

An Alternative Derivation of the Simple Relation between Melting Point and Interionic Distance of Alkali Halides

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Summary

Using a simplified form of the Gibbs free energy, an alternative method is given for the derivation of the simple relation ($\lambda T_m = \text{constant}$) originally derived by Reiss, Mayer and Katz. It is shown that the Lindemann criterion for melting is the key to the validity of the relation.

1. Introduction

Reiss et al.¹⁾ applied the corresponding state theory to a number of fused salts by assuming that the equilibrium properties of the molten salt can be treated with a reduced equation of state. Introducing a simple pair potential of the form: $\phi(r_{ij}) = z_i z_j e^2 / \kappa r_{ij}$ for $r_{ij} > \lambda$ ($\lambda = r_+ + r_-$: the sum of the ionic radii of cation and anion) and $\phi(r_{ij}) = \infty$ for $r_{ij} \leq \lambda$, they obtained the following expressions for reduced temperature τ , reduced pressure π and reduced volume Ω for a charge symmetrical salt,

$$\tau = \frac{\kappa \lambda T}{z^2 e^2}, \quad \pi = \frac{\kappa \cdot \lambda^4}{z^2 e^2} P, \quad \Omega = \frac{V}{\lambda^3} \quad (1)$$

Assuming that $\kappa = 1$ and that the melting point T_m is a corresponding state, the following simple relation is obtained

$$\lambda \cdot T_m = \text{constant} \quad (2)$$

However, their introduction of relation (2) is rather intuitive although the melting point is in fact a corresponding state. Melting occurs at the equilibrium point where the Gibbs free energies of solid and liquid phases meet each other.

In this paper, we report an alternative derivation of the relation (2) by use of a simplified equation for the Gibbs free energy, combined with a corresponding state treatment.

2. Theory

According to the simplest form of statistical mechanics²⁾, the partition function of solid phase is given by

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$$f_s = \left\{ 2 \sinh \left(\frac{\theta_E}{2T} \right) \right\}^{-3N} \exp \left\{ -\frac{\Phi_s(V_s)}{kT} \right\} \quad (3)$$

Here θ_E is the Einstein temperature of the solid, and $\Phi_s(V_s)$ the configurational potential energy. The corresponding partition function for liquid phase is expressed as

$$f_l = \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V_f \cdot e \right\} \exp \left\{ -\frac{\Phi_l(V_l)}{kT} \right\} \quad (4)$$

From thermodynamics, the following relation must hold at the melting point,

$$G_s(T_m, P) = F_s(T_m, V_s) + P \cdot V_s = G_l(T_m, P) = F_l(T_m, V_l) + P \cdot V_l \quad (5)$$

where $G(T, P)$ and $F(T, V)$ are the Gibbs free energy and the Helmholtz free energy, respectively, and the subscripts s and l denote solid and liquid, respectively. The $P \cdot V$ terms are small as compared with other terms at the atmospheric pressure and thus can be neglected in further consideration.

Using the same potential form as that used by Reiss et al.¹⁾, the total static potential of the system can be expressed by

$$\Phi(V) = \sum_{i < j} u_{ij}(r_{ij}) = \frac{1}{\lambda} \sum_{i < j} u_{ij}(\xi_{ij}) = \frac{1}{\lambda} U(\xi) \quad (6)$$

where $r_{ij} = \lambda \xi_{ij}$, $u_{ij}(r_{ij})$ the potential function between ions of i and j , and $U(\xi)$ is the reduced potential function. It is reasonably assumed that the structural changes associated with melting are the same for all alkali halides except CsBr and CsI which have the CsCl structure at the melting point. Thus the reduced potential function $U(\xi)$ can be regarded as a universal function for all alkali halides (except CsBr and CsI). Therefore,

$$\Phi_s(V_s) = \frac{1}{\lambda} U_s(\xi) = \frac{A}{\lambda}, \quad \Phi_l(V_l) = \frac{1}{\lambda} U_l(\xi) = \frac{B}{\lambda} \quad (7)$$

where A and B are constants for all alkali halides at the melting point.

Substituting eq. (6) into eqs. (3) and (4), we obtain the Helmholtz free energy of the solid

$$F_s(T, V_s) = \frac{1}{\lambda} U_s(\xi) - 3RT \ln \left\{ 2 \sinh \left(\frac{\theta_E}{2T} \right) \right\} \quad (8)$$

and for the Helmholtz free energy of the liquid phase

$$F_l(T, V_l) = \frac{1}{\lambda} U_l(\xi) + RT \ln \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V_f \cdot e \right\} \quad (9)$$

Rearranging of eq. (5) by substituting eqs. (8) and (9) into eq. (5) yields the following relation

$$\begin{aligned} & RT_m \left[3 \ln \left\{ 2 \sinh \left(\frac{\theta_E}{2T_m} \right) \right\} + \ln \left\{ \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V_f \cdot e \right\} \right] \\ &= \frac{1}{\lambda} \{ U_s(\xi) - U_l(\xi) \} = \frac{1}{\lambda} (A - B) \end{aligned} \quad (10)$$

When $\theta_E/2T_m \ll 1$, we get the approximation

$$\sinh \frac{\theta_E}{2T_m} \simeq \frac{\theta_E}{2T_m} \quad (11)$$

It is well known that the Lindemann melting criterion holds well for the compounds of the same chemical family⁴⁾

$$\frac{mV_s^{2/3} \cdot \theta_E^2}{T_m} = L, \text{ (constant)} \quad (12)$$

where L is the Lindemann parameter.

By use of eqs. (11) and (12), it is easy to show that the following equation is nearly constant

$$\begin{aligned} & 3 \ln \left\{ 2 \sinh \left(\frac{\theta_E}{2T_m} \right) \right\} + \ln \left\{ \left(\frac{2\pi mkT_m}{h^2} \right)^{3/2} V_f \cdot c \right\} \\ & = \ln \left\{ \left(\frac{2\pi kL}{h^2} \right)^{3/2} \frac{V_f \cdot c}{V_s} \right\} \simeq C, \text{ (constant)} \end{aligned} \quad (13)$$

Substituting this relation into eq. (10), we get

$$RT_m = \frac{1}{\lambda} \frac{(A-B)}{C}, \text{ i.e., } \lambda \cdot T_m = \text{constant} \quad (14)$$

3. Discussion

The significance of this derivation is the indication that the melting process is the change over of some lattice vibrations to translational motions in the system and that Lindemann's picture, a solid melts when the amplitude of the lattice vibrations becomes large enough to break down the attractive forces holding the lattice together, holds quite well for melting of alkali halides. From Table 1, we see that the product of melting point T_m and the interionic distance λ is nearly constant for all alkali halides although there are a few exceptions. Lithium halides show large deviations from the average D value given by other alkali halides. This feature is also observed in other correlations such as reduced melting curves.⁵⁾ The explanation of this departure of lithium salts can be found in the smallness of lithium ions as compared with anions, in other words, the radius ratio effect. It is pointed out⁶⁾ that when ρ (radius ratio r_+/r_-) is less than 0.35, anion contact is effective in determining the equilibrium interionic distance. The radius ratio ρ of all lithium salts but LiF is lower than 0.35.

It is interesting to examine the Lindemann parameter more closely because the validity of the relation (14) is directly linked to the applicability of the Lindemann equation. The Lindemann parameters as calculated by use of literature values are tabulated in Table 2. Again we see, as expected, that the Lindemann parameters are nearly constant for all alkali halides except lithium halides. Remarkable point is that the constancy of the Lindemann parameter is better within halides of the same cation than those of the different cations, in accord with the many simple empirical correlations.^{7,8)}

Table 1. Melting Point and Interionic Distance for Alkali Halides

Salt	T_m (K)	λ (Å)	$D(=T_m \cdot \lambda) \times 10^5$ (cm/K)
LiF	1121	2.009	2.25
LiCl	883	2.566	2.27
LiBr	823	2.747	2.26
LiI	742	3.025	2.24
NaF	1268	2.307	2.93
NaCl	1073	2.814	3.02
NaBr	1020	2.981	3.05
NaI	933	3.231	3.01
KF	1131	2.664	3.01
KCl	1043	3.139	3.27
KBr	1007	3.293	3.32
KI	954	3.526	3.36
RbF	1068	2.815	3.01
Rb	995	3.285	3.27
RbBr	965	3.434	3.31
RbI	920	3.663	3.37
CsF	976	3.005	2.93
CsCl	918	3.47	3.19
CsBr	909	3.62	3.29
CsI	899	3.83	3.44

Sources of data: T_m from L. Brewer and E. Brackett, Chem. Rev., 61, 425 (1961). λ from ref. 6, p. 526.

Table 2. Lindemann Parameters for Alkali Halides

Salt	θ_D (K)	V_s (cm ³)	$L \times 10^{-4}$
LiF	730	10.95	3.42
LiCl	422	22.56	3.84
NaF	492	16.82	2.96
NaCl	321	30.53	3.08
NaBr	225	36.20	3.14
NaI	164	45.83	3.11
KF	336	25.43	2.82
KCl	233	41.78	2.63
KBr	174	48.24	2.67
KI	132	58.99	2.50
RbCl	165	47.54	2.44
RbBr	131	54.28	2.37
RbI	103	65.24	2.23

Sources of data: θ_D M.W. Zemansky, Heat and Thermodynamics, Mc Graw-Hill, New York, (1968) p. 318. V_s : from ref. 3. There is a simple relation $\theta_E = 0.75\theta_D$ (Debye temperature).

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