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RELATIONS BETWEEN THE HEATS OF FORMATION OF MX_3 HALIDES AND THE ELECTRONEGATIVITIES OF THE HALOGEN IONS

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ABSTRACT

The heats of formation of MX_3 halides (M = B, Al, Sc, Y, La, In and Ga), $-\Delta H^0_{298}$, may be expressed empirically in terms of the electronegativities χ_A of the halogen ions

$$-\Delta H^0_{298}\frac{1}{(3e^2/r_C)} = a\chi_A + b$$

where a and b are empirical constants and the factor 3, e and r_C represent the valence of the cation, the electronic charge and the cation radius, respectively. The value of $3e^2/r_C$ corresponds to the electrostatic energy arising between the effective nuclear charge of the M^{3+} ion ($3e$) and an electron at a distance from the nucleus equal to the ionic radius r_C. The empirical constants a and b correlate with the electronegativity of the M^{3+} ion. Although its physical meaning is not clear, this empirical equation is useful in predicting the values of electronegativity and/or ionic radius from the heat of formation, and vice versa.

The heats of formation of YBr_3(solid) and BI_3(gaseous) are estimated as -200 and 6 kcal (th) mol^{-1}, respectively. Ga is more electronegative than In. This result is consistent with that obtained from a structure refinement carried out for $NaGaSi_2O_6$–pyroxene. The electronegativity of Ga^{3+} should therefore be revised to 1.9 on Pauling's scale.

INTRODUCTION

Pauling's electronegativity was introduced as an attribute of an atom in a covalent compound. Therefore, his equation $0.208\sqrt{\Delta} = |X_X - X_Y|$ does not satisfactorily describe the relation between $\sqrt{\Delta}$ and $|X_X - X_Y|$ in an ionic compound. Ohashi [1,2] has found that the ratio of the heat of formation to the potential energy ($P_E = ne^2/r$) is an effective scaling to correlate the heat of formation of the ionic compound with Pauling's electronegativity. This study examines the relation between heats of formation of MX_3 halides and the electronegativities of the halogen and trivalent metal ions concerned.

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RELATION BETWEEN HEATS OF FORMATION OF MX_3 HALIDES AND ELECTRONEGATIVITIES OF HALOGEN IONS

The electronegativities of the relevant M^{3+} and halogen ions obtained using Pauling's method are listed in Table 1, along with the ionic radii of M^{3+} (r_C) in octahedral sites and the potential energy (P_E). The P_E values correspond to the electrostatic energy between the effective nuclear charge of the M^{3+} ion (ne) and an electron at a distance from the nucleus equal to the ionic radius r. If r is given in angstroms, P_E may be evaluated, using the expression $N_A ne^2/r = 332(n/r)$ kcal (th) mol^{-1}, where N_A, n, e and r represents Avogadro's number, the valence, the electronic charge and the ionic radius, respectively. The heats of formation of the compounds MX_3 (M = trivalent metal, X = halogen), $-\Delta H^0_{298}$ (solid and/or gaseous), are listed in Table 2. Figures 1 and 2 illustrate the relation between $-\Delta H$ $(= -\Delta H^0_{298}/(3e^2/r_C))$ and χ_A.

Solid lines in Figs. 1 and 2 connect data points for $-\Delta H$(s) while the dashed lines in Fig. 1 connect data points for $-\Delta H$(g). These lines are the results of a least-squares fit to the equation

$$-\Delta H^0_{298}\frac{1}{(3e^2/r_C)} = a\chi_A + b \qquad (1)$$

where a and b are empirical constants. The values of these constants for hard-type trivalent ions are listed in Table 3. Using eqn. (1) the heats of formation of YBr_3(solid) and BI_3(gaseous) are estimated as -200 and 6 kcal (th) mol^{-1}, respectively.

The correlations shown in Fig. 1 indicate that the electronegativity of hard-type trivalent ions should decrease in the order B > Al > Sc > Y > La.

TABLE 1

Electronegativity (χ) [3], ionic radius (r) [4], potential energy (ne^2/r) and ionization potential (IP(I + II + III)) [5] for various metal and halogen ions

Ion	χ	r(Å)	ne^2/r [a]	IP(I + II + III) (eV)
La	1.1	1.032	965.1	36.21
Y	1.2	0.900	1106.7	39.11
Sc	1.3	0.745	1336.9	44.09
Al	1.5	0.535	1861.7	53.24
B	2.0	0.27	3688.9	71.37
Ga	1.6	0.620	1606.5	57.21
In	1.7	0.800	1245.0	52.68
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	

[a] kcal (th) mol^{-1} (1 cal (th) = 4.184 J).

TABLE 2

Heats of formation ($-\Delta H^0_{298}$(s)) [6] and $-\Delta H$ values for the compounds studied

Compound	$-\Delta H^0_{298}$(s) [a]	$-\Delta H$ [b]	Compound	$-\Delta H^0_{298}$(s) [a]	$-\Delta H$ [b]
LaF	426.0	0.441	BF_3(g)	271.4	0.074
$LaCl_3$	255.9	0.265	BCl_3(g)	96.3	0.026
$LaBr_3$	208.0	0.216	BBr_3(g)	48.8	0.013
LaI_3	157.0	0.163	BI_3(g)	–	–
YF_3	410.7	0.371	GaF_3	280.8 [d]	0.175
YCl_3	232.7	0.210	$GaCl_3$	125.4	0.078
YBr_3	–	–	$GaBr_3$	92.4	0.058
YI_3	147.7	0.134	GaI_3	57.2	0.036
ScF_3	396.0	0.296	InF_3	284.4 [d]	0.228
$ScCl_3$	215.0	0.161	$InCl_3$	128.4	0.103
$ScBr_3$	170.0	0.127	$InBr_3$	98.2	0.079
ScI_3	135.9 [c]	0.102	InI_3	56.1	0.045
AlF_3	361.0	0.194			
$AlCl_3$	168.7	0.091			
$AlBr_3$	122.2	0.066			
AlI_3	73.9	0.040			
AlF_3(g)	289.0	0.155			
$AlCl_3$(g)	139.7	0.075			
$AlBr_3$(g)	98.2	0.053			
AlI_3(g)	49.0	0.026			

[a] See Table 1, footnote a.

[b] $-\Delta H = -\Delta H^0_{298}/(3e^2/r_C)$.

[c] From ref. 7.

[d] From ref. 8.

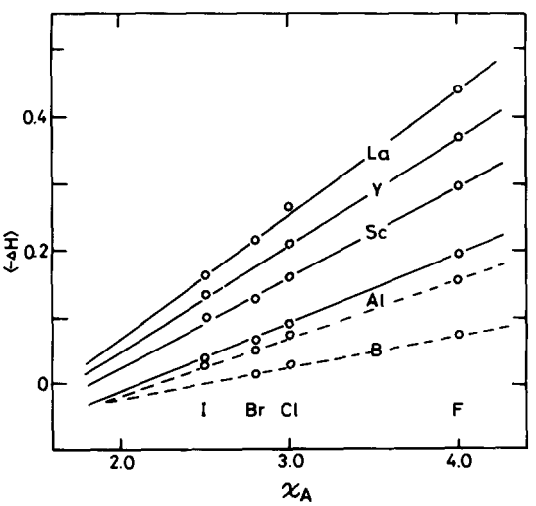

Fig. 1. $-\Delta H$ for the MX_3 halides (M = B, Al, Sc, Y, La) plotted against the electronegativities (χ_A) of the X^- ions. Solid lines connect data points for $-\Delta H$(s) and dashed lines those for $-\Delta H$(g).

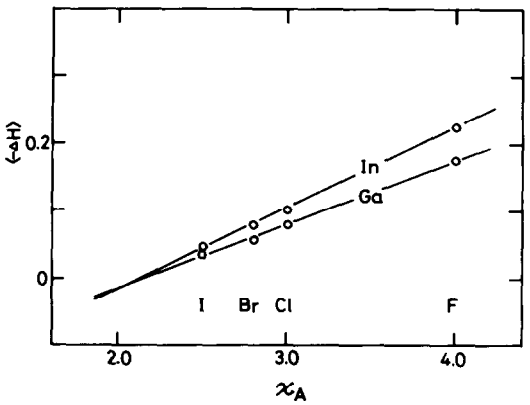

Fig. 2. $-\Delta H$ for the MX_3 halides (M = Ga, In) plotted against the electronegativities (χ_A) of the X^- ions.

TABLE 3

Values of the empirical constants a and b in eqn. (1) for various metal ions

Ion	a	b
La	0.186	−0.300
Y	0.159	−0.264
Sc	0.133	−0.237
Al	0.104	−0.222
Al(g)	0.086	−0.186
B(g)	0.049	−0.124

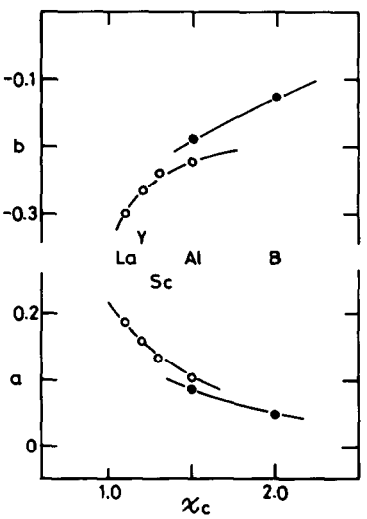

Fig. 3. Empirical constants a and b from eqn. (1) plotted against the electronegativities (χ_C) of the M^{3+} ions. Open circles represent the constants for solids and solid circles those for gaseous compounds.

This result is consistent with Pauling's table [3]. The empirical constants a and b are plotted against Pauling's electronegativity for M^{3+} ions in Fig. 3.

ELECTRONEGATIVITY OF THE Ga^{3+} ION

The correlation shown in Fig. 2 indicates that Ga is more electronegative than In. This result is not consistent with Pauling's table [3]: the electronegativities of Ga and In obtained using Pauling's method are 1.6 and 1.7, respectively [3]. On the other hand, in a structure refinement performed for $NaGaSi_2O_6$–pyroxene, the electronegativity of Ga in an octahedral site was estimated by Ohashi et al. [9] as 1.9 on Pauling's scale and thus appeared to be more electronegative than In. These latter results seem to be consistent with our own.

Figure 4 illustrates the variation in the value of $-\Delta H$ for the fluorides MF_3 with the sum of the first, second and third ionization potentials of M. These correlations indicate that $-\Delta H$ values for the group-B element compounds are related to the sum of the ionization potentials in their own specific way and that Ga is more electronegative than In. If the electronegativity of the Ga ion is revised to 1.9 on Pauling's scale, the mode of distribution of Ga^{3+} ion in melilites and garnets can be explained in terms of the higher electronegativity [10].

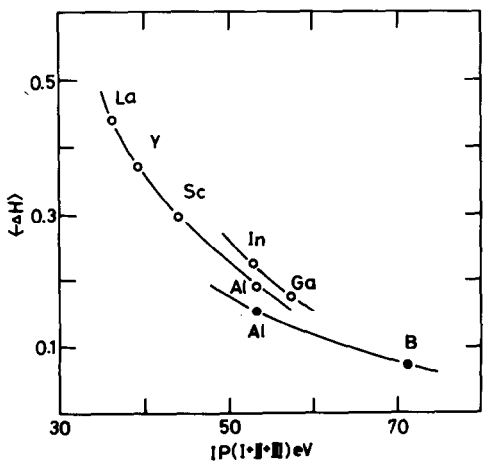

Fig. 4. $-\Delta H$ for the fluorides MF_3 plotted against the sum of the first, second and third ionization potentials of the M atoms. Open circles represent the data points for $-\Delta H$(s) and solid circles those for $-\Delta H$(g).

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