

Research article



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Halides lattice energies and cationic hydration enthalpies for superheavy elements 119 and 120

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ABSTRACT

In the present work, the cationic radius for 119^+ and 120^{2+} were estimated as 202.2 and 197.4 pm, respectively. By using such radius and Kapustinskii equation, the following lattice energies (kJmol^{-1}) were calculated: 119F (651), 119Cl (575), 119Br(555) and 119I(526); 120F_2 (1,968), 120Cl_2 (1,744), 120Br_2 (1,684) and 120I_2 (1,596). Using this values, as well as empirical equations, the following hydration enthalpies (kJmol^{-1}) were calculated: 119^+ (238.4) and 120^{2+} (1,039).

KEY WORDS: Element 119, element120, hydration enthalpies, lattice energies, empirical equations.

INTRODUCTION

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. [1]. Most recently empirical equation has been developed to calculate the lattice energies for metal monohalides from average orbital electronegativities [2]. On the other hand, hydration enthalpies is one of the fundamental quantities for the thermodynamics of aqueous systems

Furthermore, since their chemical and physical properties are difficult of even impossible to be accessed/measured directly, the so-called superheavy elements have been the subject of a lot of theoretical investigations in order to calculate or estimate their chemical and physical properties.

The present work is inserted in such context and is dedicated to obtain the hydration

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enthalpy values for the cations 119^+ and 120^{2+} as well as the lattice energies for the respective halides.

METHODOLOGY

Hydration enthalpies and lattice energies for groups 1 and 2 cations were employed as auxiliary data in order to derive empirical equations which, in conjunction with Kapustinskii equation, allows the of the hydration enthalpies for the cations 119^+ and 120^{2+} .

RESULTS AND DISCUSSION

Element 119

The up to date hydration enthalpies for group 1 monocations and group 17 monoanions [3] , as well as the lattice energies (U_{POT}) to the respective halides [4,5] are summarized in Table 1. As can be verified, the sum of cations and anion hydrations enthalpies are in very good agreement with the lattice energy for the respective metal halides. Taking into account the uncertainties that there are in both, U_{POT} and ΔH_{hyd} values, such agreement is really quite good. Hence, the following equation can be derived:

$$U_{POT} = (\Delta H_{hyd}^+ + \Delta H_{hyd}^-) \quad (1)$$

Where ΔH_{hyd}^+ and ΔH_{hyd}^- are the hydration enthalpies of the respective cation and anion.

When lattice energy is plotted as a function of the sum of the respective cation and anion hydration enthalpies, the curve shown in Figure 1 ($r = 0.9687$) is obtained, from which the following empirical equation is derived:

$$U_{POT} = 0.820 (\Delta H_{hyd}^+ + \Delta H_{hyd}^-) + 118.236 \quad (2)$$

Such phenomena ($U_{POT} = \Delta H_{hyd}^+ + \Delta H_{hyd}^-$) can be explained if we take into account that in the solid state (where cations are surrounded by anions and anions by cations, e.g. in a 6:6 environment, as in NaCl), or in solution (where both, cations and anions are

surrounded by the solvent molecules), both, cations and anions are “looking for” stability. In these systems, stability means to interact with positive or negative species in order to equalize their electronic chemical potentials [6], and such stability is achieved by exothermic interactions, with the total amount of energy required by the cation (or by the anion) been the same, no matter if the interactions occurs with another anions (or cations) in the solid state or, as in a aqueous solutions, with the negative (or positive) poles of the solvent molecules.

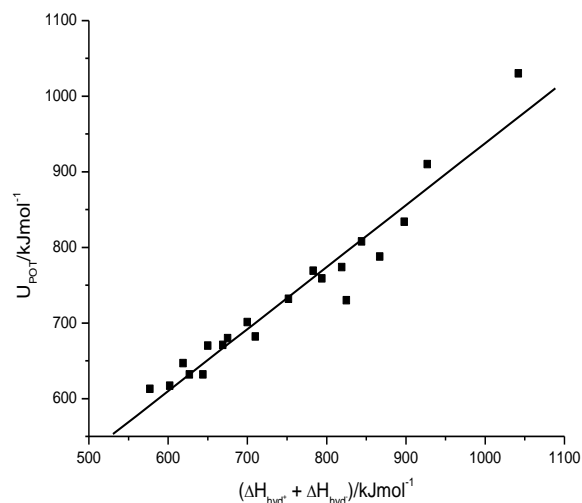


Figure 1: Lattice energies for group 1 halides, as function of the sum of the hydration enthalpies to the respective cations and anions.

By extrapolation (plotting the group 1 M^+ radius as a Z function), the 119^+ radius was estimated as 202.20 pm. This value is in good agreement with a 215.9 pm value calculated to the neutral atom [7]. Applying the estimated 199^+ radius as well as the anions radius (pm; coordination number 6): $F^- = 133$, $Cl^- = 181$, $Br^- = 196$ and $I^- = 220$ in Kapustinskii equation [8], the lattice energies ($kJmol^{-1}$) for 119^+ halides were calculated.

Table 1: Hydration enthalpies (kJmol^{-1}) for group 1 monocations and group 17 monoanions, and lattice energies (kJmol^{-1}) for group 1 halides.

	$-\Delta H_{\text{hyd}}^{\circ}$	$(\Delta H_{\text{hyd}}^{+} + \Delta H_{\text{hyd}}^{-})$	$U_{\text{POT(Ref.)}}$	$\Delta\%$
Li^{+}	578.1			
Na^{+}	463.3			
K^{+}	380.3			
Rb^{+}	355.2			
Cs^{+}	330.6			
F^{-}	463.7			
Cl^{-}	319.5			
Br^{-}	288.7			
I^{-}	246.8			
LiF		1042	1030	+1.2
LiCl		898	834	+7.7
LiBr		867	788	+10.0
LiI		825	730	+13.0
NaF		927	910	+1.9
NaCl		783	769	+1.8
NaBr		752	732	+2.7
NaI		710	682	+4.1
KF		844	808	+4.6
KCl		700	701	-0.1
KBr		669	671	-0.3
KI		627	632	-0.8
RbF		819	774	+5.8
RbCl		675	680	-0.7
RbBr		644	632	+1.9
RbI		602	617	-2.4
CsF		794	759	+4.6
CsCl		650	670	-3.0
CsBr		619	647	-4.3
CsI		577	613	-5.9

Using the calculated lattice energy values, the $\Delta H_{\text{hyd}}^{+}$ was calculated by using Eq. (1) and (2). The hydration enthalpy was also calculated by using the equation [9]:

$$\Delta H_{\text{hyd}} = -166Z^2/r_{\text{eff}} \quad (3)$$

In such equation, Z is the charge in the ion (+1, in this case) and r_{eff} is the ionic radius plus 0.85 Å (Angstroms). In such equations, the hydration enthalpy is provided in kJmol^{-1} .

Element 120

The same procedures were repeated to group 2 halides, and the respective data are summarized in Table 2. The experimental hydration enthalpies for group 2 dications are those provided by Smith [10].

The agreement between reference and lattice enthalpies calculated by using the equation:

$$U_{\text{POT}} = (\Delta H_{\text{hyd}}^{+} + 2\Delta H_{\text{hyd}}^{-}) \quad (4)$$

are very good, as verified in Table 2 data.

Table 2. Hydration enthalpies (kJmol^{-1}) for group 2 dications and group 17 monoanions, and lattice energies (kJmol^{-1}) for group 2 halides.

	$-\Delta H_{\text{hyd}}^{\circ}$	$(\Delta H_{\text{hyd}}^{+} + 2\Delta H_{\text{hyd}}^{-})$	$U_{\text{POT(Ref.)}}$	$\Delta\%$
Be^{2+}	2494			
Mg^{2+}	1921			
Ca^{2+}	1577			
Sr^{2+}	1443			
Ba^{2+}	1305			
F^{-}	463.7			
Cl^{-}	319.5			
Br^{-}	288.7			
I^{-}	246.8			
BeF_2		3421	3526	-3.0
BeCl_2		3133	3033	+3.3
BeBr_2		3069	2914	+5.3
BeI_2		2988	2813	+6.2
MgF_2		2848	2978	-4.4
MgCl_2		2560	2540	+0.8
MgBr_2		2498	2451	+1.9
MgI_2		2415	2340	+3.2
CaF_2		2504	2651	-5.5
CaCl_2		2216	2271	-2.4
CaBr_2		2154	2134	+0.9
CaI_2		2071	2087	-0.8
SrF_2		2370	2513	-5.7
SrCl_2		2082	2170	-4.1
SrBr_2		2020	2040	-1.0
SrI_2		1937	1976	-2.0
BaF_2		2232	2373	-6.2
BaCl_2		1944	2069	-6.0
BaBr_2		1882	1995	-5.7
BaI_2		1799	1890	-4.8

When lattice energy is plotted as a function of the sum of the respective cation and (plus 2) anion hydration enthalpies, the curve shown in Figure 2 ($r = 0.9775$) is obtained, from which the following empirical equation is derived:

$$U_{\text{POT}} = 0.909 (\Delta H_{\text{hyd}}^{2+} + 2\Delta H_{\text{hyd}}^{-}) + 248.573 \quad (5)$$

By extrapolation of the Ca^{2+} , Sr^{2+} and Ba^{2+} radius, a 120^{+} radius of 197.4 pm is calculated, in very good agreement with 195.8 pm, the value obtained by subtracting, from the 120H^{+} bond length (calculated by scalar relativistic Hartree-Fick approach) of 232.8

pm [7], 37 pm (half the H-H bond length in H_2).

Applying the estimated 120^{+} radius (197.4 pm) as well as the anions radius (pm): $\text{F}^{-} = 133$, $\text{Cl}^{-} = 181$, $\text{Br}^{-} = 196$ and $\text{I}^{-} = 220$ in Kapustinskii equation [8], the lattice energies (kJmol^{-1}) for 120^{+} halides were calculated, and from these values, the hydration enthalpy was calculated, by using Eq. (4) and (5). The hydration enthalpy for 120^{2+} was also calculated by using Eq. (3). The obtained results are summarized in Table 3.

Table 3. Hydration enthalpies (kJmol⁻¹) for 119⁺ and 120²⁺, and lattice energies (kJmol⁻¹) to their respective halides.

Cation/halide	$-\Delta H_{\text{hyd}}^+$	U_{POT}
119 ⁺	238.4 ^a 241.8 ^b	–
119F		651
119Cl		575
119Br		555
119I		526
	$\Delta H_{\text{hyd}}^{2+}$	U_{POT}
120 ²⁺	1,039 ^c 983 ^b 908 ^d	–
120F ₂		1,968
120Cl ₂		1,744
120Br ₂		1,684
120I ₂		1,596

^aThe arithmetic mean of eight values, using the calculated Kapustinskii lattice energies and Eq. (1) and (2). ^bUsing Eq. (3). ^cThe arithmetic mean of eight values, using the calculated Kapustinskii lattice energies and Eq. (4) and (5); ^dBy using Eq. (6) and the IE calculated by Borshevsky (Ref. 11).

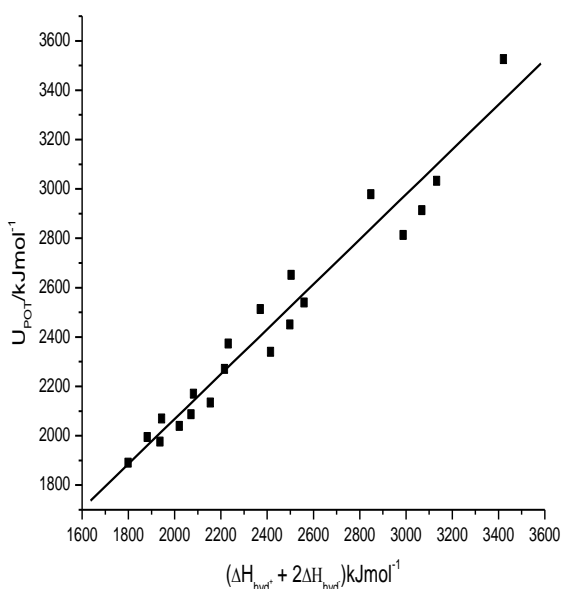


Figure 2: Lattice energies for group 2 halides, as function of the sum of the hydration enthalpies to the respective cations and (twice) the hydration enthalpies to the anions.

The presented ΔH_{hyd} values for 119⁺ and 120²⁺ are the arithmetic mean of eight values (using the U_{POT} calculated to the four halides): four calculated by Eq. (1, or 4) and four calculated by Eq.(2 or 5). As can be verified, both values are in excellent agreement with the hydration enthalpy values calculated by using Eq. (3). House [9] have found, for a series of +1, +2 and +3 cations that:

$$\Delta H_{\text{hyd}} = 0.81057 \text{ IE} + 8.8288 \quad (6)$$

in such equation, which provides de hydration enthalpy in kCalmol⁻¹, IE is the ionization energy for the considered cation.

By relativistic quantum chemical calculations, Borshevsky [11], have found a value of 11.137 eV for the second IE of element 120. Applying such value in Eq. (6), a hydration enthalpy of 908 kJ mol⁻¹ is calculated, in very good agreement with the values calculated by the other approach.

CONCLUSION

As it was demonstrated, the proposed empirical equations allows the calculation of the hydration enthalpies for the cations 119^+ and 120^+ , providing values in very good agreement with each other, as well as literature data.

REFERENCES

- 1) W.E. Dasent, Inorganic energetics, 2nd Ed., Cambridge University Press, Cambridge, 1982.
- 2) R.F. de Farias, Chem. Res. J., 2(4) (2017) 188.
- 3) C.E. Housecroft, H.D.B. Jenkins, RSC Adv., 7 (2017) 27881.
- 4) L. Glasser, H.D.B. Jenkins, J. Am. Chem. Soc., 122 (2000) 632.
- 5) L. Mu, C. Feng, H. He, Commun. Math. Comput. Chem., 56 (2000) 97.
- 6) R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, J. Chem. Phys, 68 (1878) 3801.
- 7) C. Thierfelder, T. Schwerdtfeger, A. Koers, A. Borchevsky, B. Fricke, Phys. Rev. A 80 (2009) 022501.
- 8) A.F. Kapustinskii, Q. Rev. Chem. Soc., 10 (1956) 283.
- 9) J.E. House Jr., L.A. Reif Jr., Thermochem. Acta, 66 (1983) 365.
- 10) D.W. Smith, J. Chem. Edu., 54 (9) (1977) 540.
- 11) A. Borschevsky, V. Pershina, E. Eliav, U. Kaldor, Phys. Rev. A, 87 (2013) 022502.

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