

## RELATION BETWEEN HEATS OF FORMATION OF ALKALI AND PSEUDO-ALKALI HALIDES AND ELECTRONEGATIVITIES OF HALOGEN IONS

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(Received 1 May 1986)

### ABSTRACT

The heats of formation of alkali halides (CsX, RbX, KX, NaX, LiX) and pseudo-alkali halides (NH<sub>4</sub>X, TlX, CuX, AgX, AuX),  $-\Delta H_{298}^0$ , are empirically expressed by the electronegativities ( $\chi_A$ ) of the halogen ion:

$$\frac{-\Delta H_{298}^0 \left[ (-e^2/r_A) / -100 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \right]}{(e^2/r_C)} = a\chi_A + b$$

where  $a$  and  $b$  are empirical constants;  $e$ ,  $r_C$  and  $r_A$  represent the charge on the electron, cation radius, and anion radius, respectively. The value of  $\pm e^2/r_{(C \text{ and/or } A)}$  corresponds to the electrostatic energy between the effective nuclear charge of the  $M^+$  and/or  $X^-$  ion and an electron at a distance from its nucleus equal to its ionic radius  $r_C$  and/or  $r_A$ .

The empirical constants  $a$  and  $b$  correlate with the electronegativity of the  $M^+$  ion in two different trends; one is the alkali ion series and the other is the pseudo-alkali ion series. This means that Pauling's electronegativities of alkali and pseudo-alkali ions are based on different scales. Assuming that the ( $\chi$ -IP) correlations for pseudo-alkali ions constitute the same series as the ( $\chi$ -IP) correlations for alkali ions, where  $\chi$  is the electronegativity and IP is the first ionization potential, the electronegativities of  $Tl^+$ ,  $Ag^+$ ,  $Cu^+$  and  $Au^+$  are changed to 1.1, 1.3, 1.4 and 1.7, respectively, with noticeable error. The value (1.1) for the  $Tl^+$  ion is consistent with the ionic character of the bonds formed by  $Tl^+$  in some compounds.

### INTRODUCTION

Pauling [1,2] pointed out that the bond energy,  $E(X-Y)$ , between two unlike atoms is generally greater than the arithmetic means of the energies  $E(X-X)$  and  $E(Y-Y)$ ; the difference  $\Delta$ , defined as  $\Delta = E(X-Y) - \frac{1}{2}\{E(X-X) + E(Y-Y)\}$ , is always positive, and  $\sqrt{\Delta}$  is proportional to the absolute magnitude of the difference in electronegativities of unlike atoms:

$$|\chi_X - \chi_Y| = 0.208\sqrt{\Delta} \quad (1)$$

where  $\chi_X$  and  $\chi_Y$  are the electronegativities of X and Y atoms, respectively. Furthermore, he pointed out that for many metals, even if  $E(M-M)$  is

unknown, the values of  $\Delta$  can be evaluated from the heat of formation ( $-\Delta H_{298}^0$ ) of the  $\text{MX}_n$  compound:

$$\Delta = \frac{-\Delta H_{298}^0}{n} \quad (2)$$

However, eqn. (1) does not satisfy the relation between  $\Delta$  and  $|\chi_X - \chi_Y|$  in all cases. Pritchard and Skinner [3] pointed out considerable discrepancies in the values of  $|\chi_X - \chi_Y|$  between results obtained from eqn. (1) and Pauling's scales for alkali fluorides and chlorides. Haissinsky [4] and Allred [5] have examined Pauling's method for almost all the elements out of consideration of the heat of formation of fluoride. In general, the heats of formation of fluorides obtained from eqns. (1) and (2) using Pauling's scale are surprisingly greater than the experimental heats of formation. Furthermore, the heat of formation of an alkali fluoride increases as the alkali metal becomes more electronegative, that is, as the  $|\chi_X - \chi_Y|$  value decreases.

Pauling's electronegativity was introduced as an attribute of the atom in a covalent compound. Therefore, eqn. (1) does not satisfy the relation between  $\sqrt{\Delta}$  and  $|\chi_X - \chi_Y|$  in an ionic compound. Ohashi [6,7] has found that the ratio of the heat of formation to  $P_E$  is an effective scaling to correlate the heat of formation of the ionic compound with Pauling's electronegativity, where  $P_E$  is the electrostatic energy between the effective nuclear charge of the ion and an electron at a distance from its nucleus equal to its ionic radius. The purpose of this study is to examine the relation between electronegativities and heats of formation in alkali halides and pseudo-alkali halides.

#### RELATION BETWEEN HEATS OF FORMATION OF ALKALI HALIDES AND ELECTRONEGATIVITIES OF HALOGEN IONS

The electronegativities of  $\text{M}^+$  ions and halogen ions obtained from Pauling's method are listed in Table 1, along with the ionic radii in octahedral site and potential energy ( $P_E = e^2/r$ ). The  $P_E$  (C and/or A) corresponds to electrostatic energy between the effective nuclear charge of the  $\text{M}^+$  and/or  $\text{X}^-$  ion and an electron at a distance from its nucleus equal to its ionic radius  $r$ . If  $r$  is given in angstroms, the  $P_E$  is evaluated, using  $N_A n e^2 / r = 332(n/r) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ , where  $N_A$ ,  $n$ ,  $e$ , and  $r$  represent Avogadro's number, the valence number, the charge on the electron, and the ionic radius, respectively. The heats of formation of  $\text{MX}$  ( $\text{M} = \text{Cs}, \text{Rb}, \text{K}, \text{Na}, \text{Li}; \text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ),  $-\Delta H_{298}^0$  (solid), are listed in Table 2. Figure 1 illustrates the relation between  $\langle -\Delta H \rangle \{ = -\Delta H_{298}^0 [(-e^2/r_A) / -100 \text{ kcal}_{\text{th}} \text{ mol}^{-1}] / (e^2/r_C) \}$  and  $\chi_A$ . The correlation indicates that the electronegativity of the alkali ion should decrease in the order  $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$  and that the electronegativity of  $\text{Rb}^+$  should be changed to 0.75 in Pauling's scale. Hereafter the electronegativity of  $\text{Rb}^+$  is constrained to 0.75.

TABLE 1

Electronegativity ( $\chi$ ) [12], ionic radius ( $r$ ) [13], potential energy ( $e^2/r$ ), and first ionization potential (IP) [14]

Ion	$\chi$	$r$ (Å)	$e^2/r$ <sup>a</sup>	IP (eV)
Cs	0.7	1.67	198.8	3.89
Rb	0.8	1.52	218.4	4.18
K	0.8	1.38	240.6	4.34
Na	0.9	1.02	325.5	5.14
Li	1.0	0.76	436.8	5.39
NH <sub>4</sub>	1.2 <sup>b</sup>	1.45 [15]	229.0	–
Cu	1.9	0.77	431.2	7.72
Ag	1.9	1.15	288.7	7.57
Au	2.4	1.37	242.3	9.22
Tl	1.5 [4]	1.50	221.3	6.11
F	4.0	1.33	–249.6	
Cl	3.0	1.81	–183.4	
Br	2.8	1.96	–169.4	
I	2.5	2.20	–150.9	

<sup>a</sup> kcal<sub>th</sub> mol<sup>–1</sup> (1 cal<sub>th</sub> = 4.184 J).

<sup>b</sup> Value was calculated by the present author.

The solid lines in Fig. 1 are the results of a least-squares fit to the equation:

$$\frac{-\Delta H_{298}^0 \left[ \left( -e^2/r_A \right) / -100 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \right]}{\left( e^2/r_C \right)} = a\chi_A + b \quad (3)$$

TABLE 2

Heat of formation [ $-\Delta H_{298}^0$ (s)] [16], and  $\langle -\Delta H \rangle$  values

Substance	$-\Delta H_{298}^0$ (s) <sup>a</sup>	$\langle -\Delta H \rangle$ <sup>b</sup>	Substance	$-\Delta H_{298}^0$ (s) <sup>a</sup>	$\langle -\Delta H \rangle$ <sup>b</sup>
CsF	132.6 [17]	1.665	KBr	93.7	0.661
CsCl	105.8 [17]	0.976	KI	78.3	0.492
CsBr	94.3	0.803	NaF	137.3	1.053
CsI	80.5	0.611	NaCl	98.6	0.556
RbF	131.3	1.500	NaBr	86.5	0.451
RbCl	102.9	0.864	NaI	69.3	0.321
RbBr	93.0	0.722	LiF	146.3	0.836
RbI	78.5	0.542	LiCl	96.9	0.407
KF	134.5	1.395	LiBr	83.4	0.324
KCl	104.2	0.794	LiI	64.8	0.223

<sup>a</sup> kcal<sub>th</sub> mol<sup>–1</sup> (1 cal<sub>th</sub> = 4.184 J).

<sup>b</sup>  $\langle -\Delta H \rangle = -\Delta H_{298}^0 \left[ \left( -e^2/r_A \right) / 100 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \right] / \left( e^2/r_C \right)$ .

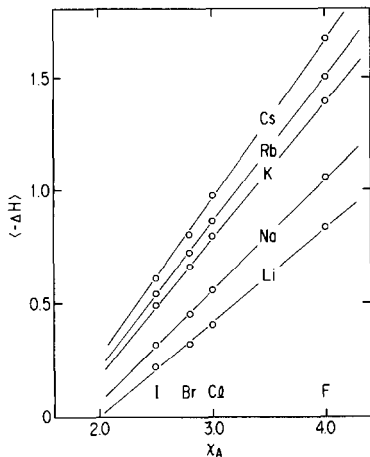


Fig. 1.  $\langle -\Delta H \rangle$  in alkali halides plotted against the electronegativity ( $\chi_A$ ) of the  $X^-$  ion.

where  $a$  and  $b$  are empirical constants. These empirical constants are listed in Table 3 and are plotted against the electronegativities of  $M^+$  ions in Fig. 2.

#### RELATION BETWEEN HEATS OF FORMATION OF PSEUDO-ALKALI HALIDES AND ELECTRONEGATIVITIES OF HALOGEN IONS

The heats of formation of pseudo-alkali halides,  $-\Delta H_{298}^0$  (solid), are listed in Table 4. Figure 3 illustrates the relation between  $\langle -\Delta H \rangle \{ = -\Delta H_{298}^0 [(-e^2/r_A)/-100 \text{ kcal}_{\text{th}} \text{ mol}^{-1}]/(e^2/r_C) \}$  and  $\chi_A$ . The correlation indicates that the electronegativity of the pseudo-alkali ion should decrease in the order  $\text{Au}^+ > \text{Cu}^+ > \text{Ag}^+ > \text{Tl}^+ > \text{NH}_4^+$ .

The solid lines in Fig. 3 are the results of a least-squares fit to eqn. (3). Values of  $a$  and  $b$  are listed in Table 5. By this empirical equation the heats of formation of  $\text{AuF}$  (solid) is estimated to be  $16 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$  and that of  $\text{NH}_4\text{Br}$  (solid) is changed to  $66 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ . The empirical constants  $a$  and  $b$  are plotted against Pauling's electronegativity of the  $M^+$  ion in Fig. 4.

TABLE 3

Empirical constants,  $a$  and  $b$ , in eqn. (3) for alkali halides

Ion	Cs	Rb	K	Na	Li
$a$	0.706	0.641	0.604	0.492	0.415
$b$	-1.157	-1.064	-1.023	-0.918	-0.827

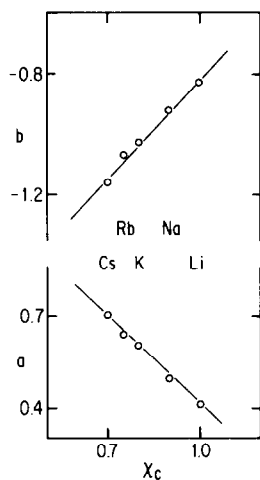


Fig. 2. Empirical constants,  $a$  and  $b$ , in eqn. (3) plotted against the electronegativity ( $\chi_C$ ) of the  $M^+$  ion for alkali halides.

TABLE 4

Heat of formation [ $-\Delta H_{298}^0$  (s)] [16], and  $\langle -\Delta H \rangle$  values

Substance	$-\Delta H_{298}^0$ (s) <sup>a</sup>	$\langle -\Delta H \rangle$ <sup>b</sup>	Substance	$-\Delta H_{298}^0$ (s) <sup>a</sup>	$\langle -\Delta H \rangle$ <sup>b</sup>
NH <sub>4</sub> F	110.8 [17]	1.208	AgBr	23.7	0.139
NH <sub>4</sub> Cl	75.1 [17]	0.601	AgI	14.9	0.078
NH <sub>4</sub> Br	56.6 [17]	0.418	AuF	(16.5) <sup>c</sup>	(0.17) <sup>c</sup>
NH <sub>4</sub> I	48.0 [17]	0.317	AuCl	8.3	0.063
CuF	60.0	0.347	AuBr	4.4	0.031
CuCl	32.2	0.137	AuI	-0.2	-0.001
CuBr	24.9	0.098	TlF	74.0	0.835
CuI	16.2	0.057	TlCl	49.0	0.406
AgF	48.5	0.419	TlBr	41.2	0.315
AgCl	30.3	0.193	TlI	29.7	0.203

<sup>a</sup> kcal<sub>th</sub> mol<sup>-1</sup> (1 cal<sub>th</sub> = 4.184 J).

<sup>b</sup>  $\langle -\Delta H \rangle = -\Delta H_{298}^0 [(-e^2/r_A)/100 \text{ kcal}_{th} \text{ mol}^{-1}] / (e^2/r_C)$ .

<sup>c</sup> Values were calculated by the present author.

TABLE 5

Empirical constants,  $a$  and  $b$ , in eqn. (3) for pseudo-alkali halides

Ion	NH <sub>4</sub>	Tl	Ag	Cu	Au
$a$	0.596	0.425	0.229	0.198	0.126
$b$	-1.178	-0.867	-0.497	-0.450	-0.319

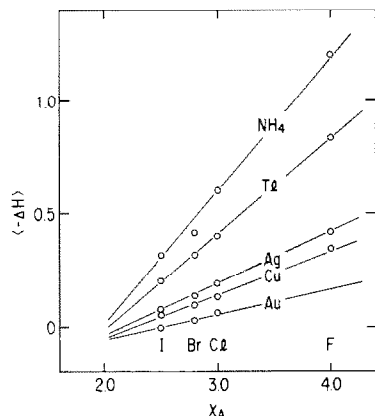


Fig. 3.  $\langle -\Delta H \rangle$  in pseudo-alkali halides plotted against the electronegativity ( $\chi_A$ ) of the  $X^-$  ion.

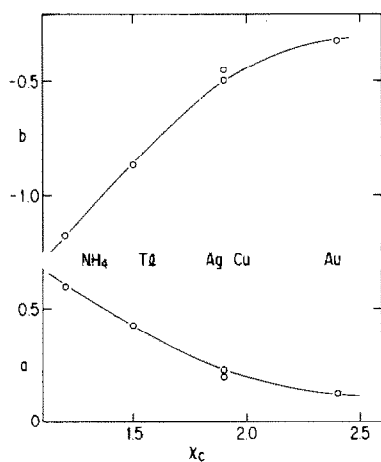


Fig. 4. Empirical constants,  $a$  and  $b$ , in eqn. (3) plotted against the electronegativity ( $\chi_C$ ) of the  $M^+$  ion for pseudo-alkali halides.

#### ELECTRONEGATIVITY OF PSEUDO-ALKALI ION

Electronegativities of the elements have been derived by various authors and by various methods. The agreement between the values obtained by the different methods is, on the whole, very good, with the exception of the Group B elements. The Group B elements are known to form compounds in which they exhibit a range of ionicity and/or covalency, depending on the range of the coordination number. Hence the most probable cause of their disagreement in the electronegativity is that the Group B elements exhibit a range of electronegativity, depending on the bonding character [8,9]. However, the discrepancies between Pauling's electronegativity and another

electronegativity (e.g. Mulliken's electronegativity) for the Group IB and/or pseudo-alkali ions may be caused by the imperfection of Pauling's method.

Pauling's electronegativities of alkali and pseudo-alkali ions were calculated from eqns. (1) and (2), using the heats of formation ( $-\Delta H_{298}^0$ ) of halides. However, comparison of Figs. 1 and 2 requires that we reconsider Pauling's method. That is, as shown in Fig. 5, the values of  $\langle -\Delta H \rangle$  for the alkali and pseudo-alkali halides are related to the electronegativities of halogen ions differently to each other. This fact means that some other factors (e.g. polarizability of the ion) affect the value of  $-\Delta H_{298}^0$  and Pauling's electronegativities of alkali and pseudo-alkali ions are based on different scales.

Ionization potentials (IP) were first used to calculate the electronegativities of atoms by Mulliken [10]. His definition is:

$$\chi_M = 1/2(I + EA) \quad (4)$$

where  $I$  is the valence-state ionization potential,  $EA$  the valence-state electron-affinity, and  $\chi_M$  the electronegativity, respectively. The ability to attract an extra valence electron, as well as the tendency to keep those already present, is built into eqn. (4). However, since electron affinities of alkali and pseudo-alkali metals are small in one order of magnitude of the ionization potential, they can be omitted from eqn. (4) with little loss of accuracy. Furthermore, since the valence electron of the alkali and pseudo-alkali metals has an  $S$  character in the halides, the valence-state ionization potential can be substituted by the first ionization potential (IP).

Figure 6 illustrates the variation of the value of  $\langle -\Delta H \rangle$  in alkali and pseudo-alkali fluorides with the first ionization potential (IP) of the alkali and pseudo-alkali atoms. There are two separate trends. The ( $\langle -\Delta H \rangle$ -IP)

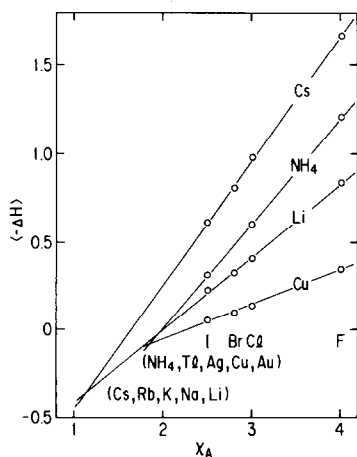


Fig. 5. Comparison of Figs. 1 and 2.

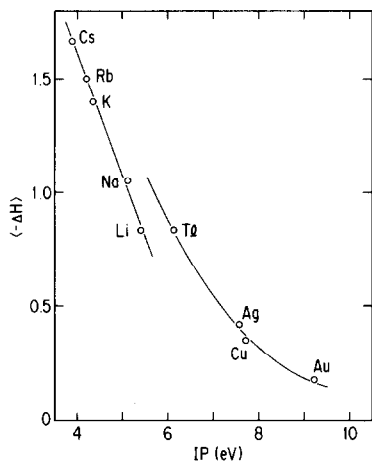


Fig. 6.  $\langle -\Delta H \rangle$  in alkali and pseudo-alkali fluorides plotted against first ionization potential of alkali and pseudo-alkali atoms.

correlations among the alkali ions constitute the same series. On the other hand, the  $Tl^+$  ion constitutes the same series with the group IB ions.

Figure 7 illustrates the variation of Pauling's electronegativity ( $\chi_p$ ) with the first ionization potential (IP) for the alkali and pseudo-alkali ions. There are two separate trends. The  $(\chi_p-IP)$  correlations among the alkali ions constitute the same series. On the other hand, the  $Tl^+$  ion constitutes the same series with the Group IB ions.

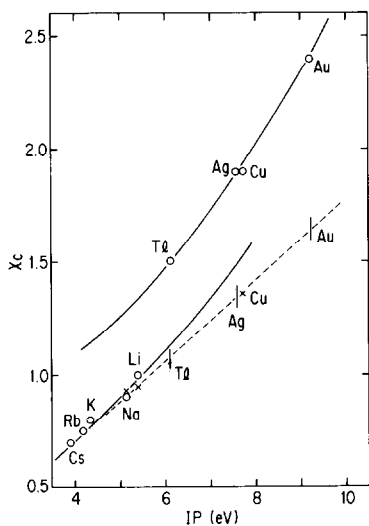


Fig. 7. Electronegativity ( $\chi_c$ ) of the  $M^+$  ion plotted against the first ionization potential of alkali and pseudo-alkali atoms.



Since Pauling's electronegativities of alkali and pseudo-alkali ions are based on different scales, as mentioned above, there is a large gap between the two trends. On the other hand, Mulliken-type values for Na, Li, and Cu are 0.93, 0.94, and 1.36 [3], and the values for Tl, Ag, and Au are estimated to be 1.1, 1.3, and 1.7 with noticeable error, as shown in Fig. 7.

#### CRYSTAL CHEMISTRY OF $Tl^+$ ION

It is well known that there is a close association of  $Tl^+$  and  $Rb^+$  in some potassium minerals [11]. The principal reasons for the close association are the equality of the radii of  $Tl^+$  (1.50 Å) and  $Rb^+$  (1.52 Å) and the fact that their chemical properties are very similar. However, the electronegativity of the  $Tl^+$  ion is 1.5 in Pauling's scale, which is more electronegative than  $Rb^+$  (0.75) and/or  $K^+$  (0.8). These facts suggest that the  $Tl-O$  bond is more covalent than the  $Rb-O$  bond. This high electronegativity was calculated by Pauling's method using the heats of formation of  $TlCl$ ,  $TlBr$  and  $TlI$  [4]. However, it becomes clear that this method is not suitable for Tl halides. As mentioned above, the Mulliken-type value for the  $Tl^+$  ion is estimated to be about 1.1. This value is consistent with the ionic character of the bonds formed by the  $Tl^+$  ion in some compounds. That is, the close association of  $Tl^+$  and  $Rb^+$  in some potassium minerals is explained by the equalities of the ionic radii and the electronegativity.

However, the  $Rb-Tl$  association can be disturbed by local geological processes (e.g. the presence of sulphide minerals). These phenomena can be caused by the variability of the Group B elements which exhibit a range of electronegativity, depending on the bonding character. Many B subgroup metals exhibit a stable valency which is 2 smaller than the group valency. This tendency is most pronounced for Tl, Pb, and Bi. The free ions corresponding to the lower valencies all have electron configurations consisting of closed shells followed by a pair of *S* electrons. Since the screening constant is connected with the number of electrons, it is generally recognized that the range of electronegativity is caused by the variation of the electron configuration of the *S* electrons outside a closed shell [9]. The electronegativity of the  $Tl^+$  ion with an inert *S* electron pair can be higher than that of spherical  $Tl^+$  ion without an inert *S* electron pair. That is, it is expected that the  $Rb-Tl$  association can be disturbed by the formation of the inert *S* electron pair in the  $Tl^+$  ion in the presence of the sulphur ion.

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