of Ships, Depret of the Navy, Washington D.C., U.S. Government Press. 1950. pp. 40-41