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Simple Relationship between Entropy Change upon Fusion or Sublimation at Melting Point, Electronic Polarizability and the Interatomic Distance for Alkali Halides

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It has been previously reported[1] that in alkali halides there is almost a linear relation between $\Delta S(m)/\alpha^{1/3}$ and r^+/r^- for a sequence LiX, NaX, KX, and RbX (X=F, Cl, Br, and I). Here $\Delta S(m)$, α, and r^+/r^- are the entropy change upon fusion, electronic polarizability of the salt, and the ionic radius ratio of cation to anion, respectively. Thus the entropy change upon melting can be given by

$$\Delta S(m) = \alpha^{1/3}\left(\frac{A}{r^-}+B\right) \qquad (1)$$

where A and B are the constants for the system.

The present author would like to point out that a similar relation also exists between the entropy change upon sublimation at melting point $\Delta S(s)$, α, and, r^+/r^-. As shown in Fig. 1, a good linear relationship between $\Delta S(s)/\alpha^{1/3}$ and r^+/r^- is obtained for the sequence LiX, NaX, KX, RbX, and CsX with exceptions of KF, RbF, and CsF.

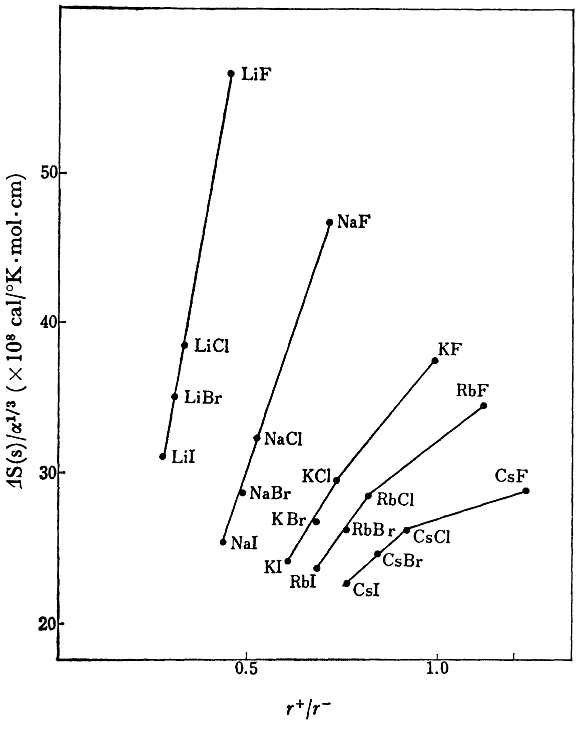

Fig. 1. Linear relationship of $\Delta S(s)/\alpha^{1/3}$ against r^+/r^- for alkali halides.
Sources of data: Heat of sublimation; S. H. Bauer and R. F. Porter, "Molten Salt Chemistry," ed. by M. Blander, Interscience Publishers, New York, N. Y. (1964), p. 627, Melting point: L. Brewer and E. Brackett, *Chem. Rev.*, **61**, 425 (1961), Electronic polarizability; J. R. Tessman, A. H. Kahn and W. Schockley, *Phys. Rev.*, **92**, 890 (1953), Ionic Radius: L. Pauling, "The Nature of the Chemical Bond," third ed., Cornell Univ. Press, Ithaca, N. Y., (1960), p. 527.

Irregular variances of KF, RbF, and CsF are also observed in the case of fusion. A posssible explanation may be found in the data obtained by Pistorius,[2] in which he found that the change of volume upon fusion is considerably smaller for the fluorides of potassium and rubidium than for other halides of potassium and rubidium. He also stated that while chloride, bromide, and iodide of both potassium and rubidium have remarkably similar melting curves, the fluorides of potassium and rubidium behave differently from the other halides. It is of interest to note that the point of CsCl falls on the extrapolated line connecting the points of CsCl and CsI. In the case of fusion, the $\Delta S(m)/\alpha^{1/3}$ value of CsCl is much lower than that expected from the extrapolation of the straight line of CsBr and CsI (Fig. 2). This may be ascribed to the fact that solid CsCl shows phase transformation from the P_m3_m (CsCl) structure to F_m3_m (NaCl) structure at 446°C with an entropy change of 0.807 cal/deg mol.[3] As shown in Fig. 2, the point corrected by including the entropy of phase transformation into the entropy change upon melting nearly falls on the extrapolated line of CsBr and CsI. On the other hand, it is considered that in the case of sublimation a small change of entropy gives little effect upon regularity.

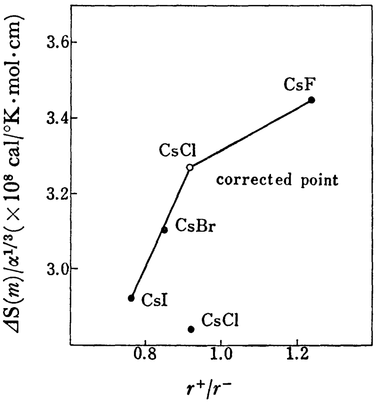

Fig. 2. Regular variation of the corrected $\Delta S(m)/\alpha^{1/3}$ of CsCl

Another interesting aspect in Fig. 1 is the linear relation of $\Delta S(s)/\alpha^{1/3}$ with r^+/r^- for the halides having same anion except for lithium halides which behave

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[1] H. Kanno, *Nature*, **218**, 765 (1968).

[2] C. W. F. T. Pistorius, *J. Chem. Phys.*, **43**, 1557 (1965).

[3] K. J. Rao, G. N. R. Rao, and C. N. R. Rao, *Trans. Faraday Soc.*, **63**, 1013 (1967).

differently. It has been experimentally shown that many thermodynamic properties of simple ionic salts, such as alkali halides and alkaline earth oxides, vary in regular fashion with change in interatomic distance.[4,5] Concurrently, much effort has been made to understand these thermodynamic properties on the basis of models.[6,7] Of the many suggested models, the most simple one is the reduced equation of state for ionic salt obtained by Reiss, Mayer, and Katz.[6] They noted that the potential function for the system can be characterized by a single distance scale factor, namely $r^+ + r^-$ $(=r)$. They postulated that the melting point of alkali halides is represented by

$$T_m = \frac{10^5}{3.19 \cdot r} \ {}^\circ\mathrm{K} \tag{2}$$

In this connection, some improvements can be made by replacing r^+/r^- with $1/r$ in Eq. (1):

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

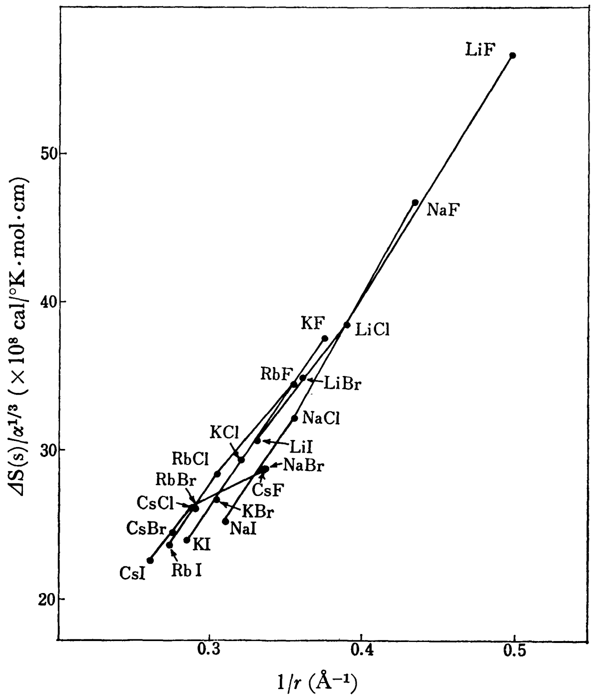

Fig. 3. Relationship of $\Delta S(s)/\alpha^{1/3}$ against $1/r$ for alkali halides. Interatomic distance; L. Pauling, "The Natune of the Chemical Bond", third ed., Cornell Univ. Press, Ithaca, N. Y., (1960), p. 527.

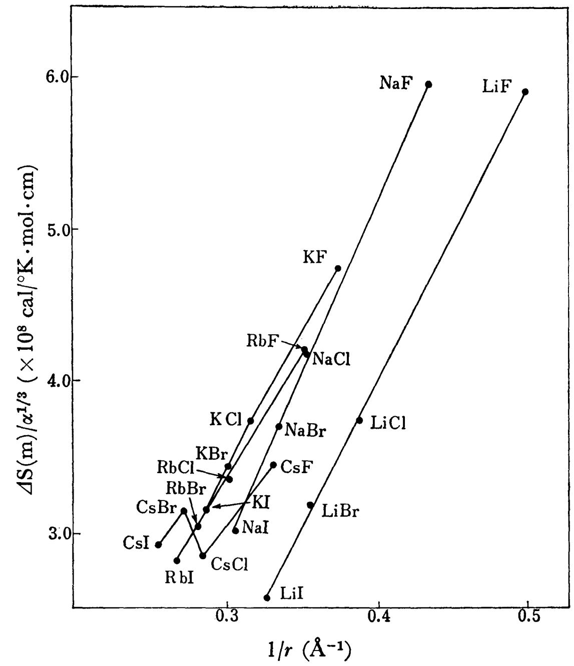

Fig. 4. Relationship of $\Delta S(m)/\alpha^{1/3}$ against $1/r$ for alkali halides. Heat of fusion; A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **64**, 269 (1960).

Substituting Eq. (2) into Eq. (3), we have

$$\Delta S = \alpha^{1/3}(A'' T_m + B'') \tag{4}$$

where A', B', A'', and B'' are the constants for the system.

The relationship between $\Delta S(s)/\alpha^{1/3}$ or $\Delta S(m)/\alpha^{1/3}$ and $1/r$ is shown in Figs. 3 and 4.

We see that all points of alkali halides are approximately represented by a linear function of the reciprocal of the interatomic distance. A significant feature of Fig. 3 is that nearly the same value of $\Delta S(s)/\alpha^{1/3}$ is given for the salts having the same value of $1/r$. Thus it is concluded that the interatomic distance is the better correlating parameter than the ionic radius ratio.

Let $\Delta S(v)$ represent the entropy change of vaporization for alkali halides at a specified temperature and we obtain the following relation at the melting point

$$\Delta S(s) = \Delta S(v) + \Delta S(m) \tag{5}$$

Thus it is expected that the linear relation also holds between $\Delta S(v)/\alpha^{1/3}$ and $1/r$.

In conclusion, we might say that the entropy change upon phase transformation is well characterized by the interatomic distance and the electronic polarizability of the salt.

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4) O. J. Kleppa and L. S. Hersh, *J. Chem. Phys.*, **34**, 351 (1961).
5) Y. P. Varshni and R. C. Shukla, *ibid.*, **35**, 582 (1961).
6) H. Reiss, S. W. Mayer, and J. L. Katz, *ibid.*, **35**, 820 (1961).
7) E. Blomgren, *Ann. N. Y. Acad. Sci.*, **79**, 781 (1960).