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A Simple Method for the Calculation of Lattice Energies of Inorganic Ionic Crystals Based on the Chemical Hardness

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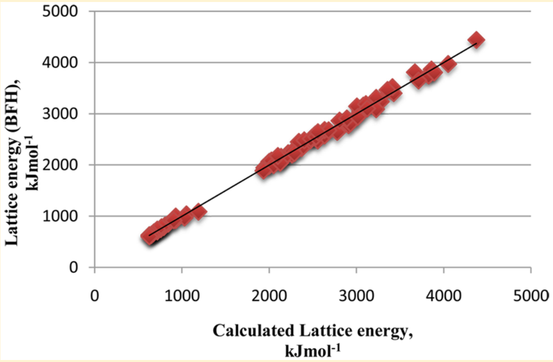
ABSTRACT: This paper presents a new technique for estimation of lattice energies of inorganic ionic compounds using a simple formula. This new method demonstrates the relationship between chemical hardness and lattice energies of ionic compounds. Here chemical hardness values of ionic compounds are calculated via our molecular hardness equation. The results obtained using the present method and comparisons made by considering experimental data and the results from other theoretical methods in the literature showed that the new method allows easy evaluation of lattice energies of inorganic ionic crystals without the need for ab initio calculations and complex calculations.



INTRODUCTION

Density functional theory[1,2] provides great convenience to chemists in the prediction of molecular properties and in the calculation of reactivity parameters such as chemical hardness (η),[3−6]softness (σ),[7] electronegativity (χ),[8,9] and chemical potential (μ).[10] In this theory, chemical hardness is defined as the second derivative of electronic energy (E) with respect to number of electrons (N) at a constant external potential $v(r)$.[11]

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \qquad (1)$$

Parr and Pearson derived equations associated with ionization energy (IE) and electron affinity (EA) values of chemical species using the finite difference method to describe quantitatively the chemical hardness as[12−14]

$$\eta = \mathrm{IE} - \mathrm{EA} \qquad (2)$$

Recently, we calculated the chemical hardness of molecules. In our work, chemical hardness of molecules was computed by means of the following equation.[15]

$$\eta_\mathrm{M} = \frac{2\sum_{i=1}^{N} \frac{b_i}{a_i}}{\sum_{i=1}^{N} \frac{1}{a_i}} \qquad (3)$$

In this equation, η_M and q_M are chemical hardness of molecule and charge of molecule, respectively. N is the total number of atoms in the molecule. a_i and b_i are parameters appearing in eq 3 and are defined as

$$a_i = \frac{\mathrm{IE} + \mathrm{EA}}{2} \qquad (4)$$

$$b_i = \frac{\mathrm{IE} - \mathrm{EA}}{2} \qquad (5)$$

Lattice energies (U) of ionic crystals have a significant function in the analysis of the thermodynamics as well as prediction of stability of ionic crystals.[16] It should be stated that this energy is an indicator of stabilities and reactivities of ionic crystals. For a crystal with A_mB_n as the general formula, the lattice energy can be expressed as change of energy for the following process.

$$A_mB_{n(c)} \rightarrow mA^{n+}{}_{(g)} + nB^{m-}{}_{(g)} \qquad (6)$$

In 1918, Born−Lande[17] proposed an equation to calculate lattice energies of ionic crystals, and then this equation was improved by Born and Mayer.[18] Disadvantage of these equations is that they can be applied only to binary systems. Kapustinskii[19−22] developed a more comprehensive equation to calculate the lattice energies of ionic crystals. Born−Mayer and Kapustinskii equations relating to the lattice energy calculations are given by eqs 7 and 8, respectively:

$$U = \frac{ALe^2}{4\pi\varepsilon_0}\frac{z^+z^-}{r_0}\left(1 - \frac{Q}{r_0}\right) \qquad (7)$$

$$U = \frac{Bz^+z^-n}{(r_+ + r_-)}\left(1 - \frac{0.345}{(r_+ + r_-)}\right) \qquad (8)$$

In the Born−Mayer equations, A represents Madelung constant, L represents Avogadro's constant, e stands for electronic charge, and z^+, z^- are cation, anion charges in electron units. r_0 is sum of cation and anion radii, and Q is softness parameter. In the Kapustinskii equation, Q = 0.345 Å is for the alkali metal NaCI-type structures, and B = 2427.8/2; n is

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the total number of ions in formula of ionic crystal, and $r^+ + r^-$ is the sum of radii of anion and cation.

Almost three decades ago, Mallouk and Barlett[23] demonstrated an entropy/volume relationship and have shown a linear correlation between lattice enthalpy and the inverse cube root of the molecular (formula unit) volume per nanometer for simple MX (1:1) salts. Then, Jenkins[24] and co-workers who developed volume-based thermodynamics method to predict thermodynamic quantities based on the molar volume presented the following equation that can be applied across an extended range of ionic salts for the estimation of lattice potential energies (U).

$$U,\ \text{kJ mol}^{-1} = 2I\left[\frac{\alpha}{V_{\mathrm{m}}^{1/3}} + \beta\right] \tag{9}$$

here, α and β are coefficients that depend on stoichiometry of salt. V_{m} represents the molecular volume, and I is ionic strength of lattice, which can be calculated by means of the equation below. In the following equation, n_i is the number of ions of type i in the formula unit with charge z_i.

$$I = \frac{1}{2}\sum n_i z_i^2 \tag{10}$$

One of the most significant correlations used to calculate the lattice energies of ionic compounds was obtained by Glasser. He has obtained a simple correlation between the condensed charge Madelung energy E_{M}' and the lattice energy and has calculated the lattice energies of ionic materials considering this correlation, which allows ready calculation of lattice energy for materials containing complex ions. According to Glasser[25] the electrostatic (Madelung) energy E_{M}' correlates well with lattice energies, and the aforementioned correlation can be given via U_{POT} (kJ mol^{-1}) = $0.963E_{\mathrm{M}}'$, with correlation coefficient R^2 = 0.976.

■ THEORETICAL MODEL

As stated above, the lattice energies of inorganic ionic solids may be considered as a measure of their reactivity or stability. Chemical hardness[26−29] is defined as a measure of the resistance toward electron cloud polarization or deformation of chemical species. According to the principle of maximum hardness,[30,31] a chemical system tends to arrange itself so as to achieve maximum hardness, and chemical hardness can be considered as a measure of stability. We decided to examine the relation with their molecular hardness values of lattice energies for inorganic ionic crystals because both chemical hardness and lattice energy are considered as measures of stability. For this purpose, first alkali halide crystals were considered. For alkali halides, molecular hardness values (η_{M}) calculated by our equation, molar volume values (V_{m}), and lattice energy (U_{BFH}) values determined by Born−Fajans−Haber (BFH)[32] cycle are given in Table 1.

As stated in the Introduction of the paper, Mallouk and Jenkins have used their molecular volume values to calculate the lattice energies of ionic solids. Especially, the method proposed by Jenkins is very useful. In this stage, some important information can be given regarding the use[33−42] of their molar volume values for simple estimation of lattice energies of ionic materials. The molar volumes of ionic compounds can be easily obtained on the basis of their chemical formulas and densities, with no structural detail required. Additionally, molar volume is an important parameter because it is associated in simple ways with many material properties. For instance, the entropies of many classes of condensed phases, lattice energies of ionic compounds are volume-based thermodynamics. Then again, many physical properties of materials such viscosity, density, and conductivity of materials are proportional to their molar volumes. In short, molar volume can be considered as a functional tool for the understanding of chemical reactivities of chemical compounds.

Table 1. Chemical Hardness, Density, Formula Mass, Molar Volume, and Experimental Lattice Energy Values for Alkali Halides

alkali halide	η_{M} (eV)	density (g/cm^3)	molar mass (g mol^{-1})	molar volume (nm^3)	BFH (kJ/mol)
LiF	6.85	2.635	25.93	0.016 34	1036
LiCl	5.99	2.068	42.39	0.034 03	853
LiBr	5.85	3.464	86.84	0.041 63	807
LiI	5.56	4.076	133.85	0.054 52	757
NaF	6.62	2.558	41.98	0.027 25	923
NaCl	5.81	2.165	58.44	0.044 82	787
NaBr	5.63	3.210	102.89	0.053 22	747
NaI	5.43	3.670	149.89	0.067 82	704
KF	5.76	2.480	58.09	0.038 89	821
KCl	5.08	1.984	74.55	0.062 39	715
KBr	4.95	2.740	119.00	0.072 12	682
KI	4.77	3.123	166.00	0.088 26	649
RbF	5.59	3.557	104.46	0.048 75	785
RbCl	4.94	2.800	120.92	0.071 70	689
RbBr	4.82	3.350	165.37	0.081 97	660
RbI	4.65	3.110	212.37	0.113 38	630
CsF	5.26	4.115	151.90	0.061 29	740
CsCl	4.66	3.990	168.36	0.070 06	659
CsBr	4.54	4.440	212.81	0.079 59	631
CsI	4.39	4.510	259.81	0.095 65	604

To verify the relation between their molecular hardness values with lattice energies of alkali halides, the data in Table 1 were plotted in Figure 1, which shows a remarkable correlation between experimental lattice energies and $\eta_{\mathrm{M}}/V_{\mathrm{m}}^{1/3}$ for alkali halide crystals. In addition to alkali halides, we investigated the relationship between lattice energies with their $\eta_{\mathrm{M}}/V_{\mathrm{m}}^{1/3}$ ratio of experimental lattice energies for simple ionic compounds that are listed in Table 4 of varying charge ratios. The graphs for both alkali halides and compounds in Table 4 are depicted in Figures 1−4.

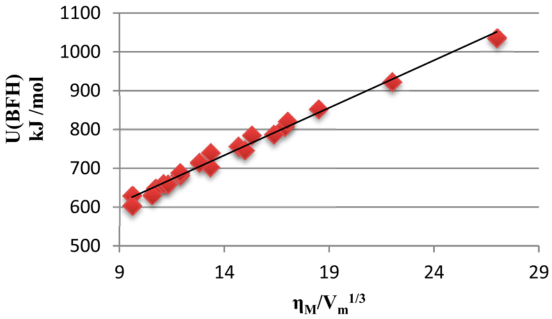

Figure 1. Plot of correlation between the lattice energies (Born−Fajans−Haber) and $\eta_{\mathrm{M}}/V_{\mathrm{m}}^{1/3}$ values for alkali halides with correlation coefficient R^2 = 0.986.

It can be seen from the linear graphs above that there is a remarkable correlation between lattice energies with $\eta_{\mathrm{M}}/V_{\mathrm{m}}^{1/3}$

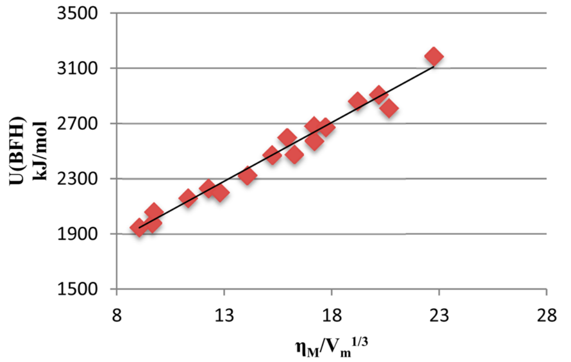

Figure 2. Plot of correlation between the lattice energies (Born–Fajans–Haber) and $\eta_M/V_m^{1/3}$ ratio for M_2X-type ionic compounds in Table 4 with correlation coefficient $R^2 = 0.974$.

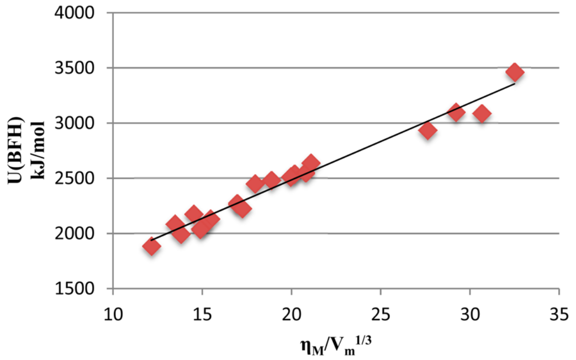

Figure 3. Plot of correlation between the lattice energies (Born–Fajans–Haber) and $\eta_M/V_m^{1/3}$ ratio for MX_2-type ionic compounds in Table 4 with correlation coefficient $R^2 = 0.971$.

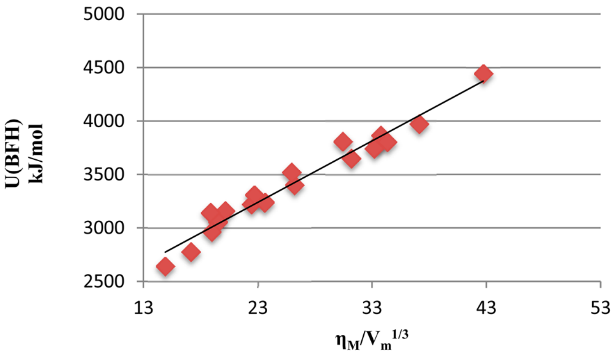

Figure 4. Plot of correlation between the lattice energies (Born–Fajans–Haber) and $\eta_M/V_m^{1/3}$ ratio for MX (charge ratio 2:2)-type ionic compounds in Table 4 with correlation coefficient $R^2 = 0.963$.

for simple ionic compounds. The existence of such considerable correlation has encouraged us to introduce a new relation for the calculation of lattice energy. It is seen from Jenkins equation given by eq 9 that it is more suitable to use the ionic strength (I) of lattice instead of using of Z^+Z^- such as eqs 7 and 8. Therefore, the relation obtained will be generalized beyond binary systems. Considering ionic strength values of crystals and by analyzing the graphs given above, we propose the following equation for calculation of lattice energies of ionic crystals.

$$U,\ \text{kJ mol}^{-1} = 2I\left[a\frac{\eta_M}{V_m^{\ 1/3}} + b\right] \tag{11}$$

In this new equation, U represents the lattice energy of ionic crystal in units of kilojoules per mole. I is ionic strength of lattice. η_M is molecular hardness of ionic crystal, and list of a and b constants for various stoichiometries is given in Table 2. The errors on a and b coefficients were determined by using Excel's regression and were reported in Table 2.

Table 2. Constants for Use in eq 11

ionic crystal (charge ratio)	ionic strength (I)	a kJ nm/mol eV	b (kJ mol^{-1})
MX (1:1)	1	12.245 ± 0.0025	195.15 ± 0.40
M_2X (1:2)	3	14.193 ± 0.035	195.5 ± 0.49
MX_2 (2:1)	3	11.598 ± 0.021	182.16 ± 0.31
MX (2:2)	4	7.186 ± 0.028	239.37 ± 0.56

■ RESULTS AND DISCUSSION

As stated in the Introduction, so far, many theoretical methods have been proposed for estimation of lattice energies of inorganic ionic crystals. To prove the reliability of new lattice energy equation proposed by us, we calculated the lattice energies of alkali halides and then compared them with results of methods frequently encountered in the literature for computing the lattice energy values for alkali halides. The predicted lattice energy values using the Born–Lande, Born–Mayer, Kapustinskii, and Glasser–Jenkins equations, the present equation, and experimental lattice energies of alkali halides are presented in Table 3.

Table 3. Comparison of Lattice Energies (kJ mol^{-1}) Determined with Various Methods for Alkali Halides

alkali halide crystal	BFH	Born–Lande	Born–Mayer	Kapustinskii	Glasser–Jenkins	present work
LiF	1036	1005	1000	952	1029	1046
LiCl	853	810	818	803	827	839
LiBr	807	765	772	792	780	800
LiI	757	713	710	713	721	746
NaF	923	899	894	885	905	924
NaCl	787	753	756	752	764	787
NaBr	747	717	719	713	727	753
NaI	704	671	670	673	678	713
KF	821	795	792	788	796	803
KCl	715	686	687	680	695	701
KBr	682	658	659	675	667	679
KI	649	622	620	613	630	650
RbF	785	758	756	760	723	761
RbCl	689	659	661	662	668	679
RbBr	660	634	635	626	644	659
RbI	630	601	600	589	610	623
CsF	740	724	714	713	723	714
CsCl	659	621	621	625	672	664
CsBr	631	598	598	602	648	646
CsI	604	568	565	563	616	623

Table 4 contains molecular hardness calculated by our equation, density, formula mass, molar volume, calculated lattice energy via eqs 9 and 11, and experimental lattice energy values (BFH). It is important to note that the correlation coefficients obtained from the graphs plotted for ionic crystals in Table 4 provided the important clue about the importance of such an approach. The agreement of experimental and

Table 4. Chemical Hardness, Density, Formula Mass, Molar Volume, Experimental Lattice Energy,[35,43,44] and Calculated Lattice Energy Values for Some Selected Inorganic Ionic Compounds

ionic compound	η_M (eV)	density (g/cm^3)	molar mass (g mol^{-1})	molar volume (nm^3)	U_{cal} (eq 11) (kJ/mol)	U_{cal} (eq 9) (kJ/mol)	U_{BFH} (kJ/mol)
BeO	10.25	3.01	25.01	0.013 80	4371	4120	4443
MgO	8.88	3.58	40.30	0.018 69	3838	3794	3791
CaO	7.85	3.34	54.07	0.026 88	3421	3445	3401
SrO	7.45	4.70	103.62	0.036 61	3204	3179	3223
BaO	6.92	5.72	153.32	0.044 50	3037	3025	3054
MgS	7.57	2.84	56.38	0.032 96	3272	3267	3238
CaS	6.81	2.59	72.43	0.046 44	3004	2993	2966
SrS	6.47	3.70	119.68	0.053 72	2900	2886	2779
BaS	6.03	4.25	169.39	0.066 19	2771	2741	2643
PbO	8.79	9.53	223.20	0.038 89	3406	3131	3520
PbS	7.53	7.60	239.30	0.052 27	3072	2905	3161
PbSe	7.32	8.10	286.16	0.058 66	2998	2823	3144
TiO	8.45	4.95	63.86	0.021 42	3664	3658	3811
MnO	9.25	5.43	70.93	0.021 68	3822	3646	3745
FeO	9.28	5.74	71.84	0.020 77	3855	3688	3865
ZnO	10.72	5.60	81.38	0.024 13	4047	3544	3971
HgO	10.92	11.14	216.59	0.032 28	3886	3284	3806
SnO	8.36	5.75	66.94	0.019 31	3706	3761	3652
CdSe	8.61	5.81	191.37	0.054 63	3219	2874	3310
Li_2O	6.00	2.013	29.88	0.024 58	2930	3232	2814
Na_2O	5.79	2.27	61.98	0.045 33	2555	2602	2478
K_2O	4.99	2.32	94.20	0.067 42	2217	2258	2232
Rb_2O	4.82	4.00	186.94	0.077 60	2135	2146	2161
Li_2S	5.45	1.66	45.95	0.045 96	2468	2590	2472
Na_2S	5.27	1.86	78.04	0.069 81	2262	2229	2203
K_2S	4.56	1.74	110.26	0.105 21	1995	1922	1979
Rb_2S	4.41	2.91	203.00	0.115 71	1943	1856	1949
Tl_2O	6.99	10.45	424.77	0.067 48	2635	2257	2575
Tl_2Se	6.29	9.05	487.72	0.089 49	2370	2038	2326
Cu_2O	7.75	6.00	143.09	0.039 60	3109	2730	3189
Cu_2S	6.93	5.60	159.16	0.047 19	2806	2565	2865
Cu_2Te	6.65	7.27	254.69	0.058 17	2634	2380	2683
Ag_2O	7.62	7.14	231.74	0.053 90	2890	2446	2910
Ag_2S	6.81	7.23	247.8	0.056 87	2681	2400	2677
Ag_2Te	6.50	8.32	341.33	0.068 13	2528	2249	2600
Cs_2O	4.52	4.65	281.81	0.100 63	2000	1953	2063
BeF_2	11.05	1.986	47.01	0.039 30	3354	2721	3464
$MgCl_2$	8.23	2.32	95.21	0.068 13	2495	2326	2540
$CaCl_2$	7.47	2.15	110.98	0.085 70	2271	2182	2271
$CaBr_2$	7.14	3.353	199.89	0.098 98	2167	2097	2134
CaI_2	6.70	3.956	293.89	0.123 36	2029	1974	2087
$BaCl_2$	6.74	3.856	208.23	0.089 67	2140	2154	2069
$BaBr_2$	6.47	4.78	297.14	0.103 22	2052	2072	1995
BaI_2	6.09	5.15	391.14	0.126 12	1938	1962	1890
$MgBr_2$	7.80	3.72	184.113	0.082 18	2341	2207	2451
$SrBr_2$	6.85	4.21	247.43	0.097 44	2128	2106	2040
CrF_2	9.4	3.79	89.99	0.039 42	3014	2718	2939
$MnBr_2$	8.17	4.385	214.75	0.081 32	2405	2214	2482
NiF_2	9.93	4.72	96.69	0.034 02	3225	2837	3089
CuF_2	9.97	4.23	101.54	0.039 85	3124	2710	3102
$TiCl_2$	7.93	3.13	118.77	0.063 02	2479	2378	2514
$MnCl_2$	8.57	2.98	125.84	0.070 19	2538	2307	2551
$FeCl_2$	8.54	3.16	126.75	0.066 60	2559	2341	2641
$PbBr_2$	7.76	6.66	367.01	0.091 49	2291	2143	2230
PbI_2	7.24	6.16	461.01	0.124 28	2102	1970	2177
CuF	8.75	7.10	82.54	0.019 29	1189	978	1088
CuCl	7.49	4.15	98.99	0.039 60	928	792	996
AgF	8.59	5.85	126.87	0.036 00	1027	814	974
AgCl	7.35	5.56	143.32	0.042 79	905	774	918

calculated lattice energies in both Tables 3 and 4 demonstrates that the present approach, which is based on molecular hardness values for the evaluation of the lattice energy of ionic crystals, is quite useful. To see more clearly the agreement between experimental lattice energies determined by BFH cycle with calculated lattice energies via our new method for all of the molecules in Tables 3 and 4, the agreement between experimental data and our results are plotted and presented in the graph below (Figure 5).

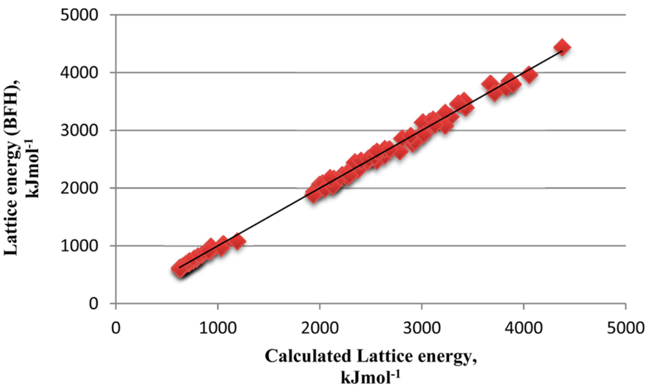

Figure 5. Comparison with the experimental lattice energies of calculated lattice energies for all of the molecules in Tables 3 and 4.

Although one of the most familiar lattice energy equations is Kapustinskii equation, there are some principal problems related to the use of the equation. First, r_o (sum of cation and anion radii) is determined without regard to structural details of the crystals. The second problem related to the use of the equation is that the lattice energies of crystals containing complex ions cannot be calculated via the equation. In 1995, Kapustinskii equation was generalized by L. Glasser[45] to provide the prediction of lattice energies of crystals containing multiple ions using thermochemical radii of complex ions. The generalized equation is presented as

$$U,\ \text{kJ mol}^{-1} = -\frac{1213.9}{\langle r\rangle}\left(1-\frac{Q}{\langle r\rangle}\right)\sum n_i z_i^{2} \tag{12}$$

where r is weighted mean ion radii sum. The meaning of other parameters in the equation has earlier been stated.

Lattice energies of crystals containing complex ion can be calculated using thermochemical radii of complex ions. Thermochemical radii[46,47] of complex anion and cation are estimated using Kapustinskii equation or generalized Kapustinskii equation introduced by L. Glasser and considering experimental lattice energies of salts including the complex anion or cation. However, it should be stated that the results obtained using molar volume value instead of thermochemical radii are more reliable. In addition to simple ionic crystals, we calculated the lattice energies of some ionic compounds containing complex ions, using eqs 11 and 9, and presented the results obtained regarding these ionic compounds in Table 5. The results showed that eq 9 is more useful for the prediction of lattice energies of compounds containing complex ion compared to eq 11.

Use of the New Methodology. In the calculation of lattice energies using the new method, we would like to draw attention to some important points. First, eq 11 is similar to eq 9. When this similarity is considered, it is obvious that $a\eta_M$ and b parameters located in the eq 11 correspond to α and β

Table 5. Chemical Hardness, Density, Formula Mass, Molar Volume, Experimental Lattice Energy, and Calculated Lattice Energy Values for Some Selected Inorganic Ionic Compound Containing Complex Ion

ionic compound	η_M (eV)	density (g/cm^3)	molar mass (g mol^{-1})	molar volume (nm^3)	U_{cal} (eq 11) (kJ/mol)	U_{cal} (eq 9) (kJ/mol)	U_{BFH} (kJ/mol)
$Ba(NO_3)_2$	10.76	3.24	261.33	0.133 92	2556	1931	2035
$Zn(OH)_2$	11.74	3.05	99.42	0.054 07	3253	2483	3151
Li_2SO_4	8.07	2.22	109.94	0.082 19	2753	2102	2142
Na_2SO_4	7.89	2.66	142.04	0.088 54	2680	2046	1938
Li_2CO_3	7.85	2.11	73.89	0.058 15	2898	2381	2523
Na_2CO_3	7.66	2.54	105.98	0.069 28	2761	2236	2301
$CaCO_3$	9.53	2.71	100.08	0.061 29	3304	2793	2814
$CaSO_4$	9.59	2.96	136.14	0.076 37	3214	2647	2480
$SrSO_4$	9.36	3.96	183.68	0.077 02	3179	2642	2484
$BaSO_4$	9.08	4.50	233.43	0.086 13	3096	2572	2374
$Sr(ClO_3)_2$	10.03	3.15	254.52	0.134 17	2456	1930	2155
$MnSO_4$	10.27	3.25	151.00	0.077 15	3301	2641	2825
$SrCO_3$	9.27	3.74	147.63	0.065 54	3236	2747	2688
$NaBrO_3$	8.58	3.34	150.89	0.075 04	888	660	791
$NaClO_3$	8.71	2.49	106.44	0.070 97	905	670	770
$KClO_3$	8.10	2.32	122.55	0.087 71	836	631	721
KIO_3	7.84	3.89	214.01	0.091 35	816	624	780
$CsMnO_4$	8.06	3.55	251.84	0.117 80	792	582	572
$KMnO_4$	8.37	2.70	158.03	0.097 08	836	614	607
K_2SO_4	7.21	2.66	174.25	0.108 78	2459	1898	1796
Rb_2SO_4	7.32	3.61	266.99	0.122 70	2427	1817	1748
Cs_2SO_4	6.78	4.24	361.87	0.141 61	2280	1723	1658
Na_2CO_3	7.66	2.54	105.98	0.069 28	2761	2236	2301
K_2PtCl_4	6.01	3.38	415.09	0.203 92	2042	1506	1574
K_2PtCl_6	6.47	3.34	485.99	0.241 33	2057	1414	1471
$LiClO_4$	9.31	2.42	106.39	0.072 99	935	665	709

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parameters located in the eq 9, respectively. It is important to note that inclusion of the hardness parameter (η) has the effect of extending the abscissa scale and somewhat improves the correlation coefficient making the new equation slightly better. Some examples about the use of hardness calculating methodology are given below. For this purpose, we considered the $NaClO_3$ and $BaSi_2O_5$ ionic compounds. For Ba, Si, O, Cl, and Na atoms, experimental IE and EA values and a_i and b_i parameters calculated via eq 4 and eq 5, respectively, for use in eq 3 are given in Table 6.

Table 6. Ionization Energy, Electron Affinity, and a_i and b_i Values for Some Selected Atoms (eV)

atom	IE	EA	a_i	b_i
Ba	5.21	0.15	2.68	2.53
Si	8.15	1.39	4.77	3.38
O	13.62	1.46	7.54	6.08
Cl	12.97	3.41	8.19	4.78
Na	5.14	0.55	2.845	2.295

We presented the use of hardness calculating methodology for $NaClO_3$ and $BaSi_2O_5$ ionic compounds considering a_i and b_i values given in Table 6 for constitutent atoms.

$$\eta_{NaClO_3} = \frac{2\left[\frac{2.295}{2.845} + \frac{4.78}{8.19} + 3 \times \frac{6.08}{7.54}\right]}{\frac{1}{2.845} + \frac{1}{8.19} + \frac{3}{7.54}} = 8.71\text{eV}$$

$$\eta_{BaSi_2O_5} = \frac{2\left[\frac{2.53}{2.68} + 2 \times \frac{3.38}{4.77} + 5 \times \frac{6.08}{7.54}\right]}{\frac{1}{2.68} + \frac{2}{4.77} + \frac{5}{7.54}} = 8.78\text{eV}$$

The new equation given by eq 11 has similar advantages to Jenkins−Glasser equation given by eq 9 in terms of applicability. However, eq 9 has been modified by Glasser and Jenkins[35] to the following form for the prediction of lattice energies of ionic compounds in cases where lattice energies are in excess of 5000 kJ mol^{-1}.

$$U,\ \text{kJ mol}^{-1} = AI(2I/V_m)^{1/3} = AI/V_{norm}^{\ 1/3}$$

$$\text{where} \quad V_{norm} = V_m/2I \qquad (13)$$

In this equation A (kJ mol^{-1} nm) = 121.19 is general electrostatic conversion factor. Note that this equation is quite successful in the evaluation of lattice energies of ionic compounds in cases where lattice energies are in excess of 5000 kJ mol^{-1}. In this study, we have not modified to such form our own equation. For this reason, we propose that eq 11 will be useful for the prediction of lattice energies of ionic compounds with less than 5000 kJ mol^{-1}. Nevertheless, we believe that we will present a more comprehensive equation in the form of eq 13 in our future studies.

CONCLUSION

In the present paper, a new lattice energy equation based on molecular hardness of inorganic ionic crystals is introduced. It is clear from the results obtained that the new lattice equation will be useful in calculating lattice energies of ionic crystals. Especially for simple inorganic ionic crystals, a remarkable agreement between experimental data and the results obtained using the new methodology was obtained. Although there are conspicuous differences in terms of lattice energies between experimental data and results obtained for ionic compounds containing complex ions, this new method will be important in solid-state chemistry.

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Notes

The authors declare no competing financial interest.

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