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## Lattice energies for metal halides from average orbital electronegativities

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**Abstract** In the present work, an empirical equation is derived, in order to allow the calculation of lattice energies for inorganic monohalides based on the cation radius and the halide average orbital electronegativity:  $U_{\text{POT}} = (-2.739 r^+ + 650.676) \bar{X} + (3.796 r^+ - 370.851)$ , where  $r^+$  = cation radius (pm) and  $\bar{X}$  is the average electronegativity for the considered monohalide. The obtained equation was applied to Li, Na, K, Rb, Cs, Fr, Cu, Tl and Au monohalides, with good results. For gold, a relativistic correction factor is applied.

**Keywords** Lattice energy, average orbital electronegativity, halides, gold, empirical equation

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### Introduction

Thermochemical data are of prominent importance to a most profound understanding of the nature and behaviour of inorganic compounds, as shown for  $\text{PtF}_6$  [1].

Among the thermochemical parameters, one of the most important is lattice energy, which can provide information about the nature (ionic, covalent) of the interactions between neighbours species in a solid lattice, providing insights about fundamental properties such as solubility, etc.

Lattice energies have been calculated by using a lot of approach, such as in volume based thermodynamics [2, 3].

In the present work, an empirical equation is derived, in order to allow the calculation of lattice energies for inorganic monohalides based on the cation radius and the halide average orbital electronegativity.

### Methodology

The average orbital electronegativity of molecules, as introduced by Viting [4] can be calculated by

$$\bar{X} = \frac{\sum n_i \chi_i}{\sum n_i} \quad (1)$$

Where  $\chi_i$  is the electronegativity of the  $i$ th atom and  $n_i$  is the number of this sort in the formula unit.

In the present work, the concept of average orbital electronegativity was extended to metal monohalides. To calculate the values of  $\bar{X}$ , the revised Pauling electronegativities [5] have been employed.

For sodium halides, lattice energy as a function of average orbital electronegativity (Figure 1) provides the equation:  $U_{\text{POT}} = 346.287 \bar{X} + 2.582$  ( $r = 0.9999$ ). For other mono halides analogous equations can be obtained.

However, the interest here is to obtain a general equation.

Using the  $\bar{X}$  values, the following empirical equation was derived:

$$U_{\text{POT}} = (-2.739 r^+ + 650.676) \bar{X} + (3.796 r^+ - 370.851) \quad (2)$$

where  $r^+$  = cation radius (pm) and  $\bar{X}$  is the average orbital electronegativity for the considered monohalide. So, using only the cation radius [5] (pm):  $\text{Li}^+$  (76),  $\text{Na}^+$  (102),  $\text{K}^+$ (138),  $\text{Rb}^+$ (152),  $\text{Cs}^+$ (167);  $\text{Cu}^+$ (77),  $\text{Ag}^+$  (115),  $\text{Tl}^+$ (150) and  $\text{Au}^+$ (137), as well as the  $\bar{X}$  values, lattice energies for Li, Na, K, Rb, Cs, Fr, Cu, Tl and Au mono halides were calculated and compared with reference values from literature [3,6].



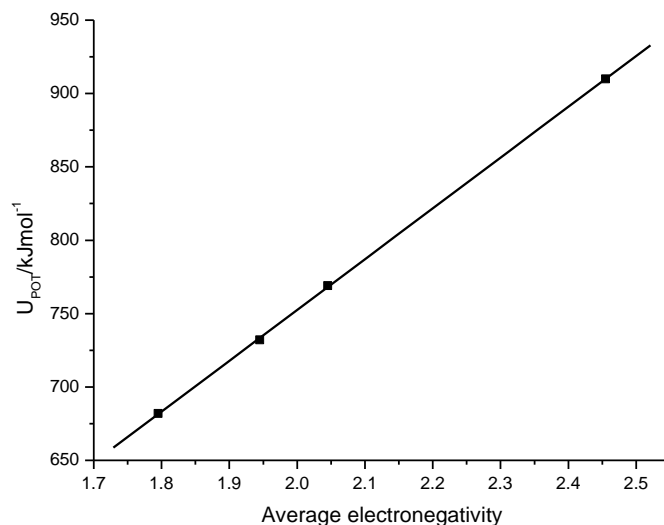


Figure 1: Lattice energies as function of average electronegativities for sodium halides

### Results and Discussion

The obtained results are summarized in Table 1. As can be verified, the equation works very well for group 1 halides, as well as for Cu(I) and Ag(I) halides. Considering Cu and Ag monohalides, the worst results are obtained to the respective fluorides. Such fact could be explained taking into account that  $F^-$  is the hardest base (compared with  $Cl^-$ ,  $Br^-$  and  $I^-$ ), and so, the proposed equation is calculating a most effective acid-base interaction than the real one ( $Cu^+$  and  $Ag^+$  are soft acids).

Table 1: Lattice energies ( $kJmol^{-1}$ ) for metals monohalides

Salt	$\bar{X}$	$U_{(ref)}/kJmol^{-1}$	$U_{(pred)}/kJmol^{-1}$	$\Delta\%$
LiF	2.48	1030	1015	-1.5
LiCl	2.07	834	834	0.0
LiBr	1.97	788	789	+0.1
LiI	1.82	730	723	-1.0
NaF	2.46	910	930	+2.2
NaCl	2.05	769	778	+1.2
NaBr	1.95	732	740	+1.1
NaI	1.80	682	685	+0.4
KF	2.40	808	807	-0.1
KCl	1.99	701	696	-0.7
KBr	1.89	671	668	-0.4
KI	1.74	632	627	-0.8
RbF	2.40	774	769	-0.6
RbCl	1.99	680	672	-1.2
RbBr	1.89	632	649	+2.7
RbI	1.74	617	614	-0.5
CsF	2.39	744	725	-2.6
CsCl	1.98	670	646	-3.6
CsBr	1.88	647	626	-3.2
CsI	1.73	613	597	-2.6
CuF	2.94	1088	1214	+11.6
CuCl	2.53	996	1034	+3.8



CuBr	2.43	978	988	+1.0
CuI	2.28	966	924	-4.3
AgF	2.96	974	1059	+8.7
AgCl	2.55	918	922	+0.4
AgBr	2.45	905	888	-1.9
AgI	2.30	892	834	-6.5
AuCl	2.85	1066	934 (1143)	-12.4 (+7.2)
AuBr	2.75	1059	907 (1110)	-14.4 (+4.8)
AuI	2.60	1070	865 (1059)	-19.2 (-1.0)
TlF	3.01	850	920	+8.2
TlCl	2.60	751	822	+9.5
TlBr	2.50	734	798	+8.7
TlI	2.35	710	762	+7.3

For Au(I) halides the obtained results are really not good. However, it is necessary to remember that for gold, ( $Z = 79$ ), relativistic contributions matter [7], and that gold is the element with the (proportionally) higher relativistic contraction/effects.

The relativistic and non-relativistic equations can be related by using  $\gamma = 1/[1-(v^2/c^2)]$ , where  $v$  is the velocity of the considered body (in our case, an electron). The velocity of the 1s electron is  $\approx Z/137$ , where  $Z$  is the atomic number. Hence,  $\gamma = 1/[1-((Z/137)^2/c^2)]^{1/2}$ . For gold ( $Z = 79$ ),  $\gamma = 1.224$ .

Multiplying the lattice energy values calculated using Eq. (2), by  $\gamma$ , “corrected” lattice energy values are calculated for gold, and are shown between parenthesis in Table 1.

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