

# Linear Relation between the Initial Slope of Melting Curve and the Volume of Liquid at the Melting Point

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## Summary

A theoretical attempt is given for interpreting the linear relation between the initial slope of melting curve ( $dT_m/dP$ ) and the volume of liquid at the melting point ( $V_l$ ).

It is shown that the substances giving the same Lindemann constant constitute the same group in the linear relation.

## 1. Introduction

Interest in melting phenomenon is long standing, and there have been many analytical and theoretical attempts<sup>1-5</sup> to interpret this first order phase transition in terms of the equalization of the Gibbs free energies of coexisting phases. Yet no satisfactory theory of melting has been presented because of the theoretical difficulties for describing liquid state, in particular, at high density although recent perturbation theory seems to have some promising aspects in describing high density liquid state<sup>6,7</sup>. Thus we have to be contented at the moment with empirical approaches and/or computer experiments<sup>8,9,10</sup> in clarifying the basic mechanism of melting.

In the previous paper<sup>11</sup>, the author reported that there is a simple relation between the initial slope of melting curve ( $dT_m/dP$ ) <sub>$p=1atm$</sub>  and the volume of the solid at the melting point ( $V_s$ ) for the sequence of alkali halides of the same cation,

$$\frac{dT_m}{dP} = aV_s + b \quad (1)$$

where  $a$  and  $b$  are constants.

It is well known that in a series of elements or compounds of the same chemical family the values of the relative volume change on melting ( $\Delta V_m/V_s$ ) and the entropy change on melting ( $\Delta S_m$ ) are nearly constant for all members of that family. However, this simple rule does not hold in alkali halide series; e.g., the  $\Delta V_m/V_s$  values of LiX (X=F, Cl, Br and I) are ranging from 0.32 in LiF to 0.20 in LiI and the  $\Delta S_m$  values from 24.1 J/(K mol) in LiF to 19.7 J/(K mol) in LiI.

The applicability of eq 1 to alkali halides with the same cation suggests therefore that eq 1 may be a more general rule than the aforementioned empirical rule that the  $\Delta V_m/V_s$  and  $\Delta S_m$  values are nearly constant for all members of the same chemical family. It is interesting to find out a criterion (or criteria) for the applicability of

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eq 1 and to investigate the underlying mechanism by which the relation can be accounted for.

Furthermore, if we can correlate this relation with any other well-known formula or law, we may get some insight about the factors governing melting phenomenon.

In this paper the author has tried to interpret eq 1 by a modified significant structure theory of liquid<sup>5</sup>, the original form of which was developed by Eyring and his coworkers<sup>12</sup>. It is shown that the compounds which give the same Lindemann constant constitute the same group in the linear relation.

## 2. Theoretical Section

The partition function of a monatomic liquid  $Z_l(T, V_l)$  is given by

$$Z_l(T, V_l) = \left\{ \prod_{i=1}^{3N_t} \left[ 2 \sinh \left( \frac{h\nu_i}{2kT} \right) \right]^{-1} \right\} \left\{ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{eV_f}{N_t} \right\}^{N_t} \exp \left\{ -\frac{\Phi_l(V_l)}{kT} \right\} \quad (2)$$

where  $N_t$  and  $N_v$ , ( $N_t + N_v = N$ : Avogadro number), are the numbers of molecules (atoms) in the translational and vibrational motions, respectively,  $\nu_i$  normal vibration of the  $i$ -th freedom in the vibrational motions,  $m$  mass of molecule (atom),  $V_f$  free volume of the liquid, and  $\Phi_l(V_l)$  static configurational potential energy of the liquid. When we apply the Einstein approximation to the vibrational terms, we get the Helmholtz free energy of liquid by the equation,

$$F_l(T, V_l) = 3N_v kT \ln \left\{ 2 \sinh \left( \frac{\theta_l}{2T} \right) \right\} - N_t kT \ln \left\{ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{eV_f}{N_t} \right\} + \Phi_l(V_l) \quad (3)$$

where  $\theta_l = h\nu_l/k$  is a characteristic temperature of liquid (corresponding to Einstein temperature) and  $\nu_l$  is the average vibrational frequency.

According to the significant structure theory<sup>12</sup>,  $N_t$ ,  $N_v$  and  $V_f$  are represented by

$$\begin{aligned} N_t &= N \left( \frac{V_l - V_s}{V_l} \right) = Nx_t \\ N_v &= N - N_t = Nx_v = N(1 - x_t) \\ V_f &= V_l - V_s \end{aligned} \quad (4)$$

where  $V_s$  and  $V_l$  are respectively the volumes of solid and liquid at the melting point, and  $x_t$  and  $x_v$  are the mole fractions of the molecules in the translational and vibrational motions, respectively. These relations are derived on the assumption that in one mole of liquid there are  $(V_l - V_s)/V_s$  moles of holes of molecular size and that the whole excess volume (the sum of the volumes of all movable holes) is communally utilized by the molecules in the translational motions. This picture has often been criticized: Bernal<sup>13</sup> pictured liquid as a homogeneous coherent assembly of movable molecules, and his picture seems to be supported by recent computer simulations<sup>14,15</sup>, rejecting the existence of holes of molecular size in liquid. However, it is possible to consider that the free spaces introduced on melting can confer translational motions on some molecules in liquid, the number of which being approximately equal to that given by eq 4. In fact, as is shown in Figure 1, the sum of

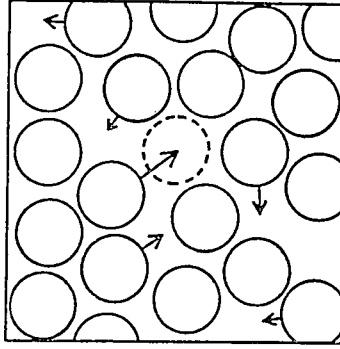


Figure 1.

Schematic diagram of liquid structure.  
 Circles with an arrow are the molecules (atoms)  
 in the translational motions and those without an  
 arrow are the ones in the vibrational motions.

several translational motions bestowed by small fractional voids can amount to the magnitude of a translational momentum gained by a single molecule jumping into a hole of molecular size, i. e.,

$$\frac{1}{2}(p_1^2 + p_2^2 + \dots) = \frac{1}{2}p_h^2$$

where  $p_h$  is the translational momentum acquired when a molecule jumps into a hole of molecular size, and  $p_i$  ( $i=1,2,\dots$ ) the translational momenta due to small fractional voids. Therefore the approximations given by eq 4 are reasonable and effective for the present purpose. Recent molecular dynamics calculations<sup>16</sup> show that in a molten KCl the diffusivity  $D$  of  $K^+$  and  $Cl^-$  can be represented by

$$D = K(V - V_0)$$

where  $K$  is a constant,  $V_0$  the volume at  $0K$ , and  $V$  the volume of molten KCl. This clearly indicates that the translational motions in a simple liquid is closely linked to the free space introduced by either melting or thermal expansion.

Differentiation of eq 3 with respect to temperature gives the entropy of liquid

$$\begin{aligned} S_l(T, V_l) = & -\frac{\partial F_l(T, V_l)}{\partial T} = -3Nkx_v \ln \{2 \sinh (\theta_l/2T)\} \\ & + 1.5Nkx_v(\theta_l/T) \coth (\theta_l/2T) + 1.5Nkx_l \\ & + Nkx_l \ln \left\{ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{eV_l}{N} \right\} \end{aligned} \quad (6)$$

The corresponding entropy of solid phase is

$$S_s(T, V_s) = -3Nk \ln \{2 \sinh (\theta_E/2T)\} + 1.5Nk(\theta_E/T) \coth (\theta_E/2T) \quad (7)$$

where  $\theta_E$  is the Einstein temperature. The number of nearest neighbors changes a little on melting: e. g., 12 to about 10.8 for rare gas elements and a little less for metals<sup>17</sup>. Therefore the approximation of  $\theta_l$  by  $\theta_E$  may be validated when the temperature of liquid is not far from the melting point. From eqs 6 and 7, we obtain the entropy change on melting  $\Delta S_m$  by the equation

$$\begin{aligned}
\Delta S_m &= S_l(T_m, V_l) - S_s(T_m, V_s) \\
&= 3Nkx_l \ln \{2 \sinh (\theta_E/2T_m)\} - 1.5Nkx_l(\theta_E/T_m) \coth (\theta_E/2T_m) \\
&\quad + 1.5Nkx_l + Nkx_l \ln \left\{ \left( \frac{2\pi mkT_m}{h^2} \right)^{3/2} \frac{eV_l}{N} \right\}
\end{aligned} \tag{8}$$

Lindemann<sup>18</sup> proposed that solid melts when the vibrational amplitude of atoms (molecules) in the crystal reaches a certain critical value, which is formulated as follows,

$$\frac{mV_s^{2/3}\theta_E^2}{T_m} = C \tag{9}$$

Here  $C$  is the Lindemann parameter. Using this relation (9), we can prove that the following formula is nearly constant under the condition  $(\theta_E/2T_m) \ll 1$  for the compounds having the same Lindemann parameter

$$\begin{aligned}
&3 \ln \{2 \sinh (\theta_E/2T_m)\} + \ln \left\{ \left( \frac{2\pi mkT_m}{h^2} \right)^{3/2} \frac{eV_l}{N} \right\} \\
&\simeq 3 \ln (\theta_E/T_m) + \ln \left\{ \left( \frac{2\pi mkT_m}{h^2} \right)^{3/2} \frac{eV_l}{N} \right\} \\
&= \ln \left\{ \left( \frac{2\pi kC}{h^2} \right)^{3/2} \frac{eV_l}{NV_s} \right\} \simeq \text{constant}
\end{aligned} \tag{10}$$

It is easy to show that the following term in eq 8 is nearly constant when  $(\theta_E/2T_m) < 1$ ,

$$(\theta_E/T_m) \coth (\theta_E/2T_m) \simeq 2 \tag{11}$$

Substitution of eqs 10 and 11 into eq 8 results

$$\begin{aligned}
\Delta S_m &= x_l R \left[ \ln \left\{ \left( \frac{2\pi kC}{h^2} \right)^{3/2} \frac{eV_l}{NV_s} \right\} - 1.5 \right] \\
&= \left( \frac{V_l - V_s}{V_l} \right) K(C, V_l/V_s)
\end{aligned} \tag{12}$$

where

$$K(C, V_l/V_s) = R \ln \{ (2\pi kC/h^2) 1.5 (eV_l/NV_s) \} - 1.5R.$$

It is to be noted that the constancy of  $K(C, V_l/V_s)$  is little affected by the variation of the term  $(V_l/V_s)$ ; i. e.,

$$\ln (V_l/V_s) = \ln (1 + x_l) \simeq x_l = 0.1 \sim 0.15$$

Therefore we get

$$\frac{dT_m}{dP} = \frac{\Delta V_m}{\Delta S_m} = \frac{V_l}{K(C, V_l/V_s)} \tag{13}$$

From this equation, it is evident that the compounds which give the same Lindemann parameter have the same slope for the  $(dT_m/dP)$  vs  $V_l$  plotting.

### 3. Discussion

Our purpose in this study has been to demonstrate that a careful examination of the linear relation between the initial slope of melting curve and the volume at the melting point would provide some basic aspects of melting phenomenon in general. In fact we have shown that eq 1 holds for compounds giving the same Lindemann parameter. Eq 13 tells us that  $V_l$  is the better parameter than  $V_s$  in eq 1. The

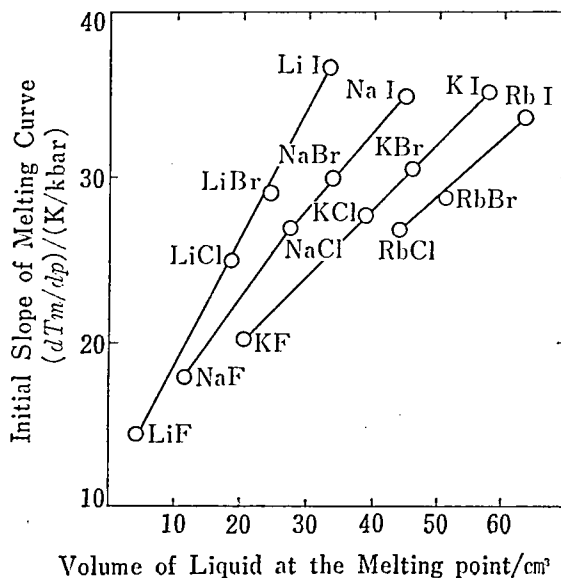


Figure 2.

The linear relation between  $(dT_m/dP)$  and  $V_l$  for alkali halides.

All  $(dT_m/dP)$  values were calculated from  $\Delta V_m$  and  $\Delta S_m$  values.  $\Delta S_m$  from ref. (29), and  $\Delta V_m$  and  $V$  from ref. (30).

Table 1. Lindemann parameters for alkali halides

Salt	$\theta_D(K)^a$	$T_m(K)^b$	$V_s(\text{cm}^3/\text{mol})^c$	$C \times 10^{-4}$
LiF	730	1121	10.95	3.42
LiCl	422	883	22.56	3.84
NaF	492	1268	16.82	2.96
NaCl	321	1073	30.53	3.08
NaBr	225	1020	36.20	3.14
NaI	164	933	45.83	3.11
KF	336	1131	25.43	2.82
KCl	233	1043	41.78	2.63
KBr	174	1007	48.24	2.67
KI	132	954	58.99	2.50
RbCl	165	995	47.54	2.44
RbBr	131	965	54.28	2.37
RbI	103	920	65.24	2.23

a: from ref. (28). b: from ref. (29). c: from ref. (30).

There is a simple relation  $\theta_E = 0.75\theta_D$  (Debye temperature)

$(dT_m/dP)$  vs  $V_l$  plotting for alkali halides are shown in Figure 2.

It is remarkable to notice that the Lindemann criterion for melting is a key to the justification of many empirical formulae: e.g., Salter<sup>19</sup> used the Lindemann law

and the Grüneisen equation to derive theoretically the Simon equation, and the recent Kraut-Kennedy empirical formula<sup>20</sup> is also derivable from the combination of the Lindemann law and the Grüneisen relation. From the fact that Lindemann's criterion plays a key role for the justification of eq 1, we easily know that eq 1 holds only within the alkali halides of the same cation group because each cation group has a different Lindemann parameter, as is shown in Table 1. In this connection, Jackson and Libermann<sup>21</sup> have recently shown that the critical temperatures of alkali halides ( $T_c$ ) for shear instability exhibit remarkable correlations with the melting temperatures. Expressed as the ratio of the absolute temperature ( $T_c/T_m$ ), they have the same groupings as discussed above.

Another interesting point is that a similar linear relation does not hold for the halides of the same anion, and this would suggest that cations play a major role in melting process of alkali halides. In this connection, the general rule that the smaller ions are more mobile than the larger ions in ionic compounds and melts deserves special attention because melting of an ionic compound occurs at the temperature at which an appreciable fraction of ions in the salt begins to make the translational motions accompanied with the loss of long range order in the structure. An interesting case is the silver iodide crystal in which silver ions move around

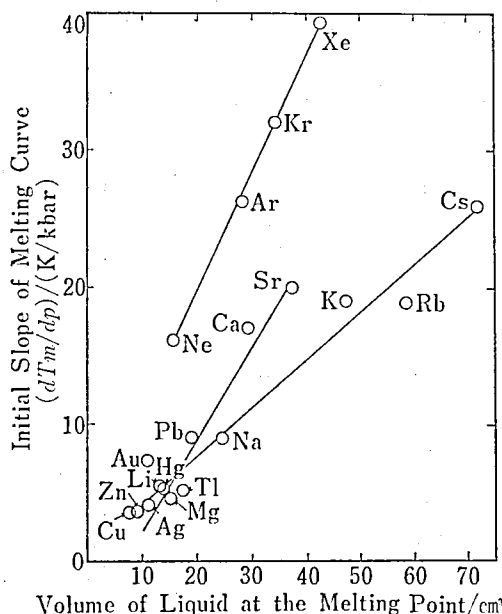


Figure 3.

The linear relations between  $(dT_m/dP)$  and  $V_l$  for metals and rare gas elements.

$\Delta S_m$  from ref. (25),  $V_s$  and  $V_l$  for metals from refs. (31) and (32).  $(dT_m/dP)$  values for Ca and Sr from ref. (33).

All data for rare gas elements are from ref. (34).

rather freely above 148°C while iodide ions still stay at their lattice points up to 555°C<sup>22</sup>: in other words, AgI has two melting points, one for cations (148°C) and the other for iodide ions (555°C). In molten salts electricity is carried by either cations or anions and it is well known that cations are the major entity for ionic conduction in fused alkali halides<sup>23</sup>. It thus appears that initiation of melting in alkali halides depends primarily on the thermodynamic stability of cations against the translational motions in the salts.

Figure 3 shows the plots of the data presently available for metals and rare gas elements. As the data of metals for the volume change on melting are scarce and sometimes not accurate enough because of the experimental difficulties associated with high temperatures, the stringent test of eq 13 is difficult. However, we see the good applicability of eq 1 to metals and rare gas elements. In the case of metals it seems that they are divided into two groups, one for monovalent metals (alkali metals, Cu and Ag) and the other for divalent metals (alkaline earth metals, Zn, Cd, Hg and Pb) although distinction is very obscure for some metals. In the theoretical analysis of the Lindemann equation, Shapiro<sup>24</sup> used the following version of the equation

$$\frac{\langle x^2 \rangle}{R_0^2} = \delta^2$$

where  $\langle x^2 \rangle$  is the mean square amplitude of the atomic vibration,  $R_0$  the closest atomic distance and  $\delta$  the critical fraction of the nearest-neighbor distance, and he obtained  $\delta=0.113$  (average) for five alkali metals (body-centered cubic structure) and  $\delta=0.071$  (average) for metals of the face centered cubic structure (Al, Cu, Ag Au). It is reasonable that the Lindemann parameter strongly depends on the crystal structure and the nature of crystal binding although Gshneider<sup>25</sup> gave the only one Lindemann parameter for almost all metals in his analysis of experimental thermodynamic data of metals.

The good applicability of eq 13 combined with the theoretical consideration given here would suggest that melting phenomenon is closely associated with the free space (or holes) acquired by either thermal expansion and/or volume increase on melting. There is strong evidence that melting initiates from the surface of crystal<sup>26,27</sup>, supporting the view that holes, including fractional voids, confer the translational motions on some molecules adjoining them. The translational motions thus acquired give rise to the indistinguishability of these identical particles which is the cause of the communal entropy. The communal entropy is the main factor for lowering the Gibbs free energy of liquid phase as compared with that of solid phase near the melting point<sup>5</sup>.

It is interesting to test the applicability of eq 1 (or 13) to melting at high pressures and indeed it seems, as is shown in Figure 4, that the linear relation holds at high pressures unless phase transition or another would destroy the condition (the same Lindemann parameter). Deviation of Xe from the linearity at high pressures

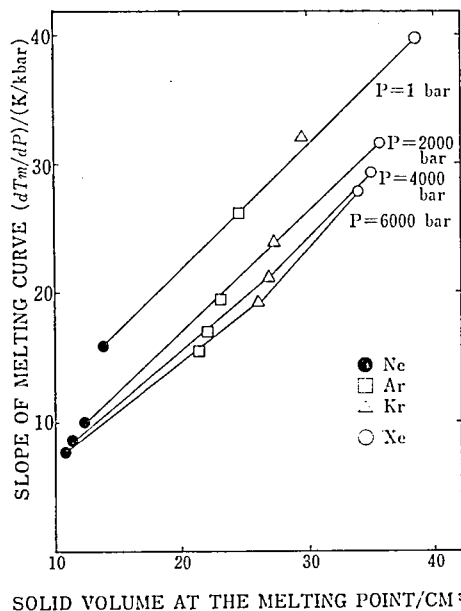


Figure 4.

The linear relations for rare gas elements at high pressures.  $(dT_m/dP)$  values at pressure  $P$  were calculated from the Simon equations in ref. (34).  $V_s$  values at pressure  $P$  were calculated by the corresponding treatments with one atomospheric  $V_s$  versus  $T$  data and isothermal compressibility data in refs. (34) and (35)

(>4 kbars) is interesting. However, we must see this deviation with some precaution because the experimental data for Xe are rather scanty and less reliable than those for other rare gas elements. One conceivable cause for this deviation might be due to a possible melting-curve maximum of Xe, though not yet discovered, in the pressure range not far from 7 kbar (the maximum pressure at which experiment has been done). In fact, many heavy elements (e.g., Rb, Cs, Ba) show melting-curve maxima at relatively low pressures<sup>36</sup>.

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