

## **Empirical formula for the parameters of metallic monovalent halides**

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### *Abstract*

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*By collating the data on melting properties and transport coefficients obtained from various experiments and theories for certain halides of monovalent metals, all-inclusive linear relationship has been fashioned out. This expression holds between the change in entropy and volume on melting; it is approximately obeyed by the majority of halides considered and leads to a deficit of entropy on melting for a number of samples. The observed anomalies found explanation in the structural and transport phenomena. The deviating systems e.g. Ag-I belongs to the group of fast-ion conductors in the high temperature crystal phase.*

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### *Keywords*

Alkali halide melts, empirical formula and melting properties

## **1.0 Introduction**

The molten salts are of special interest because of their technological importance especially in liquid electrolyte. There has been continuous study of the structures of molten salts with the aid of neutron and X-ray diffraction techniques for several years. The aspect of study on monovalent and divalent metallic halides has been reviewed at different times experimentally, theoretically and particularly by computer simulation procedure (cf. Rovere and Tosi [1], Enderby and Barnes [2], Ichikawa and Matsumoto [3], Mochinaga et al [4], Mathew-Ojelabi [5].

The pioneering works (experiment and theory) have been able to provide reasonable data for a large number of alkali halide melts under certain conditions. A very close examination of these data or properties reveal an important trend which if properly harnessed, will bring about a reliable empirical expression that can reproduce similar data for newly discovered members of the family of the alkali-halides. Recourse to macroscopic thermodynamic and transport data was made in the past to infer gross structural characters of many melts and to characterize the solid electrolyte state of fast-ion conductors as an ion-disordered phase see Ubbelodhe [6], O'Keefe and Hyde [7].

It is the aim of the present work to extend the inference-making approach to a quantitative level for the monovalent halides as a first step. To this end, we shall adopt an approximate linear relationship between the entropy change  $\Delta S$  and the volume change  $\Delta V$  on melting as suggested by Stishov et. al. [8] and established for certain metals by Lasoka [9]. The approximate linear relationship is such that for monatomic systems,  $\Delta S$  is found to extrapolate, in the limit  $\Delta V \rightarrow 0$ , to  $R \ln 2$  where  $R$  is the universal gas constant. This

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limiting value is said to be due to the localization of shear modes at melting or topological line defects in the liquid Tallon [10], Rivier and Duffy [11].

The plan of work is as follows: we shall develop briefly in Section 2, the important expressions needed for the work while the following section summarizes the calculation procedures. Estimated values of some thermodynamic properties for the alkali-halide melts are presented in Section 3 before conclusion.

## 2.0 Theory

The discussion here holds for classical ionic substance such as the alkali-halides which readily exhibit two important features namely:

- (i) Coulomb force effect which induces charge alternation, say in  $Cl^-$  surrounded by  $Na^+$  in  $NaCl$  structure and vice-versa
- (ii) Short-range repulsive effect that prevents the collapse of structure under Coulomb attraction

Ordinarily, these two features are insufficient for the local coordination number specification since two different structures ( $NaCl$  and  $CsCl$ ) exist for the alkali-halides in the crystalline phase. There is need for chemical bonding to be accounted for in the treatment of a more complex ionic material than the alkali-halides.

An appropriate model for the two features outlined above is the one based on the Born theory for the cohesive energy  $E$  of a crystal per molecule.  $E$  is given as the sum of the Madelung (mainly determined by the Coulomb forces between point-like ions and a repulsive contribution from the overlap of the ion cores. The dependence of  $E$  on the lattice parameter  $a$  is expressed as

$$E(a) = a_m \frac{e^2}{a} + \frac{B}{a^n}, \quad a_m = \text{Madelung constant} \quad (2.1)$$

We shall explore the simplicity of Equation (2.1) for important quantitative discussion. At equilibrium, the lattice spacing  $a_0$  can be derived by setting  $\left[ \frac{dE}{da} \right]_{a=a_0} = 0$  at zero pressure yielding

$$a_0 = \left( \frac{nB}{a_m e^2} \right)^{\frac{1}{n-1}} \quad (2.2)$$

and consequently

$$E(a) = -a_m \frac{e^2}{a} \left[ 1 - \frac{1}{n} \left( \frac{a_0}{a} \right)^{n-1} \right] \quad (2.3)$$

The repulsive exponent can be determined from the compressibility  $K$  given by

$$K^{-1} = v_0 \left( \frac{d^2 E}{dv^2} \right)_{a=a_0} = (n-1) \frac{a_m e^2}{9v_0 a_0} \quad (2.4)$$

The Madelung energy contributes dominantly to the cohesive energy while the repulsive term dominates the determination of the compressibility. Thus, the repulsive exponent is fixed at  $n \sim 10$ .

The repulsive term falls off as  $r^{-10}$  and hence the nearest-neighbours dominate the contribution such that  $B$  becomes roughly proportional to the coordination number  $n_c$  of a given structure. If the cohesive energy is derived from an inter-ionic pair potential  $\varphi_{ij}(r)$ , then one can write

$$\varphi_{+-}(r) = -\frac{e^2}{r} + \frac{b}{r^n} \text{ and } \varphi_{--}(r) = \varphi_{++}(r) = \frac{e^2}{r} \quad (2.5)$$

We have set  $B = n_c b$  while introducing  $\lambda \left[ = \left( \frac{n_c b}{e^2} \right)^{\frac{1}{(n-1)}} = \left( \frac{a_m}{n_c} \right)^{\frac{1}{(n-1)}} a_0 \right]$  and  $\frac{\lambda}{e^2}$  as the scales of length and energy respectively. Then, the equation of state assumes form

$$p = -\frac{e^2}{\lambda^4} f\left(\frac{v}{\lambda^3}, \frac{\lambda k_B T}{e^2}\right) \quad (2.6)$$

In Equation (2.6),  $f$  is the universal function of the indicated variables. The value of  $\frac{\lambda k_B T}{e^2}$  at the melting point is the same for all the alkali-halides thus providing a good correlation between the melting temperatures of the family. The melting temperature can accurately be estimated from

$$T_m = \left( \frac{3 \times 10^{-5}}{\lambda} \right) \text{deg} \quad (2.7)$$

Equation (2.7) excludes the Lithium salts because the neglect of short-range repulsion between relatively large anions cannot be justified for them.

Important physical parameters are the fractional volume change  $\Delta V/V$  and entropy change  $\Delta S$  on melting. The generalized form of the extrapolation value of  $\Delta S$  as  $\Delta V \rightarrow 0$  is Tallon and Robinson [10]

$$\Delta S \approx nR \ln 2 + \alpha B_T \Delta V \quad (2.8)$$

where  $n$  is the number of components in a formula unit,  $\alpha$  is the coefficient of thermal expansion and  $B_T$  is the isothermal bulk modulus.

Equation (2.8) is important because, apart from its role as a fundamental limiting value, it also assigns the same value of the Grüneisen parameter  $\gamma = \alpha B_T V / C_v$  ( $C_v$  = heat capacity at constant volume) to similar systems. Quantity  $\alpha B_T V$  at liquid-solid coexistence does not vary significantly from system to system within a given family of salts. Equation (2.7) is taken approximately as a linear relationship between the melting properties  $\Delta S$  and  $\Delta V/V$ ; it extrapolates for  $\Delta V/V \rightarrow 0$  to a value in the ratio 2 for the alkali-halides.

### 3.0 Calculation procedure

The table below displays some collated data for 21 mono-halides with a prevalence of chlorides. The data on  $\Delta S$ , the molar volume  $V_m$  of the liquid phase and the melting temperature  $T_m$  emanated from Barn et. al. [12], Chase et al [13], Janz [14], Igarashi and Mochinaga [15]. For those systems whose molar volume of solid at melting are unknown we assume the difference between  $V_m$  and molar volume  $V_{RT}$  of the solid at room temperature in the manner of ref [7], i.e.  $(V_m - V_{RT})$  provides a reasonable and presumably an upper estimate for the volume change on melting. Accordingly,  $\Delta V/V$  is taken as  $(V_m - V_{RT})/V_m$ . The listed data are in order of increasing value of the chemical activity  $\chi_m$  for the metals as suggested by Pettifor [16]. This arrangement introduces a correlation via the nature of bonding i.e. it roughly estimates the increasing weight of covalency versus ionicity as one proceeds downward within the table.

**Table 3.1:** Melting and transport properties of selected monovalent metal halides: the crystal structures are for the high temperature phase while  $\Delta V/V = (V_m - V_{RT})/V_m$  represents the relative volume at  $T_m$ .

Salt	$\chi_m$	Structure	$T_m$ (K)	$\Delta S_m$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta V/V$	$\sigma$ ( $\Omega^{-1} \text{cm}^{-1}$ )	$H$ (cp)
<i>CsCl</i>	0.25	<i>NaCl</i>	918	5.29	0.30	1.1	1.6
<i>CsBr</i>	0.25	<i>CsCl</i>	909	6.20	0.30	0.80	1.8
<i>RbCl</i>	0.30	<i>NaCl</i>	988	4.45	0.24	1.5	1.4
<i>RbBr</i>	0.30	<i>NaCl</i>	953	3.88	0.19	1.1	1.6
<i>KCl</i>	0.35	<i>NaCl</i>	1045	5.98	0.23	2.2	1.1
<i>KBr</i>	0.35	<i>NaCl</i>	1007	6.06	0.23	1.6	1.2
<i>KI</i>	0.35	<i>NaCl</i>	954	6.02	0.22	1.3	1.4
<i>NaCl</i>	0.40	<i>NaCl</i>	1074	6.30	0.28	3.6	1.0
<i>NaBr</i>	0.40	<i>NaCl</i>	1020	6.15	0.27	2.9	1.2
<i>NaI</i>	0.40	<i>NaCl</i>	934	6.08	0.25	2.2	1.2
<i>LiF</i>	0.45	<i>NaCl</i>	1121	5.77	0.32	8.6	1.9
<i>LiCl</i>	0.45	<i>NaCl</i>	883	5.28	0.27	5.7	1.5
<i>LiBr</i>	0.45	<i>NaCl</i>	823	5.12	0.27	4.7	1.7
<i>Li-I</i>	0.45	<i>NaCl</i>	742	4.72	0.23	3.9	2.1
<i>AgCl</i>	1.18	<i>NaCl</i>	728	4.26	0.13	3.7	2.3
<i>AgBr</i>	1.18	<i>NaCl</i>	703	3.12	0.14	2.9	3.5
<i>Ag-I</i>	1.18	$\beta$ - <i>AgI</i>	831	2.70	0.071	2.3	3.6
<i>CuCl</i>	1.20	Wurtzite	696	2.43	0.16	3.7	4.1
<i>TlBr</i>	1.56	<i>CsCl</i>	733	5.35	0.20	0.82	2.2
<i>Tl-I</i>	1.56	<i>CsCl</i>	715	4.92	0.17	0.53	2.6
<i>InCl</i>	1.60	<i>Yellow Tl</i>	498	4.42	0.11	0.85	-

Of special importance to our calculation is the crystal structure of the solid at the melting point which is also listed on the table (column 3) as given by Wyckoff [17] and Wells [18] for each metal considered.

#### 4.0 Results and discussion

Numerical values of columns 5 and 6 on the table have been used to construct the graph of the figure below. For the family of salts considered, the circles represent the systems whose entropy and volume change conform, approximately, with the linear entropy-volume relation of Equation (2.8). The best fit to the data is shown by the straight line on the figure. The trendline is represented by equation

$$\frac{\Delta S}{R} = 2 \cdot 2 \ln 2 + 4 \cdot 9 \frac{\Delta V}{V} \quad (4.1)$$

On the figure, about 3 systems have their entropies deviate from the norm (equation 2.8). Out of the 3 systems, only *RbBr* shows significant deviation from the rule (Equation 2.8). The deviation of the intercept of Equation (4.1) from  $2 \ln 2$  is certainly not significant since the slope of Equation (2.8) is a rough estimate from the high temperature data (cf. Tallon and Robinson [10]).

The Pettifor parameter  $\chi_m$  (column (2)) clearly separates the alkali-halides from the less ionic halides of Silver, Copper, Thallium and Indium mono-chlorides. The less ionic chlorides transform before melting into the layer-type yellow *Tl-I* structure. The liquid state of these systems exhibits similar values of the ionic conductivity ( $\sigma$ ) and shear viscosity ( $\eta$ ) of particular magnitudes for loosely coordinated ionic melts whose major structural features arise from the excluded volume effects and from relative Coulomb ordering of the two component species.

Recalcitrant alkali-halides such as *Ag-I*, *Ag-Br* and *Cu-Cl* as presented on the graph are in order of increasing  $\Delta V/V$ . In any case, *Ag-I* is well known for its high temperature crystal phase super-ionic conductivity. However, within *Ag-Br* and *Cu-Cl* before melting, the ionic conductivities attain values that are comparable to those displayed on the table. Any deficit in entropy is attributable to the fact

that the entropy of the crystal of these salts increases abnormally before melting due to disorder of the cationic component.

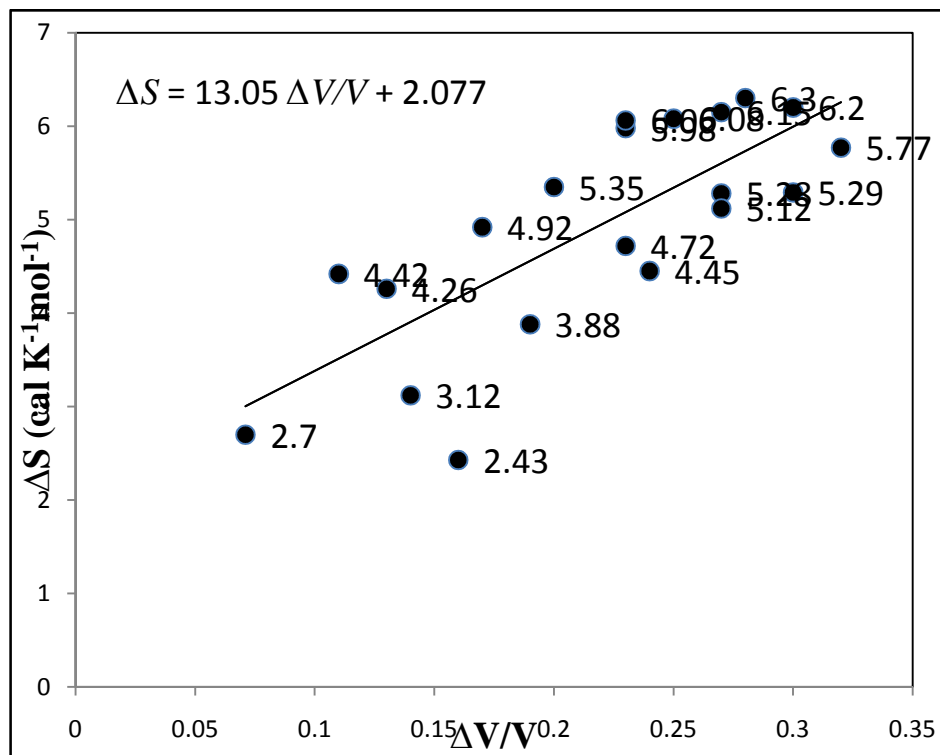


Figure 4.1: Entropy of melting as a function of relative volume

## 5.0 Conclusion

By examining the relationship between the entropy and volume of melting for mono-chlorides we have been able to fashion out an empirical expression that unifies virtually all materials in this category. This rule turns out to be approximately obeyed by the majority of the salts considered. Those systems showing a deficit of entropy on melting fall into well defined pockets within the ordering of systems adopted here. The present work on mono-chlorides is expected to set the stage for further investigation of the polyvalent metal halides.

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