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RELATIONS BETWEEN HEATS OF FORMATION OF MX_2 HALIDES AND ELECTRONEGATIVITIES OF HALOGEN IONS

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ABSTRACT

The heats of formation of MX_2 halides (M being Ba, Sr, Ca, Mg, Be, Mn Fe, Co, Ni, Cu, Zn, Cd and Hg), $-\Delta H^0_{298}$, are expressed empirically by electronegativities (χ_A) of halogen ion:

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

where a and b are empirical constants; factor 2, e, r_C and r_A represent the valence number of the cation, the charge on the electron, cationic radius, and anionic radius, respectively. The value of $2e^2/r_C$ corresponds to the electrostatic energy between the effective nuclear charge of the M^{2+} ion ($2e$) and an electron at a distance from its nucleus equal to its ionic radius r_C. The empirical constants a and b correlate with the electronegativity of the M^{2+} ion as three different trends; Ba, Sr, Ca, Mg, Be series, Mn, Fe, Co, Ni, Cu series and Zn, Cd, Hg series. Although physical meaning is not clear, this empirical equation is useful to predict the values of electronegativity and/or ionic radius from the heat of formation, and vice versa. The electronegativity of Cd^{2+} in halides is found to be 1.3 in Pauling's scale. This value is consistent with that obtained from the structure refinement of $Cd_3Al_2Si_3O_{12}$ garnet.

INTRODUCTION

Pauling's electronegativity was introduced as an attribute of the atom in a covalent compound. Therefore, his equation, $0.208\sqrt{\Delta} = |\chi_x - \chi_y|$, does not satisfy the relation between $\sqrt{\Delta}$ and $|\chi_x - \chi_y|$ in an ionic compound. Ohashi [1–3] 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. The

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purpose of this study is to examine the relation between heats of formation of MX_2 halides and electronegativities of halogen and divalent metal ions.

RELATION BETWEEN HEATS OF FORMATION OF MX_2 HALIDES AND ELECTRONEGATIVITIES OF HALOGEN IONS

The electronegativities of M^{2+} and halogen ions obtained from Pauling's method are listed in Table 1, along with the ionic radii of M^{2+} (r_C) and X^- ions (r_A) in octahedral site and potential energy ($P_E = ne^2/r$). The P_E corresponds to electrostatic energy between effective nuclear charge of the M^{2+} ion (ne) and an electron at a distance from its nucleus equal to its ionic radius r. If r is given in ångström, the P_E is evaluated, using $N_A ne^2/r = 332(n/r)$ kcal_{th} 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 MX_2 (M: divalent metal; X: halogen), $-\Delta H^0_{298}$(solid), are listed in Tables 2–4. Figures 1–3 illustrate the relation between $\langle -\Delta H \rangle$ and χ_A (where $\langle -\Delta H \rangle = -\Delta H^0_{298}\{(-e^2/r_A)/(-100\ \text{kcal}_{\text{th}}\ \text{mol}^{-1})\}^{1/2}/(2e^2/r_C)$).

The correlation shown in Fig. 1 indicates that the electronegativity of alkali-earth ion should decrease in the order Be > Mg > Ca > Sr > Ba and

TABLE 1

Electronegativity (χ) [4], ionic radius (r) [5], potential energy (ne^2/r), and ionization potential {IP(I+II)} [6]

Ion	χ	r (Å)	ne^2/r [a]	IP(I+II) eV
Ba	0.9	1.35	491.9	15.21
Sr	1.0	1.18	562.7	16.72
Ca	1.0	1.00	664.0	17.98
Mg	1.2	0.72	922.2	22.67
Be	1.5	0.45	1475.6	27.53
Mn	1.4 [b]	0.83	800.0	23.07
Fe	1.65 [b]	0.78	851.3	24.05
Co	1.8	0.745	891.3	24.91
Ni	1.8	0.690	962.3	25.78
Cu	2.0 [b]	0.73	909.6	28.01
Zn	1.5 [b]	0.740	897.3	27.32
Cd	1.5 [b]	0.95	699.0	25.89
Hg	1.9	1.02	651.0	29.18
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] $\text{kcal}_{\text{th}}\ \text{mol}^{-1}$ ($1\ \text{cal}_{\text{th}} = 4.184$ J).
[b] From ref. 8.

TABLE 2

Heat of formation $\{-\Delta H^0_{298}(s)\}$ [7] and $\langle -\Delta H \rangle$ value

Substance	$-\Delta H^0_{298}(s)$ [a]	$\langle -\Delta H \rangle$ [b]
BaF_2	287.7	0.924
$BaCl_2$	205.4	0.565
$BaBr_2$	180.5	0.478
BaI_2	144.5	0.361
SrF_2	289.0	0.811
$SrCl_2$	198.2	0.477
$SrBr_2$	171.2	0.396
SrI_2	134.0	0.292
CaF_2	292.0	0.695
$CaCl_2$	191.4	0.390
$CaBr_2$	163.2	0.320
CaI_2	128.0	0.237
MgF_2	266.0	0.456
$MgCl_2$	153.4	0.225
$MgBr_2$	123.7	0.175
MgI_2	86.0	0.115
BeF_2	243.0	0.260
$BeCl_2$	118.0	0.108
$BeBr_2$	79.4	0.070
BeI_2	39.4	0.033

[a] See footnote a Table 1.
[b] For $\langle -\Delta H \rangle$, see text.

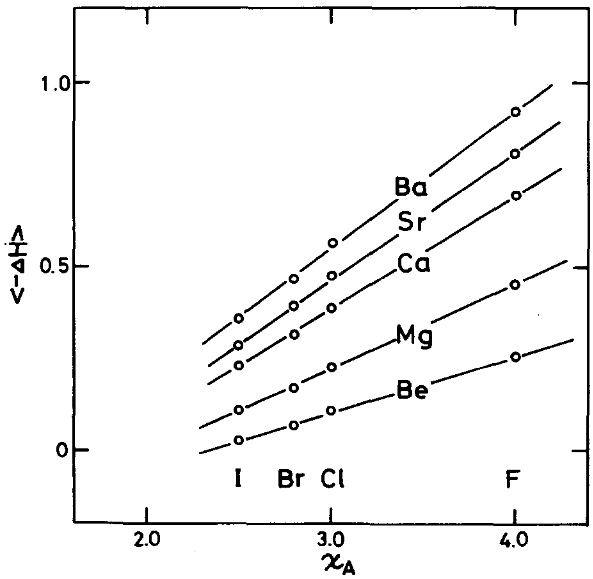

Fig. 1. $\langle -\Delta H \rangle$ in alkali earth halides plotted against the electronegativity (χ_A) of X^- ion.

TABLE 3

Heat of formation $\{-\Delta H^0_{298}(s)\}$ [7] and $\langle -\Delta H \rangle$ value

Substance	$-\Delta H^0_{298}(s)$ [a]	$\langle -\Delta H \rangle$ [b]
MnF_2	204.6 [c]	0.404
$MnCl_2$	115.2	0.195
$MnBr_2$	90.0	0.146
MnI_2	58.0	0.089
FeF_2	168.0	0.312
$FeCl_2$	81.8	0.130
$FeBr_2$	59.1	0.090
FeI_2	30.0	0.043
CoF_2	159.0	0.282
$CoCl_2$	77.8	0.118
$CoBr_2$	51.0	0.074
CoI_2	21.0	0.029
NiF_2	158.0	0.259
$NiCl_2$	73.0	0.103
$NiBr_2$	51.8	0.070
NiI_2	23.0	0.029
CuF_2	128.0	0.222
$CuCl_2$	49.2	0.073
$CuBr_2$	33.2	0.048
CuI_2	1.7	0.002

[a] See footnote a Table 1.
[b] See footnote b Table 2.
[c] From ref. 9.

TABLE 4

Heat of formation $\{-\Delta H^0_{298}(s)\}$ [7] and $\langle -\Delta H \rangle$ value

Substance	$-\Delta H^0_{298}(s)$ [a]	$\langle -\Delta H \rangle$ [b]
ZnF_2	182.7	0.322
$ZnCl_2$	99.5	0.150
$ZnBr_2$	78.3	0.114
ZnI_2	50.0	0.068
CdF_2	167.4	0.378
$CdCl_2$	93.0	0.180
$CdBr_2$	75.2	0.140
CdI_2	48.0	0.084
HgF_2	101.0 [c]	0.245
$HgCl_2$	55.0	0.114
$HgBr_2$	40.5	0.081
HgI_2	25.2	0.048

[a] See footnote a Table 1.
[b] See footnote b Table 2.
[c] From ref. 10.

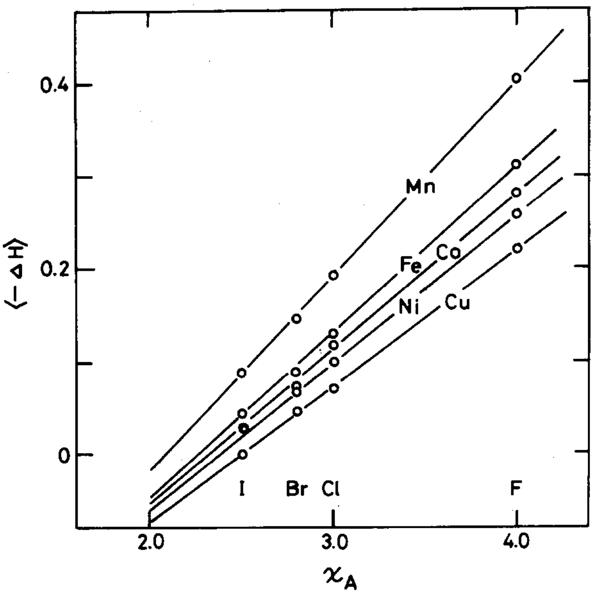

Fig. 2. $\langle -\Delta H \rangle$ in MX_2 halides (M = Mn, Fe, Co, Ni, Cu) plotted against the electronegativity (χ_A) of X^- ion.

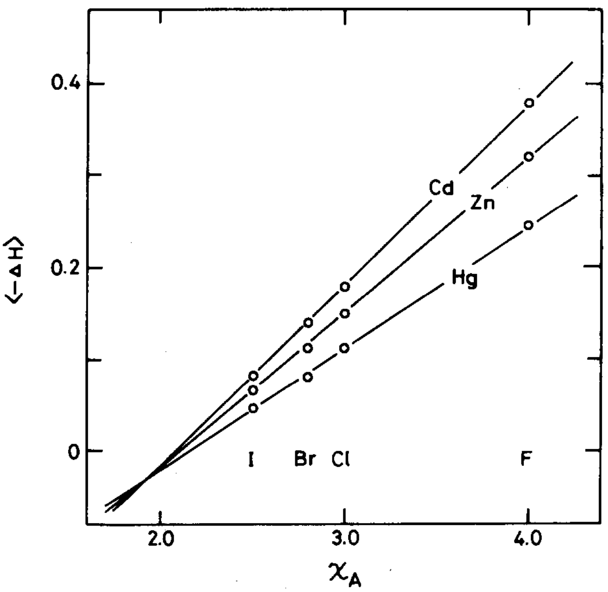

Fig. 3. $\langle -\Delta H \rangle$ in MX_2 halides (M = Zn, Cd, Hg) plotted against the electronegativity (χ_A) of X^- ion.

the electronegativity of Sr^{2+} should be revised to be 0.95 in Pauling's scale. On the other hand, the correlation shown in Fig. 3 indicates that the electronegativity of Group IIb ion should decrease in the order Hg > Zn > Cd. In the structure refinement of $Cd_3Al_2Si_3O_{12}$ garnet, the electronegativity of Cd in dodecahedral site has been estimated to be 1.3 in Pauling's scale and appeared to be more electropositive than Zn [11]. Their results seem to be consistent with ours. Hereafter the electronegativities of Sr and Cd are constrained to 0.95 and 1.3, respectively.

RELATION BETWEEN HEATS OF FORMATION OF MX_2 HALIDES AND ELECTRONEGATIVITIES OF DIVALENT METAL IONS

Solid lines in Figs. 1–3 are the least-mean-square fit to the equation:

$$\frac{-\Delta H^0_{298}\{(-e^2/r_A)/(-100\ \mathrm{kcal_{th}\ mol^{-1}})\}^{1/2}}{(2e^2/r_C)} = a\chi_A + b, \qquad (1)$$

where a and b are empirical constants. They are listed in Table 5 and are plotted against the electronegativities of M^{2+} ions in Fig. 4. The empirical constants a and b correlate with the electronegativity of the M^{2+} ion as three different trends. These facts indicate that some other factors (e.g. polarizability of the ion) affect the heat of formation.

The plots for Ni halides in Fig. 4 deviate from the trends among the transition metal ion series. The deviation requires a re-examination for the heats of formation of Ni halides (e.g. NiI_2).

TABLE 5

Empirical constants, a and b, in eqn. (1)

Ion	a	b
Ba	0.373	−0.566
Sr	0.345	−0.568
Ca	0.307	−0.534
Mg	0.229	−0.462
Be	0.153	−0.353
Mn	0.211	−0.441
Fe	0.181	−0.412
Co	0.169	−0.395
Ni	0.155	−0.360
Cu	0.147	−0.364
Zn	0.170	−0.360
Cd	0.197	−0.410
Hg	0.133	−0.287

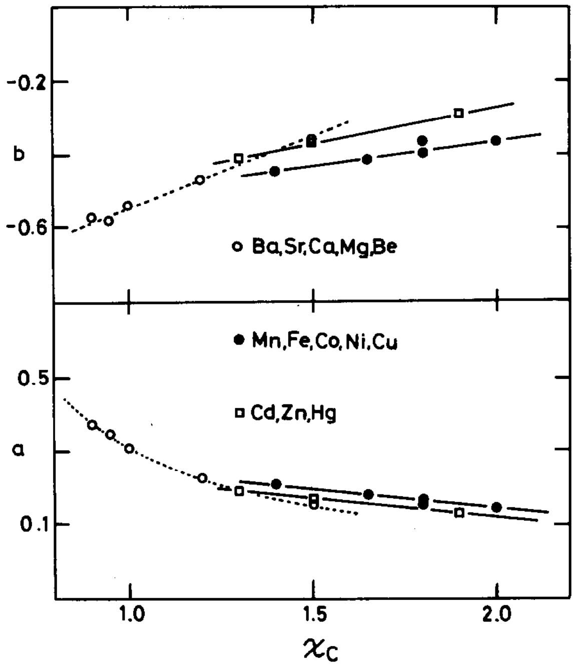

Fig. 4. Empirical constants, a and b, in eqn. 1 plotted against the electronegativity (χ_C) of M^{2+} ion.

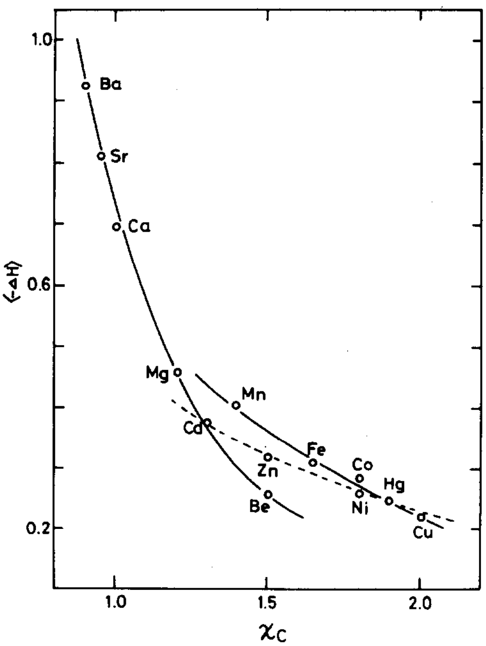

Fig. 5. $\langle -\Delta H \rangle$ in MF_2 plotted against the electronegativity (χ_C) of M^{2+} ion.

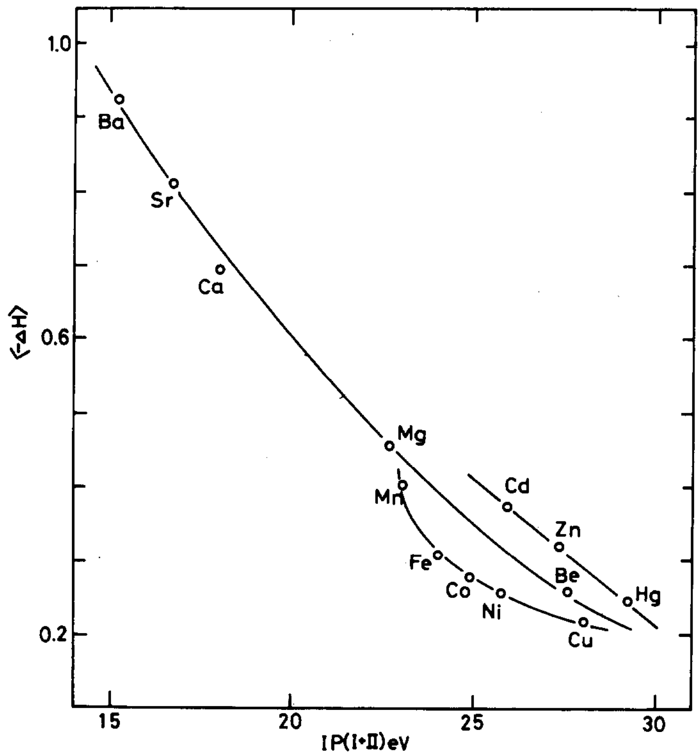

Fig. 6. $\langle -\Delta H \rangle$ in MF_2 plotted against the sum of first and second ionization potentials of M atoms.

Figures 5 and 6 illustrate the variation of the value of $\langle -\Delta H \rangle$ of MF_2 with the electronegativity of M^{2+} ion and with the sum of the first and second ionization potentials, respectively. These correlations indicate that Ni is more electronegative than Co. The electronegativities of Co and Ni ions are estimated to be 1.75 and 1.85, respectively.

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