# Calculation of the Melting Curves of some Alkali-halides with CsCl Structure and their Thermodynamic Properties along these Curves

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The paper presents a study of three semi-empirical laws of melting. The study utilises the Improved Unsymmetrized Self-Consistent Field Method (IUSCFM) for strongly anharmonic crystals with complex lattice and the energy criterion in calculating the melting curves of some alkali-halides. The energy criterion was proven correct along the melting curves particularly in the case of CsCl type of structure. The calculations of the melting curves for crystals of nine alkali-halides (KCl, KBr, KI, RbCl, RbBr, RbI, CsCl, CsBr, CsI) are presented. The thermodynamic properties of these salts along the curves are also determined. A comparison of the calculated results and the experimental data is included.

*Key words:* Melting curves, Alkali-halides, Thermodynamic properties, Energy criterion, CsCl structure.

## 1. Introduction

The absence of an exact universal statistical theory describing the different phases of matter adds to the difficulty of formulating a precise microscopic theory of melting, even for monoatomic substances.

This is further complicated when polyatomic substances are investigated. Therefore it is justifiable to adopt semi-empirical laws of melting [1 – 6]. These laws are usually formulated with the thermodynamic functions of the crystalline phase only [1].

Ross [2] showed that the coefficient

$$\varrho(T, V_s) = \frac{\psi(T, V_s) - U_0(V_s)}{RT} = \varrho_s = \text{const} \qquad (1)$$

is constant along the melting binodale, where $V_s$ is the molecular volume of the crystal in equilibrium with the liquid at the temperature $T$, $U_0(V)$ the potential energy of the static lattice, and

$$\psi(T, V) = F(T, V) - F_{\text{id}}(T, V) \qquad (2)$$

the configurational free energy with $F(T, V)$ the free energy of the crystal and $F_{\text{id}}(T, V)$ the free energy of the ideal gas of the studied material.

The second semi-empirical law of melting includes the constancy of the configurational entropy of solids along the melting curves [1, 3]:

$$\sigma(T, V_s) = \frac{S - S_{\text{id}}}{R} = \frac{1}{R}\left(\frac{\partial \psi}{\partial T}\right)_{V = V_s} = \sigma_s = \text{const}, \qquad (3)$$

where $S$ is the entropy of the crystal and $S_{\text{id}}$ the entropy of the ideal gas. Equation (3) was used in [4] to calculate the volume of Ar and Na crystals along their melting curve.

The third one is

$$\tau(T, V_s) = \frac{\bar{U}(T, V_s) - U_0(V_s)}{RT} = \tau_s = \text{const} \qquad (4)$$

which can be obtained from (1) and (3) according to the second thermodynamic law with $\bar{U}(T, V_s)$ the potential energy of the crystal [5].

In the classical quasi-harmonic approximation, (1) and (3) can be derived from the Lindemann criterion. (Some times (1) and (3) are called the generalized Lindemann melting laws [1 – 3].) In this approximation, (4) is actually an identity ($\tau = 1.5\,n$ at any $T$ and $V$, where $n$ is the number of atoms (ions) in the elementary cell). It is, however, not possible to use this relation for anharmonic crystal melting curves since it is not permissible in this case to adopt the quasi-harmonic approximation even as a zeroth approximation [7 – 9].

In this paper, (1), (3) and (4) have been analysed for their applicability in case of CsCl type structures. By

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using the energy criterion (formula (4)) and the improved unsymmetrized self-consistent field method (IUSCFM) for strongly anharmonic multi-compound crystals with complex lattice [9–14], the melting curves of nine alkali-halides and the thermodynamic properties of these salts along the curves were calculated.

## 2. Self-Consistent Potentials. Helmholtz Free Energy

In solids the deviations of atoms from their equilibrium sites are small in comparison with the interatomic distances up to the melting temperatures. This enables the potential energy of a crystal lattice $U$ to be expanded in a Taylor series in powers of the ionic displacements:

$$U = U_0 + \sum_{l=2}^{\infty} U_l \,. \tag{5}$$

This series, by virtue of its convergence can be approximated by a partial sum:

$$U \approx U^{\mathrm{PS}} = U_0 + \sum_{l=2}^{s} U_l \,. \tag{6}$$

It is well known that the exact calculation of the statistical integral of a crystal can be made only when $s=2$ (harmonic or quasi-harmonic approximation [15–17]). But at high temperatures the anharmonic effects in crystals are large, and the lowest anharmonic terms can become equal to or even greater than those of the second order [7–9]. So, in the vicinity of the melting temperatures, the quasi-harmonic approximation cannot be used as a basis for the perturbation theory.

As a zeroth-order approximation for strongly anharmonic crystals, the unsymmetrized self-consistent field method can be used [8–12, 18, 19]. This method was suggested for the first time by Terletsky and Zubov [18] to describe the thermodynamic properties of strongly anharmonic monoatomic cystals. In this approximation the Helmholtz free energy of the ionic crystal is given by

$$F_0 = -\theta \ln \int \exp\left\{-\frac{1}{\theta}\left[\sum_{i,\mu} \frac{(\boldsymbol{P}_\mu^i)^2}{2m_\mu} + U^0\right]\right\} \frac{\mathrm{d}\boldsymbol{r}_1^1 \dots \mathrm{d}\boldsymbol{P}_n^N}{(2\pi\hbar)^{3Nn}} , \tag{7}$$

$\mathrm{d}\boldsymbol{r}_1^1 \dots \mathrm{d}\boldsymbol{P}_n^N$ being the phase-space volume element,

$$U^0 = \sum_{i,\mu} u_\mu^i \equiv \sum_{i,\mu} u_\mu(\boldsymbol{q}_\mu^i) \tag{8}$$

is the self-consistent potential energy of a crystal, and $\boldsymbol{q}_\mu^i$ are the displacement of the ions from the lattice points.

The self-consistent potentials $u_\mu(\boldsymbol{q}_\mu)$ obey a set of non-linear integral equations [10, 12] which, in the case of pairwise interactions $(\phi^{\mu\nu})$

$$U = \tfrac{1}{2} \sum_{i=1}^{N} \sum_{\mu=1}^{n} \sum_{j,\nu}{}' \phi^{\mu\nu}(|\boldsymbol{r}_i^\mu - \boldsymbol{r}_j^\nu|) , \tag{9}$$

can be written in the form [10, 12]

$$u_\mu(\boldsymbol{q}_\mu) = \sum_{j,\nu} \left[\int \phi^{\mu\nu} w_\nu \, \mathrm{d}\boldsymbol{q}'_\nu - \tfrac{1}{2} \iint \phi^{\mu\nu} w_\mu w_\nu \, \mathrm{d}\boldsymbol{q}'_\mu \, \mathrm{d}\boldsymbol{q}'_\nu\right] , \tag{10}$$

where $\phi^{\mu\nu}(\boldsymbol{r}_\mu^i, \boldsymbol{r}_\nu^j)$ is the interaction potential between ions $\mu$ and $\nu$,

$$w_\mu(\boldsymbol{q}_\mu) = \exp\left[\frac{f_\mu - u_\mu(\boldsymbol{q}_\mu)}{\theta}\right] \tag{11}$$

and $f_\mu$ is defined by the normalization

$$f_\mu = -\theta \ln \exp\{-u_\mu(\boldsymbol{q}_\mu)/\theta\} \, \mathrm{d}\boldsymbol{q}_\mu \,. \tag{12}$$

Many-body forces can also be considered without any specific problems [20].

For arbitrary $s$, in (6) the set of non-linear integral equations (10) reduces to a finite set of transcendental equations [10] in the moments of the one-particle distribution function (11). These moments define the self consistent potentials $u_\mu(\boldsymbol{q}_\mu)$ and, hence, the zeroth-order Helmholtz free energy (7).

In principle, the unsymmetrized self-consistent field method enables one to include the strong anharmonicity of any even order in the Helmholtz free energy and in the thermodynamic properties of the crystals.

The statistical perturbation theory can be used to improve the unsymmetrized self-consistent field approximation [9, 12, 19]. If the power series expansions of $U$ and $U^0$ are truncated after terms of the same order $s$ $(s \geq 4)$, the relation $\overline{U^{\mathrm{PS}} - U^0} = 0$ is valid, where the bar implies averaging over the system with the self-consistent potential energy $U^0$. The first non-zero correction to the Helmholtz free energy of a crystal with the potential energy $U^{\mathrm{PS}}$ is of the form

$$F_2 = -\frac{1}{2\theta} \overline{(U^{\mathrm{PS}} - U^0)^2} \,. \tag{13}$$

The effect of higher anharmonicities on the thermodynamic functions of a strongly anharmonic crystal can be calculated by the statistical perturbation theory too. In the first- and second-order perturbation theory the higher-anharmonicity correction to the Helmholtz free energy is defined by the formula [19]

$$F_{\mathrm{H}} = \overline{U^{\mathrm{H}}} - \frac{1}{2\theta}\left[2\,\overline{U^{\mathrm{H}}(U^{\mathrm{PS}} - U^0)} + \overline{(U^{\mathrm{H}})^2}\right], \qquad (14)$$

where $U^{\mathrm{H}}$ contains the anharmonicities of orders higher than $U^{\mathrm{PS}}$.

According to the above, the Helmholtz free energy, in the quasi-classical approximation, can be expressed by

$$F = F_0 + F_2 + F_{\mathrm{H}} + F_{\mathrm{Q}}\,, \qquad (15)$$

where

$$F_{\mathrm{Q}} = \frac{\hbar^2}{24\,\theta}\sum_{i=1}^{N}\sum_{\mu=1}^{n}\frac{1}{m_\mu}\,\overline{\nabla^2_{r^i_\mu} U^0} \qquad (16)$$

is the first quantum correction [11].

## 3. Validity of the Energy Criterion

The relations (1), (3) and (4) were used by Zubov [5, 21] to calculate the melting curves of Argon, Krypton and Xenon, where it was found that (1) and (3) gave almost identical results. The results obtained with all three rules were comparable with the experimental data. Magalinskii and Zubov [22] studied the changes of the configurational entropy $\sigma$ along the melting curve of Argon. Here it was found that $\sigma_s$ varies by no more than 1.17% when the temperature increases by a factor of five. In this case the concept of constant configurational entropy is valid.

However the validity of (1), (3) and (4) for strongly anharmonic mono-atomic crystals does not mean that they can be used for strongly anharmonic polyatomic crystals with complex lattice. And as the alkali-halides with CsCl type structure are the subject of this study, $\varrho$, $\sigma$ and $\tau$ have been studied along the experimental melting curves of seven alkali-halides (KCl, KBr, KI, RbCl, RbBr, RbI, and CsCl) at the high temperature modification. Experimental data were taken from [23–26].

It was noticed that $\varrho_s$ and $\tau_s$ are always positive and $\sigma_s$ is always negative. This finding is in good agreement with that of Magalinskii and Zubov [16]. In addition to that, $\varrho_s$ and $|\sigma_s|$ decrease along the melting curves continuously, but $\tau_s$ initially decreases to its minimum value ($\tau_{s\,\min}$) and then begins to increase. At the same time the rates of decrease and increase of $\tau_s$ are smaller than $7 \times 10^{-5}$ per Kelvin.

Table 1. The change of $\varrho$, $\sigma$, and $\tau$ along the melting curves.

| Salt | KCl | KBr | KI | RbCl | RbBr | RbI | CsCl |
|---|---|---|---|---|---|---|---|
| $\Delta\varrho$ | 2.18 | 2.24 | 1.56 | 5.24 | 5.62 | 4.39 | 7.34 |
| $\Delta\sigma$ | 2.82 | 2.92 | 1.98 | 6.55 | 7.03 | 5.44 | 9.12 |
| $\Delta\tau$ | 0.29 | 0.54 | 0.38 | 0.43 | 0.61 | 0.55 | 0.84 |
| $\Delta T$ (K)* | 500 | 600 | 600 | 700 | 800 | 800 | 900 |

* $\Delta T$ is the temperature interval ranges in question.

The changes of $\varrho$, $\sigma$, and $\tau$ along the melting curves can be enhanced by investigating

$$\Delta\eta = \frac{\eta_{\max} - \eta_{\min}}{\eta_{\min}} \times 100\,, \qquad (17)$$

where $\eta = (\varrho_s,\ |\sigma_s|$ or $\tau_s)$ for each salt. This helps in choosing either (1), (3) or (4) as the best one.

It is clear from Table 1 that $\tau_s$ changes by less than 0.84% along the melting curve of all the studied salts, whereas $\varrho_s$ and $\sigma_s$ change by more than 4 times the $\tau_s$ changes, and their changes reach 7.34% and 9.12%, respectively. This proves the validity of the energy criterion for crystals with CsCl type of structure. In addition to that, the changes of $\varrho_s$ and $|\sigma_s|$ are near to each other (see Table 1). This is why the results of the melting curve calculations, which depend on $\varrho_s$ and $\sigma_s$, are close to each other [21].

Therefore, rule (4) is used for calculating the melting curves and the thermodynamic properties of the crystals KCl, KBr, KI, RbCl, RbBr, RbI, CsCl, CsBr, and CSI depending on IUSCFM along these curves.

## 4. Numerical Results and Discussion

To obtain the melting curves we first solve the equation of state

$$P = -\frac{a}{3V}\left(\frac{\partial F}{\partial a}\right)_T \qquad (18)$$

for a single experimental melting point in relation to the volume "$V$". Then, we calculate $\tau$ for this melting point. After that, depending on (4) and (18), we can calculate the melting curves

$$P_{\mathrm{m}} = P_{\mathrm{m}}(T); \quad V = V_s(T)\,, \qquad (19)$$

where $P_{\mathrm{m}}$ is the pressure along the melting curve. In (18), $a$ is the distance between the nearest neighbours and $P$ the pressure.

Table 2. The parameters of pair (20) and three body (22) potentials.

| | KCl | KBr | KI | RbCl | RbBr | RbI | CsCl | Unit | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| $\varrho'$ | 0.3269 | 0.3365 | 0.3437 | 0.3420 | 0.3555 | 0.3570 | 0.3393 | Å | [30] |
| $b \times 10^{13}$ | 3.441 | 3.673 | 4.675 | 3.270 | 3.417 | 3.527 | 2.876 | erg | [30] |
| $-A \times 10^{9}$ | 1.40 | 2.25 | 7.00 | 1.18 | 1.50 | 3.66 | 1.83 | erg | [30] |
| $C_{++} \times 10^{60}$ | 24.3 | 24.3 | 24.3 | 59.4 | 59.4 | 59.4 | 152.0 | erg × cm$^6$ | [27] |
| $C_{+-} \times 10^{60}$ | 48.0 | 60.0 | 82.0 | 79.0 | 99.0 | 135.0 | 129.0 | erg × cm$^6$ | [27] |
| $C_{--} \times 10^{60}$ | 124.5 | 206.0 | 403.0 | 130.0 | 215.0 | 428.0 | 129.0 | erg × cm$^6$ | [27] |
| $D_{++} \times 10^{76}$ | 24.0 | 24.0 | 24.0 | 82.0 | 82.0 | 82.0 | 278.0 | erg × cm$^8$ | [27] |
| $D_{+-} \times 10^{76}$ | 73.0 | 99.0 | 156.0 | 134.0 | 180.0 | 280.0 | 250.0 | erg × cm$^8$ | [27] |
| $D_{--} \times 10^{76}$ | 250.0 | 470.0 | 1130.0 | 260.0 | 490.0 | 1200.0 | 260.0 | erg × cm$^8$ | [27] |

In the present calculations the Born-Mayer-Huggins potential [27, 28] was used to describe the effective force between two ions. This potential can be expressed, as suggested in [27, 28, 29], as follows:

$$\phi_{\mu\nu}(r)=\frac{e_\mu e_\nu}{r}+b_{\mu\nu}^{kk'}\,e^{-(r/\varrho')}-\frac{C_{\mu\nu}}{r^6}-\frac{D_{\mu\nu}}{r^8}, \tag{20}$$

where

$$b_{\mu\nu}^{kk'}=b\,\beta_{kk'}\exp\left[-(R_\mu+R_\nu)/\varrho'\right]. \tag{21}$$

The factor $\beta_{kk'}$ originates from certain quantum-mechanical considerations and depends only on charges of interacting ions, namely: $\beta_{++}=1.25$, $\beta_{+-}=1$, $\beta_{--}=0.75$. $R_\mu$ are the Pauling ionic radii with the following values: 1.33, 1.48, 1.69, 1.81, 1.95, 2.16 Å for K, Rb, Cs, Cl, Br, and I respectively. The other parameters of the pair potential are listed in Table 2. Three body interactions can be expressed, according to [30], by

$$\phi^{\lambda\mu\nu}=A\exp\left[-(r_{\mu\nu}+r_{\nu\lambda}+r_{\lambda\mu})/(3\,\varrho')\right], \tag{22}$$

where $r_{\mu\nu}$ is the distance between $\mu$ and $\nu$ ions. The values of the parameter $A$ are listed in Table 2. Here it must be mentioned that the parameters of the pair and three body potentials, used in our calculation, were calculated from experimental results for $T\to 0$ [27–30].

The values of $\tau$ for KCl, KBr, KI,. RbCl, RbBr, RbI, CsCl, CsBr and CsI at the experimental melting points are 2.7774, 2.7678, 2.7471, 2.7876, 2,7762, 2.7425, 2.7815, 2.8011 and 2.7995 respectively. These values are used to calculate the melting curves of these salts.

Figure 1 shows the theoretical values of $P_m$ along the melting curves of the studied salts. The comparison of the theoretical with the experimental is not given here in the case of CsBr and CsI as the experimental results for these two salts are not available to us. The calculated values for $P_m$ can be compared to available results [23–26], where the experimental errors are also indicated. It is clear from Fig. 1 that the agreement between the experimental and theoretical results is excellent, as the calculated values are within the experimental errors [23–26]. Because of taking the angular dependent part of the self-consistent potential in consideration we have reached better agreement with the experimental data for $P_m$ than Zubov and Soulayman [31].

It was found that there are semi-linear relations between volume $V_s$, potential energy $U$ and temperature $T$ along the melting curves. These relations can be expressed over a wide range of temperature changes in a very precise manner as

$$\bar{U}=\bar{U}(T_0)+\chi(T-T_0) \tag{23}$$

and

$$V_s(T)=V_s(T_0)-\gamma(T-T_0), \tag{24}$$

where $\chi$ and $\gamma$ are constants and $T_0$ is the lowest experimental melting temperature where the studied salt has CsCl type structure. $V_s(T_0)$ and $\bar{U}(T_0)$ are the molecular volume and the potential energy, respectively, when $T=T_0$. The obtained results for $V_s$ agree with the experimental results of Vaidya and Kennedy [26].

It must be mentioned here that the obtained molecular volume-temperature dependence of the studied ionic compounds along the melting curves has, indeed, a very slight curvature toward the volume axis. This result agrees with experimental [32] and theoretical [33] results.

The isothermal bulk modulus $B_T$ along the melting curves is basically a function of volume. This function can be expressed as

$$B_T=B_T(V_0)\exp\{-\delta(V_s-V_0)\}, \tag{25}$$

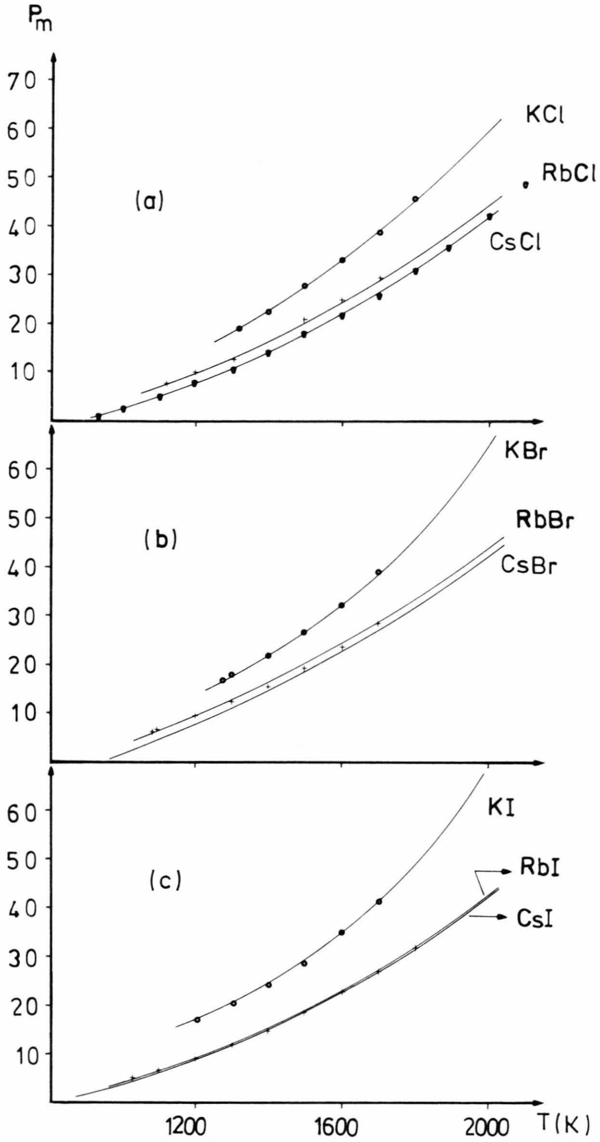

Fig. 1. Melting pressure vs. temperature dependence for alkali-halides (MX), where M is K, Rb or Cs and X is Cl (a), Br (b) or I (c). —— Theoretical results, o experimental data for KX [23, 25], + experimental data for RbX [24, 25], ▿ experimental data for CsCl [25, 26].

where $\delta$ is a constant and $B_T(V_0)$ is the isothermal bulk modulus when $V_s = V_s(T_0) = V_0$.

The relative differences between the calculated values of $\bar{U}$, $V_s$ and $B_T$ depending on (23), (24), and (25), respectively, and depending on (18) and (4), along the experimental melting curve do not exceed 1.2% over a wide range of temperature changes.

Table 3. The calculated linear expansion coefficient $\alpha \times 10^6$ K$^{-1}$ of the studied salts along the melting curve.

| Salt ($T_0$) | $T$ (K) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $T_0$ | 1000 | 1200 | 1400 | 1600 | 1800 | 2000 |
| CsCl (933) | 62.16 | 61.70 | 58.21 | 52.49 | 46.00 | 39.74 | 34.18 |
| CsBr (909) | 66.38 | 63.78 | 53.15 | 45.52 | 39.79 | 35.31 | 31.72 |
| CsI (894) | 68.97 | 60.22 | 48.77 | 40.87 | 35.11 | 30.74 | 27.35 |
| RbCl (1123) | 51.76 | – | 50.40 | 46.38 | 41.94 | 37.54 | 33.46 |
| RbBr (1081) | 53.61 | – | 52.05 | 47.34 | 41.19 | 34.97 | 29.37 |
| RbI (1033) | 53.11 | – | 50.02 | 44.22 | 37.62 | 31.42 | 26.16 |
| KCl (1323) | 42.70 | – | – | 40.66 | 35.63 | 31.15 | 27.31 |
| Kbr (1270) | 40.92 | – | – | 38.28 | 33.02 | 27.45 | 22.43 |
| KI (1207) | 34.06 | – | – | 30.66 | 26.07 | 21.40 | 17.31 |

It was also noticed that changes in the isochoric heat capacity, $C_v$, along the melting curves are very small (less than 0.2%). This is why no special data for $\bar{U}$, $V_s$, $B_T$ or $C_v$ are presented in Table 3, which includes the numerical results of the linear expansion coefficient, only.

The isobaric heat capacity, $C_p$, and the adiabatic bulk modulus $B_s$ of the studied strongly anharmonic crystals along the melting curves can be easily calculated by the relations

$$C_p = C_v + 9\,T\,V B_T\,\alpha^2 \tag{26}$$

and

$$B_s = \frac{B_T\,C_p}{C_v}, \tag{27}$$

where $B_T$ can be calculated by (25), $\alpha$ is obtained in Table 3, and $V$ can be calculated by (24). All other values are presented in Table 4.

## 5. Conclusion

We can conclude that, owing to the anharmonic effects, (4), (1) and (3) do not follow from the Lindemann criterion because $\tau_s \neq 1.5\,n$; rather in case of CsCl, $\tau_s = 2.7815$. In addition it was found that $\tau_s$

Table 4. Some thermodynamic parameters at the triple points.

| Salt | $-U(T_0)$ kcal/mol | $V_0$ cm$^3$/mol | $B_T(V_0)$ kbar | $C_v(T_0)$ J/K mol | $\chi \times 10^3$ kcal/mol | $-\gamma \times 10^3$ cm$^3$/K mol | $-\delta \times 10^3$ mol/cm$^3$ |
|---|---|---|---|---|---|---|---|
| KCl | 159.6 | 33.37 | 187.4 | 46.55 | 4.3389 | 4.613 | 168.01 |
| KBr | 152.6 | 38.53 | 170.4 | 46.49 | 6.2911 | 6.514 | 145.26 |
| KI | 143.5 | 47.12 | 169.3 | 46.24 | 7.9262 | 8.143 | 122.26 |
| RbCl | 155.4 | 37.87 | 136.0 | 46.90 | 4.7011 | 3.938 | 155.15 |
| RbBr | 148.5 | 43.95 | 113.8 | 46.82 | 4.8591 | 5.765 | 124.89 |
| RbI | 140.6 | 53.81 | 99.10 | 46.43 | 4.9795 | 7.521 | 80.46 |
| CsCl | 149.7 | 45.63 | 101.8 | 46.97 | 4.3389 | 5.031 | 138.88 |
| CsBr | 143.7 | 51.86 | 83.11 | 46.95 | 4.4545 | 6.759 | 120.61 |
| CsI | 135.6 | 63.058 | 67.72 | 46.843 | 4.5944 | 9.275 | 101.71 |

changes very little along the melting binodale of all the studied ionic compounds in the high pressure solid phase. On the other hand, the energy criterion gives a better fit to experimental data for crystal having simple cubic sublattices (CsCl-type modification of the alkali-halides).

The validity of the semi-empirical relations with other types of structure will hopefully be considered in another work.

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