



Lattice Energies for Groups 1 and 2 Halides from Absolute Hardness

Robson Fernandes de FARIAS¹, Savaş KAYA^{2*}

¹Universidade Federal do Rio Grande do Norte, Cx. Postal 1664, 59078-970, Natal/RN, BRASIL

²Department of Chemistry, Faculty of Science, Cumhuriyet University, 58140, Sivas, TURKEY

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Abstract: In this work, we presented new empirical equations to calculate the lattice energy values of groups 1 and 2 halides based on absolute hardness values of cations and anions forming the ionic compound.

For group 1 halides: $U_{POT} = (-0.494r^+ + 122.392)(\eta^+ + \eta^-) - 109.514\eta^+ + 1191.694$

and for group 2 halides: $U_{POT} = (-0.781r^{+2} + 251.255)(\eta^{+2} + \eta^-) - 222.245\eta^{+2} + 2427.356$

In the given equations, r^+ and r^{+2} = cation radius (pm); η^+ and η^{+2} = cation absolute hardness (eV) and η^- = anion absolute hardness (eV). Here, it should be noted that calculated lattice energy values for mentioned ionic compounds are in good agreement with the reference values obtained from the literature.

Keywords: Lattice energy, Absolute hardness, Empirical equation, Halides

Kimyasal Sertlikten Grup 1 ve 2 Halojenürlerin Örgü Enerjileri

Özet: Bu çalışmada grup 1 ve 2 halojenürlerin örgü enerjilerini hesaplamak için iyonik bileşiği oluşturan katyon ve anyonların mutlak sertlik değerlerine dayalı yeni denklemler türetilmiştir.

Grup 1 halojenürler için: $U_{POT} = (-0.494r^+ + 122.392)(\eta^+ + \eta^-) - 109.514\eta^+ + 1191.694$

Grup 2 halojenürler için: $U_{POT} = (-0.781r^{+2} + 251.255)(\eta^{+2} + \eta^-) - 222.245\eta^{+2} + 2427.356$

Verilen denklemlerde, r^+ ve r^{+2} = katyon yarıçapı (pm); η^+ ve η^{+2} = katyon mutlak sertliği (eV). η^- = anyon mutlak sertliği (eV). Belirtmelidir ki, çalışmada dikkate alınan iyonik bileşikler için elde edilen denklemler aracılığıyla hesaplanan örgü enerjisi değerleri, literatürden elde edilen referans değerler ile uyum içerisinde.

Anahtar Kelimeler: Örgü enerjisi, mutlak sertlik, yeni denklemler, halojenürler

1. INTRODUCTION

It is known that lattice energy (U) is the energy required to decompose the solid into its constituent independent gaseous ions and this energy is a measure of the stability of inorganic ionic solids. Lattice energy is a prominent parameter in chemistry, since it could be related

with a series of properties of a given compound, such as solubility, melting point, etc. Recently, R.F de Farias used the lattice energies to provide the thermochemical explanation for the stability of unusual compounds such as NaCl₃ and NaCl₇ [1].

* Corresponding author. Email address: savaskaya@cumhuriyet.edu.tr
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In the current literature, there are many empirical equations proposed to calculate the lattice energies of inorganic ionic solids. Glasser-Jenkins [2] and Kaya [3] equations are some of well-known lattice energy equations and they provide very compatible results with experimental data reported. Glasser-Jenkins and Kaya lattice energy equations are given below, respectively.

$$U / kJ mol^{-1} = 2I \left[\frac{\alpha}{V_m^{1/3}} + \beta \right] \quad (1)$$

$$U / kJ mol^{-1} = 2I \left[a \frac{\eta_M}{V_m^{1/3}} + b \right] \quad (2)$$

In these equations, U , V_m and η_M represent the lattice energy, molar volume and molecular hardness, respectively. a , b , α and β parameters appearing in the mentioned equations are constants that take different numerical values for various stoichiometries. I is the ionic strength of the lattice which is simply calculated in terms of the number and type of ions with charge z_i entering the unit formula, namely,

$$I = 1/2 \sum n_i z_i^2 .$$

$$U_{POT} = (-0.494r^+ + 122.392)(\eta^+ + \eta^-) - 109.514\eta^+ + 1191.694 \quad (3)$$

where r^+ = cation radius (pm); η^+ = cation absolute hardness (eV) and η^- = anion absolute hardness (eV). For each group of halides, a specific empirical equation with very high accuracy can be derived. For Li^+ halides, for instance,

$$U_{POT} = 89.232 (\eta^+ + \eta^-) - 2726.668 (r = 0.999) \quad U_{POT} = 191.777 (\eta^+ + \eta^-) - 4609.108 (r = 0.999).$$

However, despite some lack of accuracy, the main interest here is to obtain general equations, such as Eq. (1).

For group 2 cations, the absolute hardness values

$$U_{POT} = (-0.781r^{+2} + 251.255)(\eta^{+2} + \eta^-) - 222.245\eta^{+2} + 2427.356 \quad (4)$$

where r^{+2} = cation radius (pm); η^{+2} = cation absolute hardness (eV) and η^- = anion absolute hardness (eV). To prove the validity of Eq.3 and

Most recently, Farias [4] developed an empirical equation to calculate the lattice energies of metal monohalides from average orbital electronegativities. The aim of the present work is to derive new and useful formulas to calculate the lattice energies of groups 1 and 2 halides based on absolute hardness [5] values of cations and anions in the solids.

2. METHODOLOGY

In the Conceptual Density Functional Theory, absolute hardness (η) is calculated with the help of ground state ionization energy (I) and ground state electron affinity values (A) [6] of chemical species as $\eta = (I-A)/2$. Using ionization energy and electron affinity values reported in the literature, absolute hardness values for Li^+ (35.12), Na^+ (21.08), K^+ (13.64), Rb^+ (11.56) and Cs^+ (9.61); F^- (7.01), Cl^- (4.70), Br^- (4.24) and I^- (3.70) were calculated. Using such values, as well as reference values [2,7] for the lattice energies for the respective halides, an empirical equation was derived:

(eV) were calculated as Be^{2+} (67.84), Mg^{2+} (32.56), Ca^{2+} (19.52), Sr^{2+} (15.93) and Ba^{2+} (13.66). For each group of halides, very accurate equations can be obtained. For Mg^{2+} halides, for example,

However, as stated previously, the main purpose here is to obtain general equations. So, for the group 2 halides, the following equation was derived:

Eq.4, we compared our results with reference values. For all cations, the employed ionic radius (pm) was for coordination number 6, as follows

[8,9]: Li⁺ (76), Na⁺ (102), K⁺ (138), Rb⁺ (152), Cs⁺ (167), Be²⁺ (45), Mg²⁺ (72), Ca²⁺ (100), Sr²⁺ (118) and Ba²⁺ (135).

3. RESULTS and DISCUSSION

Chemical hardness is defined as resistance towards electron cloud polarization or deformation of chemical species. Hard and Soft Acid-Base Principle and Maximum Hardness Principle are the electronic structure principles based on chemical hardness concept. The obtained results are summarized in Tables 1 and 2. The derived equation shows that, given a certain cation, the lattice energy is dependent only on the anion absolute hardness. Furthermore, differing from Kapustinskii [10] equation, Eq. (3) and (4) do not require the anion radius. Furthermore, differing from Kaya equation [3] there is not a molar volume (V_m) term. Hence, no information about the lattice parameters of the considered halide is necessary.

As can be verified, Eq. (3) and (4) works very well, specially Eq.(4). In Figure 1, graphical comparison with reference values of the results obtained using Eq.4 is given. For group 2 halides. For the shown curve, $r = 0.995$.

The great advantage of the proposed equations is their simplicity: only cation radius and ionization energies (to calculate the absolute hardness for cations and anions) are required, and such data are easily available for almost all elements of the periodic table. Hence, Eq. (3) and (4) are easily employable.

In conjunction with Kapustinskii equation, Equation (3) was successfully employed to calculate the first and second ionization energies for the super heavy element 119 [11], attesting their reliability and usefulness.

Table 1. Lattice energy values for Li to Cs halides (using Eq. 3).

	$U_{POT}(kJmol^{-1})_{Ref.}$	$U_{POT}(kJmol^{-1})_{Eq.3}$	$\Delta\%$
LiF	1030	920	-10.7
LiCl	834	724	-13.2
LiBr	788	685	-13.1
LiI	730	639	-12.5
NaF	910	906	0.4
NaCl	769	739	-3.9
NaBr	732	706	-3.6
NaI	682	667	-2.2
KF	808	818	+1.2
KCl	701	692	-1.3
KBr	671	667	-0.6
KI	632	638	+0.9
RbF	774	804	+3.9
RbCl	680	695	+2.2
RbBr	632	673	+6.5
RbI	617	648	+5.0
CsF	759	802	+5.7
CsCl	670	710	+6.0
CsBr	647	692	+7.0
CsI	613	670	+9.3

Table 2. Lattice energy values for Be to Ba halides (using Eq. 4).

	$U_{POT}(kJmol^{-1})_{Ref.}$	$U_{POT}(kJmol^{-1})_{Eq.4}$	$\Delta\%$
BeF₂	3526	3526	0.0
BeCl₂	3033	3027	-0.2
BeBr₂	2914	2927	+0.4
BeI₂	2813	2811	-0.1
MgF₂	2978	2908	-2.4
MgCl₂	2540	2458	-3.2
MgBr₂	2451	2368	-3.4
MgI₂	2340	2263	-3.3
CaF₂	2651	2683	+1.2
CaCl₂	2271	2283	-0.5
CaBr₂	2134	2203	+3.2
CaI₂	2087	2110	+1.1
SrF₂	2513	2537	+1.0
SrCl₂	2170	2169	0.0
SrBr₂	2040	2096	+2.7
SrI₂	1976	2010	+1.7
BaF₂	2373	2406	+1.4
BaCl₂	2069	2069	0.0
BaBr₂	1995	2002	+0.4
BaI₂	1890	1923	+1.7

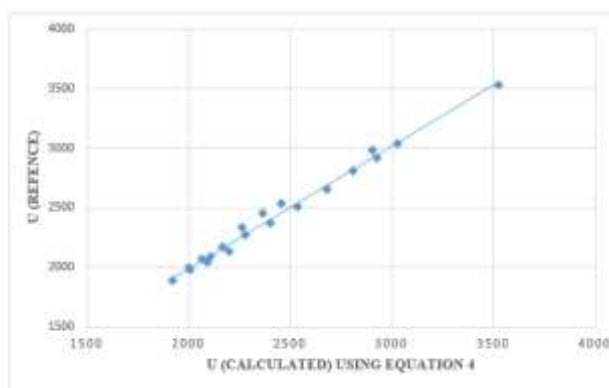


Figure 1. Comparison with reference values of the results obtained using Eq.4.

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