

Relations between the Thermodynamic Properties of Alkali Halides at the Melting Point

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Synopsis. Two new empirical formulas are presented for alkali halides at the melting point. There is a set of linear relations between the initial slope of melting curve (dT_m/dP) and the solid volume (V_s) for the sequences LiX, NaX, KX, and RbX (X=F, Cl, Br, and I).

Alkali halides are the most typical ionic salt for which theoretical and analytical studies have been made in order to clarify the melting of ionic compounds.¹⁻³⁾ However, the phenomenon of melting still remains unclarified. It is expected that the relations between various thermodynamic properties associated with fusion might help us understand the mechanism of melting of ionic crystals.

In a previous paper,⁴⁾ the following empirical formula was given for the entropy change on fusion (ΔS_m) for the sequences of LiX, NaX, KX, and RbX (X=F, Cl, Br, and I).

$$\Delta S_m = \alpha^{1/3} \left(\frac{A}{r} + B \right) \quad (1)$$

where α and r are the electronic polarizability and interionic distance of the salt, respectively; A and B are constants.

A similar relation holds for the relative volume change on fusion:

$$\frac{\Delta V_m}{V_s} = \alpha^{1/3} \left(\frac{C}{r} + D \right), \quad (2)$$

where ΔV_m and V_s are the volume change on melting and the volume of the solid salt at the melting point, respectively; C and D are constants for the salts with the same cation (LiX, NaX, KX, and RbX, X=halogen ion). Although a small deviation from the straight line is seen for a few salts, good linear correlation for the halides of the same cation (Fig. 1) indicates that electronic polarizability, a measure of the deformation of electron cloud in ion, is a very important factor for characterizing melting of these salts in contrast to the argument of Pauling⁵⁾ that apparent irregular variation of thermodynamic properties (melting point, boiling point) of alkali halides is ascribed to the radius-ratio effect. Obviously, regular or irregular variation of a certain property depends on the choice of a set of parameters and coordinates.

Irregular variation of cesium halides (CsCl, CsBr, and CsI) is presumably due to the difference in crystal structure between CsCl (face-centered cubic structure at the melting point) and CsBr and CsI (both simple cubic structure at their melting points). The percentage volume expansion of CsCl on melting (10.0%) is considerably smaller than that of the bromide and iodide (26.8 and 28.5%, respectively).^{6,7)} However, an

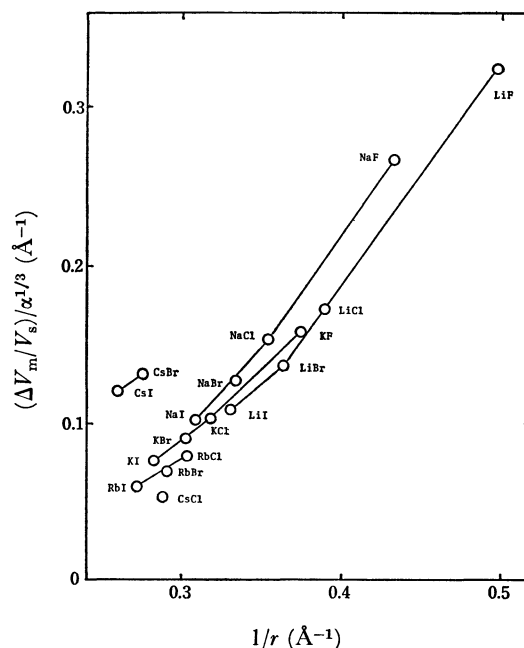


Fig. 1. Relative volume expansion of alkali halide at the melting point. Sources of data: ΔV_m and V_s ; H. Spindler and F. Sauerwald, *Z. Anorg. Allg. Chem.*, **335**, 267 (1965), electronic polarizability; J. R. Tessman, A. H. Kahn, and W. Schockley, *Phys. Rev.*, **92**, 890 (1953), Interionic distance; L. Pauling, "The Nature of the Chemical Bond," third ed, Cornell Univ. Press, Ithaca, N. Y. (1960), p. 527.

extrapolation of the molar volume of the low temperature form of CsCl up to the melting point would give a volume expansion on fusion of 28.3%. Conversely, if the volume expansion (17.6%) associated with the transition in CsCl from simple cubic to face-centered cubic structure is applied to the bromide and iodide, hypothetical cesium bromide and iodide would result in a volume expansion on melting of 9.2 and 10.3%, similar to the value of 10.0% for the chloride. This fact was pointed out by Johnson *et al.*⁸⁾ who reasoned that large volume expansion of CsBr and CsI is attributed to the reduction in coordination number from eight to about five on melting, whereas the melting from NaCl structure involves only small change in coordination number (from six to about five). It was proposed and verified by X-ray diffraction study^{6,9)} that the structure of liquid cesium bromide and iodide is very similar to that of the chloride. It is noteworthy that relations (1) and (2) include lithium halides because it has often been pointed out that lithium salts do not obey the corresponding-state law of other alkali halides.^{9,10)}

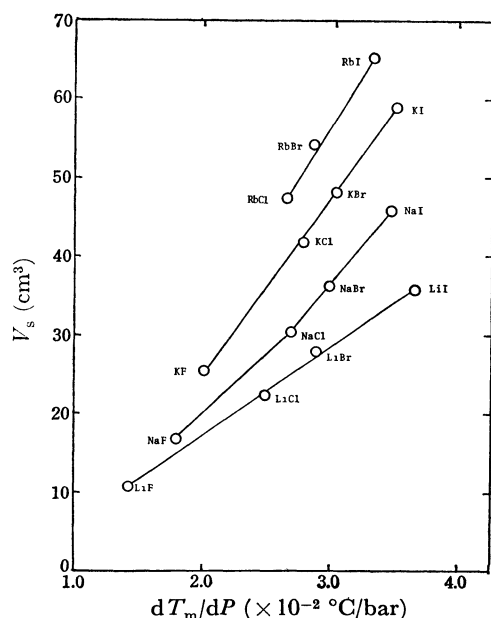


Fig. 2. Linear relation of (dT_m/dP) with solid volume at the melting point (V_s) for the sequences LiX, NaX, KX, and RbX. Source of data: ΔS_m values are calculated from ΔH_m and T_m data compiled by L. Brewer and E. Brackett, *Chem. Rev.*, **61**, 425 (1961).

From relations (1) and (2), we get

$$\left(\frac{dT_m}{dP}\right)_{p=1\text{ atm}} = \frac{\Delta V_m}{\Delta S_m} = \frac{V_s \left(\frac{C}{r} + D\right)}{\left(\frac{A}{r} + B\right)} = \frac{V_s(C+Dr)}{(A+Br)} \quad (3)$$

$$\simeq EV_s$$

where E is a constant for the sequence (LiX, NaX, KX, or RbX). Formula (3) suggests that the initial slope of melting curve $(dT_m/dP)_{p=1\text{ atm}}$ is proportional, as a first approximation, to the volume of the solid salt at the melting point (V_s). As is shown in Fig. 2, there is a good linear relation between the initial slope of the melting curve and the volume of the salt for a sequence of alkali halides of the same cation. It is expected from this relation that at certain high pressures the salt having larger volume should have higher melting point than those of smaller volume if the relation (3) holds up to high pressures. In fact the normal order of melting points of sodium halides is reversed above ca. 60 kbars with NaF having the lowest and NaI the highest melting point,¹¹ and a similar behavior is found for the potassium and rubidium halides at lower pres-

ures.^{12,13}

The initial slope of the melting curve $(dT_m/dP)_{p=p_0}$ is expressed as T_0/a^c by differentiation of the well-known Simon equation, $P-P_0=a\{(T/T_0)^c-1\}$, where T_0 and P_0 are the triple-point temperature and pressure, respectively; a and c are constants. From the corresponding law developed by Reiss *et al.*,⁹ the melting point of alkali halide is inversely proportional to ionic distance, *i.e.*, $T_0 \propto 1/r$. Combining this relation and formula (3), we see that a^c is inversely proportional to r^4 , in accord with the conclusion given by Owens¹⁰ in his analysis of melting curves of alkali halides.

Finally it should be pointed out that the calorimetric heats of fusion of NaI, KI, RbI, and CsI redetermined by Bousquet *et al.*¹⁴ are considerably higher than those of Dworkin and Bredig.¹⁵ However, a comparison of the observed values of the initial slopes of the melting curves of alkali halides¹⁶ with those calculated by means of the Clapeyron-Clausius equation indicates that the data of Dworkin and Bredig are more accurate.

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