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Correlation between standard enthalpy of formation, structural parameters and ionicity for alkali halides

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Abstract: The standard enthalpy of formation (ΔH^\ominus) is considered to be an interesting and useful parameter for the correlation of various properties of alkali halides. The interrelation between ΔH^\ominus and structural parameters for the halides of Li, Na, K and Rb has been thoroughly analyzed. When the cationic component element is kept constant in a homologous series of alkali halides, the negative value of ΔH^\ominus was observed to decrease linearly with increasing interionic distance (d). Accordingly, the following empirical equation $\Delta H^\ominus = \alpha + \beta d$ (where α and β are empirical constants) was established. However, for common anionic series of alkali halides, an opposing non-linear trend was observed, with the exception of common fluorides. The correlation study on the standard enthalpy of formation was extended in term of the radius ratio and also discussed in the light of ionization energy of the metal, electron affinity of the halogen, size of the ions, ionic character of the bond and the lattice energy of the compound.

Keywords: thermodynamic properties; exothermicity; interionic distance; radius ratio; interrelation.

INTRODUCTION

Alkali halides are crystalline ionic solids that are of great interest for both theoretical and experimental studies. In recent years, they have gained increased interest due to their prominent applications in the fabrication of various electronic, optical and optoelectronic devices.¹ They have also received considerable attention due to their potential role in emerging nano-scale technologies and importance in environmental chemistry, such as ozone layer depletion and precipitation.² During the past few years, considerable efforts, *e.g.*, see references^{3–22}, have been made to understand the interrelation between their various structural, optical and electronic properties, such as lattice constants, interionic distance, radius ratio, refractive index, electronic polarizability, dielectric constant, cohe-

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sive energy, bond energy, magnetic susceptibility, energy gap, bulk modulus, *etc.* Although thermodynamic properties are of considerable importance for an understanding of the nature of a compound against a changing environment, limited attempts have been made to study the interrelation of the thermodynamic properties of alkali halides with their other properties. Shanker *et al.*²³ studied the relationship between solid state parameters and melting parameters for alkali halides and reported that melting temperature and relative change in volume after melting vary in a systematic manner with the ionic character of bond. Kanno^{24,25} observed the relationship between enthalpy of fusion, entropy change upon fusion or sublimation upon melting, melting point, electronic polarizability, interionic distance and the ionic radius ratio for some alkali halides. He also developed an empirical relation between the relative volume changes upon melting with the interionic distance.²⁶ In a relatively recent work of Rozman,²⁷ correlations between thermodynamic parameters (such as melting point, melting energy and jump in entropy upon melting) and the binding energy of dipolons were established for the halides of lithium, sodium, potassium and rubidium. Ohashi²⁸ expressed an empirical relation between the heats of formation and the electronegativity of halogen ions. Recently Vasiliu *et al.*²⁹ predicted the geometric parameters, frequencies, enthalpies of formation and bond dissociation energies for some simple alkali metal compounds by employing the coupled cluster theory. A second order empirical polynomial relation between standard enthalpy of formation and refractive index for all the twenty alkali halides has also been developed.³⁰

A literature survey reveals that no systematic effort has hitherto been made to correlate the thermodynamic properties of alkali halides with their structural, physical, optical and electronic properties. The available work in this direction is very limited and scanty. Since structural parameters are basic constants that are involved in most theoretical calculations and also in predicting the behaviour of a compound, it is worth correlating them with the thermodynamic properties of alkali halides. As the enthalpy of formation throws light on the nature of the bond and the intrinsic stability of the compound in the condensed phase, it was decided to study the correlation of the enthalpy of formation with the structural and ionic parameters of alkali halides.

BASIC INPUT DATA AND THEIR TREND IN THE HOMOLOGOUS SERIES OF ALKALI HALIDES

The values of room temperature standard enthalpy of formation³¹ and interionic distance¹ are listed in Table I for the common cationic and anionic homologous series of alkali halides. The radius ratio in a crystal having the NaCl structure as presented in Table I is calculated from the effective ionic radii of the cationic and anionic constituent elements of the compound with a coordination number 6.³¹ Table I indicates that the negative value of standard enthalpy of formation ($-\Delta H^\ominus$), *i.e.*, exothermicity, decreases with increasing of

interionic distance (d) and decreasing radius ratio (r^+/r^-) in the homologous series of compounds when the cationic component element is kept constant. On the other hand, for the common anionic homologous series of compounds (Table I), the exothermicity ($-\Delta H^\ominus$) generally increases with increasing of both d and r^+/r^- , with the exception of the common fluorides, which obey the reverse trend.

TABLE I. Standard enthalpy of formation and structural parameters of alkali halides

Compound	$-\Delta H^\ominus / \text{kJ mol}^{-1}$	$d / \text{\AA}$	r^+/r^-
Common cationic series			
LiF	616.0	2.0131	0.5714
LiCl	408.6	2.5699	0.4199
LiBr	351.2	2.7508	0.3878
LiI	270.4	3.0060	0.3455
NaF	576.6	2.3164	0.7699
NaCl	411.2	2.8200	0.5635
NaBr	361.1	2.9865	0.5204
NaI	287.9	3.2364	0.4636
KF	567.2	2.6720	1.0376
KCl	436.5	3.1464	0.7624
KBr	393.8	3.2991	0.7041
KI	327.9	3.5327	0.6273
RbF	557.7	2.8258	1.1429
RbCl	435.4	3.2949	0.8398
RbBr	394.6	3.4454	0.7755
RbI	333.8	3.6710	0.6909
Common anionic series			
LiF	616.0	2.0131	0.5714
NaF	576.6	2.3164	0.7699
KF	567.2	2.6720	1.0376
RbF	557.7	2.8258	1.1429
LiCl	408.6	2.5699	0.4199
NaCl	411.2	2.8200	0.5635
KCl	436.5	3.1464	0.7624
RbCl	435.4	3.2949	0.8398
LiBr	351.2	2.7508	0.3878
NaBr	361.1	2.9865	0.5204
KBr	393.8	3.2991	0.7041
RbBr	394.6	3.4454	0.7755
LiI	270.4	3.0060	0.3455
NaI	287.9	3.2364	0.4636
KI	327.9	3.5327	0.6273
RbI	333.8	3.6710	0.6909

DISCUSSION

The values of the room temperature standard enthalpy of formation are plotted against interionic distance for different homologous series of alkali halides in Fig. 1. It could be inferred from Fig. 1 that when the cationic component element

is kept constant in a given homologous series of the compounds, there is almost linear decrease in the negative value of standard enthalpy of formation with increasing d . Thus, the exothermicity of compound formation decreases with increasing anion size. Based on the linear variation between ΔH^\ominus and d , the following empirical relation was established:

$$\Delta H^\ominus = \alpha + \beta d \quad (1)$$

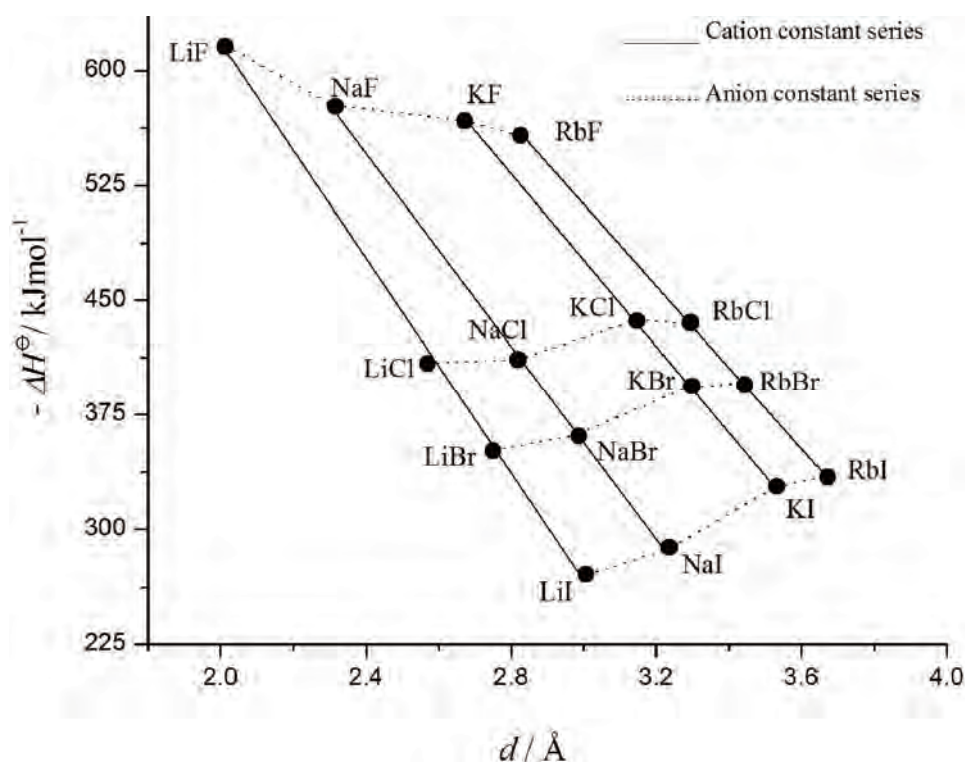


Fig. 1. Plot of the standard enthalpy of formation vs. the interionic distance for alkali halides.

where α and β are empirical constants that are presented in Table II for the different cationic series of alkali halides. The values of square of the correlation coefficient, *i.e.*, R^2 , which can be used to judge the effectiveness of the correlation equation, are also incorporated in this Table. Table II clearly indicates that the R^2 value (≥ 0.9980) was very satisfactory for each case. The values for standard enthalpy of formation ($\Delta H^\ominus_{\text{cal}}$) as calculated from Eq. (1) are compared with the known values³¹ in Table III. The percent deviations for the different compounds, as obtained using the relation:

$$\text{percent deviation} = 100 \left| \frac{\Delta H^\ominus_{\text{known}} - \Delta H^\ominus_{\text{cal}}}{\Delta H^\ominus_{\text{known}}} \right| \quad (2)$$

are also incorporated in Table III. This table clearly shows that there is excellent agreement between the calculated and the known values with the percent deviation ranging from 0.04 to 2.33. Moreover, the average percent deviation is only 0.65.

TABLE II. Empirical constants (α and β) for different series of alkali halides (Eq. (1)); X represents F, Cl, Br or I

Compound series	$-\alpha / \text{kJ mol}^{-1}$	$\beta / \text{kJ mol}^{-1} \text{ \AA}^{-1}$	R^2
LiX	1316.8	350.2	0.9980
NaX	1304.3	315.2	0.9991
KX	1309.7	277.8	1.0000
RbX	1306.1	264.6	0.9999

TABLE III. Known and calculated values of the standard enthalpy of formation of alkali halides

Compound	$-\Delta H^\ominus / \text{kJ mol}^{-1}$		Deviation, %
	Literature ³¹	Calculated (Eq. (1))	
LiF	616.0	611.8	0.68
LiCl	408.6	416.8	2.01
LiBr	351.2	353.5	0.66
LiI	270.4	264.1	2.33
NaF	576.6	574.2	0.42
NaCl	411.2	415.4	1.02
NaBr	361.1	363.0	0.55
NaI	287.9	284.2	1.29
KF	567.2	567.4	0.04
KCl	436.5	435.6	0.21
KBr	393.8	393.2	0.15
KI	327.9	328.3	0.12
RbF	557.7	558.4	0.13
RbCl	435.4	433.3	0.48
RbBr	394.6	394.4	0.05
RbI	333.8	334.8	0.30

Furthermore, it is very interesting and surprising to note that the value of empirical constant α , listed in Table II, remains the same (average: $-1309.2 \text{ kJ mol}^{-1}$) for all the sixteen halides of Li, Na, K and Rb. In fact, this constant is the standard enthalpy of formation of an imaginary compound in the series having zero interionic distance. It is the limiting value and exists only under the hypothetical situation. Although it appears practically impossible for a compound to have zero interionic distance, its implication for future studies cannot be ruled out.

On the other hand, for the common anionic series of compounds, an opposite non-linear trend for the variation of ΔH^\ominus with d was observed with the exception of the common fluorides (Fig. 1). Thus the exothermicity of compound formation increases with increasing size of cationic component element for the common an-

ionic series of alkali halides, except for the fluorides which exhibit the opposite trend. The general increase of exothermic enthalpy of formation with increasing cationic size of chlorides, bromides and iodides is due to the decreasing value of the ionization energy of the metals, which facilitates the formation of the respective cations in the same order. It is also inferred from Table I that the homologous series of same anion do not show any unambiguous general trend for in the ΔH^\ominus values. This observation is consistent with the finding of Shenkin³² who theoretically showed that only the anion size plays a decisive role in thermodynamic relationships for alkali halides. The anomalous behaviour of fluorides is presumably due to the small size and high electronegativity of fluorine compared to other halogens. In fact, the ionic radius of the fluoride anion is similar to that of the oxide anion; thus, fluorides often resemble oxides while other halides resemble sulphides in many respects.³³

The anomalous behaviour of fluorides can be explained in the light of the unusually lower value of the electron affinity of fluorine compared to the other higher halogens. The numerical value of electron affinity is 115.0 kJ mol⁻¹ lower than the value expected from the linear extrapolation of the plot between electron affinity and ionization energy for other halogens (Fig. 2). The values of electron affinity and ionization energy for the halogens were taken from the literature.³¹ In a similar way, a 110.0 kJ mol⁻¹ discrepancy was reported Politzer.³⁴ Thus, fluorides are accompanied by anomalously lower bond energies of about 115.0 kJ mol⁻¹ than would be predicted from the trends of the other halides. The lower value of electron affinity for fluorine is due to the small size of the atom as putting an extra electron into a region of space already crowded with electrons offers a significant amount of repulsion. This repulsion decreases the attraction of an incoming electron and accordingly lowers the electron affinity.

Based on the thermodynamic Born–Haber cycle, the standard enthalpy of formation (ΔH^\ominus) can be related to the electron affinity (EA) of the halogen, the ionization energy (EI) of the metal, the enthalpy of atomization (ΔH_{ax}) of the halogen, the enthalpy of atomization (ΔH_{am}) of the metal and the lattice energy (ΔH_1) of the compound by the following equation:

$$\Delta H^\ominus = EA + EI + \Delta H_{ax} + \Delta H_{am} + \Delta H_1 \quad (3)$$

Thus, the trend of the lattice energy is expected to be more regular than that of the standard enthalpy of formation because the former is obtained by subtracting the irregular value of the electron affinity along with other parameters from the latter. The plot of lattice energy³⁵ vs. interionic distance for alkali halides shown in Fig. 3 can be best represented by the following second order polynomial equation:

$$\Delta H_1 = 1962.9 - 602.7d + 65.2d^2 \quad (R^2 = 0.9958) \quad (4)$$

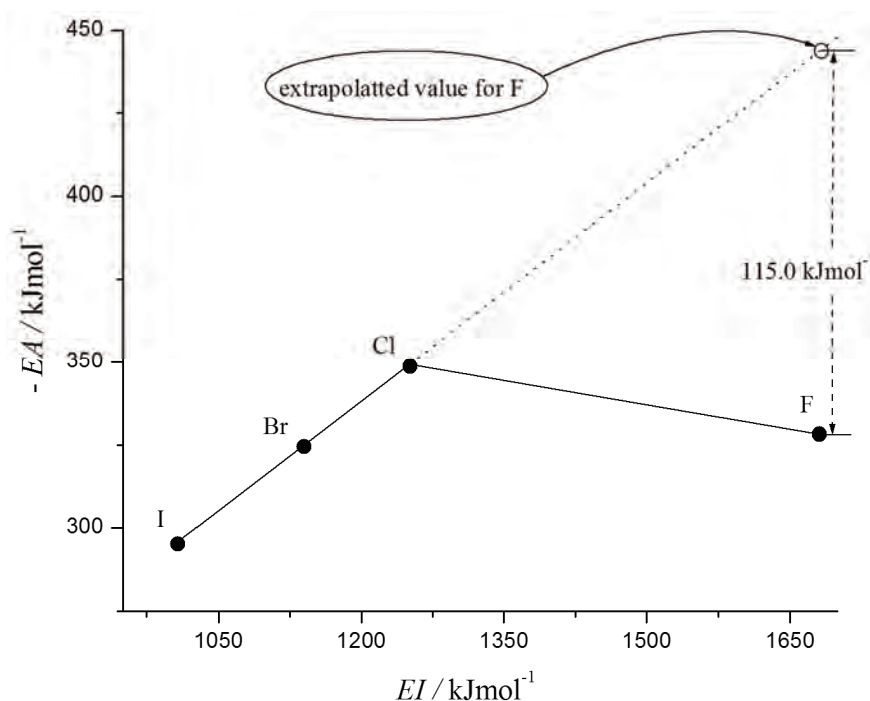


Fig. 2. Plot of electron affinity vs. ionization energy of the halogens.

Figure 3 clearly indicates that the variation of lattice energy with interionic distance is very regular and does not show any anomalous or irregular behaviour of fluorides. Thus, the electron affinity plays a dominant role for the anomalous nature of fluorides. However, further work is required in this direction.

The correlation studies of standard enthalpy of formation were extended to the radius ratio (r^+/r^-). The variation plot shown in Fig. 4 indicates that $-\Delta H^\ominus$ increases regularly with increasing radius ratio of the compounds for different homologous series when either of the component elements is fixed, again with the exception of the common fluorides. The common fluorides show a regular decrease in the value of $-\Delta H^\ominus$ with the radius ratio. In fact, the enthalpy of formation of any fluoride is less exothermic than that expected from the extrapolation of linear plot obtained for the other halides. The possible reasons have already been discussed.

Since F is the most electronegative, the fluoride is more ionic in nature than any of the other respective halides. Thus, it appeared quite interesting to study the correlation between the standard enthalpy of formation and the ionic character of the bond. The ionic character of the bond of a particular compound may be calculated from the value of electronegativity difference ($\Delta\chi$) of its constituent elements by employing the Pauling Equation:³⁶

$$\text{Fractional ionic character of bond } (f^i) = 1 - \exp \{-1/4 (\Delta\chi)^2\} \quad (5)$$

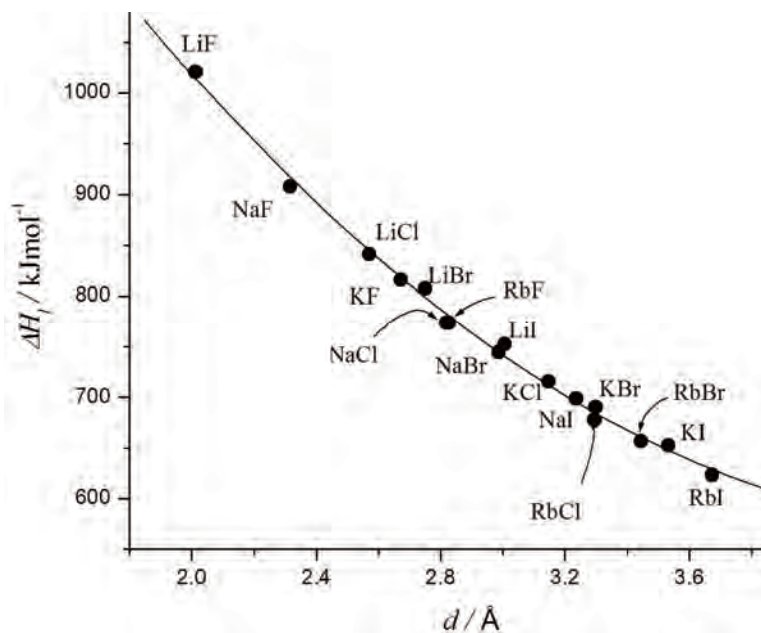


Fig. 3. Plot of lattice energy vs. interionic distance for the alkali halides.

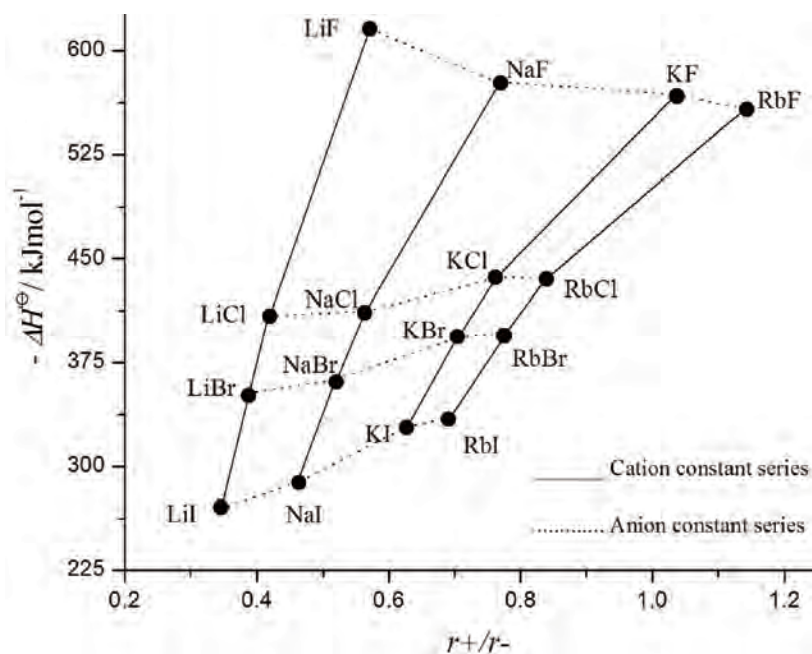


Fig. 4. Plot of standard enthalpy of formation vs. radius ratio for the alkali halides.

The electronegativity values (χ) of atoms are available on a number of scales, including the popular ones Pauling,³⁶ Pauling revised,³¹ Allred and Rochow,³⁷ Gordy,³⁸ Sanderson,³⁹ Allen⁴⁰ and Mulliken.⁴⁰ These scales are prepared by independent methods and have different values of χ for a particular atom. Since χ is a measure of the tendency of an atom to attract bonding electrons towards itself, smaller atoms, as a rule, should have higher values of χ . The electronegativities of alkali metals as proposed by Sanderson, Gordy, Mulliken and Allen are in conformity with the criterion of increase in value with decreasing atomic size and therefore these scales were considered in the calculation of the fractional ionic character of the bond for the different compounds. The values of fractional ionic character of bond for alkali halides as calculated using different electronegativity scales are presented in Table IV. This Table shows that the value of the fractional ionicity for any compound is different for the different scales. However, for any common cationic series of compounds, the trend of the variation with size of the anionic component element remains the same. Hence, for the sake of simplicity, average values were used for further analysis. It can be inferred from Table IV that the fractional ionic character of the bond in a compound decreases with increasing size of the anionic component elements in a common cationic series. However, for the common anionic series of the compounds, an opposite trend was obtained, *i.e.*, the ionicity increases with increasing size of the cationic component elements. Thus the following generalization was established for all the halides of Li, Na, K and Rb: "ionicity increases with decreasing size of the anionic and increasing size of cationic component elements in a given common cationic or anionic series of compounds, respectively".

TABLE IV. Fractional ionic character of the bond in alkali halides

Compound	Gordy ³⁸	Sanderson ³⁹	Mulliken ⁴⁰	Allen ⁴⁰	Average (used)
LiF	0.891	0.937	0.917	0.932	0.919
LiCl	0.647	0.860	0.719	0.616	0.711
LiBr	0.523	0.803	0.615	0.544	0.621
LiI	0.387	0.671	0.472	0.408	0.485
NaF	0.901	0.948	0.926	0.937	0.928
NaCl	0.668	0.880	0.741	0.632	0.730
NaBr	0.547	0.829	0.703	0.562	0.660
NaI	0.431	0.708	0.501	0.426	0.512
KF	0.912	0.957	0.945	0.950	0.941
KCl	0.695	0.899	0.791	0.680	0.766
KBr	0.579	0.854	0.703	0.614	0.688
KI	0.447	0.744	0.574	0.483	0.562
RbF	0.916	0.967	0.948	0.952	0.946
RbCl	0.705	0.918	0.801	0.690	0.779
RbBr	0.591	0.879	0.715	0.624	0.702
RbI	0.460	0.781	0.589	0.495	0.581

The validity of this generalization is very clearly observed in Fig. 5. The plot also indicates that the ionic character of bond increases with increase of radius ratio for the homologous series of compounds when either of the component elements is kept constant. Besides this it is also inferred from this figure that the variation is almost linear for the common anionic and common cationic series of compound with the exception of fluorides.

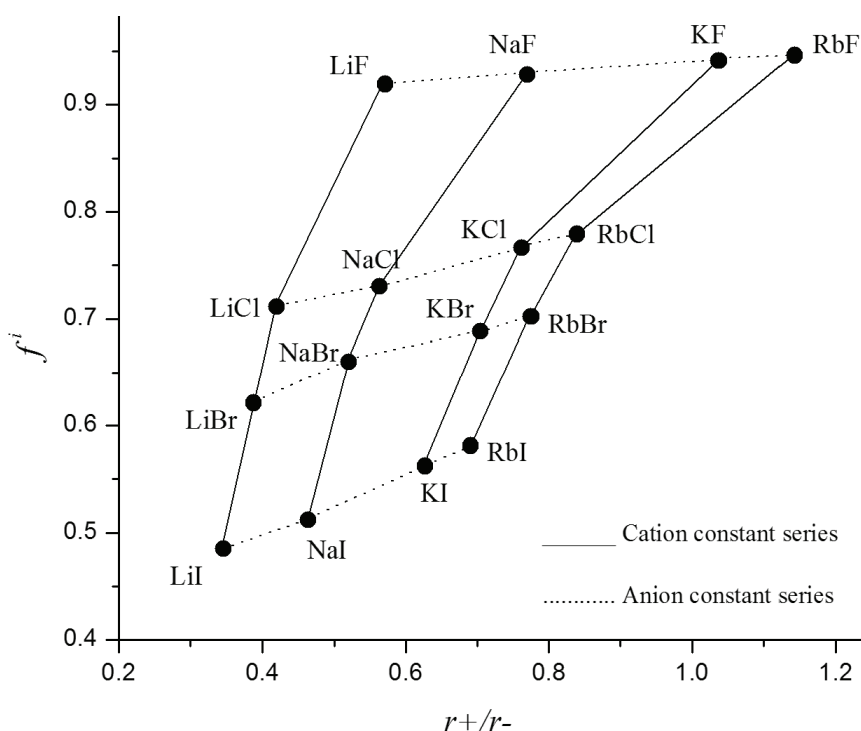


Fig. 5. Plot of fractional ionic character of the bond vs. radius ratio for the alkali halides.

The standard enthalpy of formation of a compound throws light on the type of bonding. A large value of exothermic enthalpy of formation of compound indicates that the nature of bonding is different from that in the constituent elements. The exothermicity has been observed to be generally increased with the degree of ionicity of bond. The plot of standard enthalpy of formation with fractional ionic character of bond shown in Fig. 6 indicates that there is a general linear relation between these two parameters and variation may be represented as:

$$\Delta H^\ominus = 74.4 - 686.9 f^i \quad (R^2 = 0.9629) \quad (6)$$

Since in most cases fluorides exhibit exceptional behaviour, Eq. (6) can be presented in a better way by excluding the fluorides. The empirical equation between ΔH^\ominus and f^i as obtained for the plot represented by line B in Fig. 6 is:

$$\Delta H^{\ominus} = -3.2 - 561.0f^i \quad (R^2 = 0.9878) \quad (7)$$

The linear variation indicates that there exists a very good correlation between standard enthalpy of formation and the ionic character of the bond. Thus, the hypothesis of increasing ionicity with exothermicity is valid for the alkali halides with an NaCl structure. However, this generalization is not valid within the alkali fluorides.

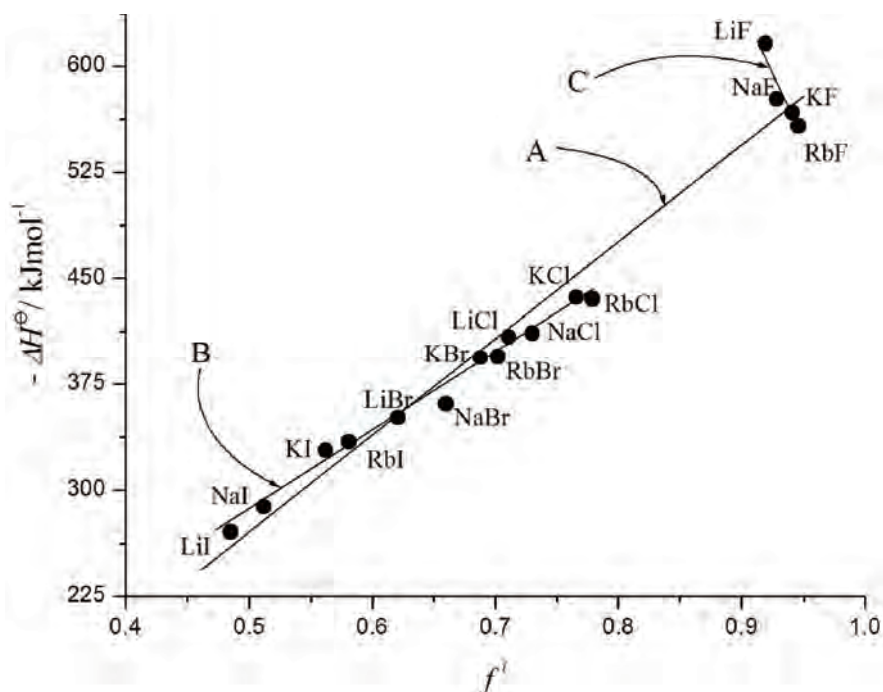


Fig. 6. Plot of the standard enthalpy of formation vs. the fractional ionic character of the bond for alkali halides.

CONCLUSIONS

Systematic variation between the standard enthalpy of formation and structural parameters (interionic distance and radius ratio) for all the sixteen halides of Li, Na, K and Rb were observed. It was established that the exothermicity decreases with increasing or decreasing size of the anionic or cationic component element for the common cationic or anionic series of alkali halides. However, common fluorides show the opposite behaviour to that of the other common halides. Empirical relationships between the standard enthalpy of formation and the interionic distance were proposed for the different common cationic series of compounds.

It was found that the ionicity increases with decreasing size of the anionic and increasing size of cationic component elements in a given common cationic or anionic series of the compounds, respectively. Furthermore, a general linear relation between the standard enthalpy of formation and ionicity was observed to exist for the alkali halides, except for the fluorides. It was proposed that the anomalous behaviour of fluorides with respect to other halides is due to the small size of the fluorine atom, which leads to lower values of the electron affinity than those expected from the trend of the other halogens.

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ИЗВОД

КОРЕЛАЦИЈА ИЗМЕЂУ СТАНДАРДНЕ ЕНТАЛПИЈЕ ФОРМИРАЊА, СТРУКТУРНИХ ПАРАМЕТАРА И ЈОНСКОГ КАРАКТЕРА АЛКАЛНИХ ХАЛОГЕНИДА

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Стандардна енталпија формирања (ΔH^\ominus) је значајан и веома користан параметар за корелацију са различитим особинама алкалних халогенида. Веза између ΔH^\ominus и структурних параметара халогенида Li, Na, K и Rb у овом раду је детаљно анализирана. У случају када је у хомологној серији алкалних халогенида катјонска компонента соли иста, нађено је да се негативна вредност ΔH^\ominus линеарно смањује са повећањем интерјонског растојања и да се ова релација може изразити следећом емпријском формулом: $\Delta H^\ominus = \alpha + \beta d$ (α и β су емпиријске константе). Међутим, супротан нелинеаран тренд промене негативне вредности ΔH^\ominus је нађен у солима алкалних халогенида за исту серију халогенидних анјона, осим у случају флуорида. Поред тога, у овом раду дискутована је веза између стандардне енталпије формирања и јонског радијуса, као промене јонизационе енергије алкалног метала, електронског афинитета халогена, величине јона, јонског карактера везе и енергије кристалне решетке јонског једињења.

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