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RELATIONS BETWEEN THE HEATS OF FORMATION OF LANTHANIDE TRIHALIDES AND THE ELECTRONEGATIVITIES OF THE HALOGEN IONS

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ABSTRACT

The heats of formation of lanthanide trihalides $-\Delta H_{298}^{\ominus}$ may be expressed empirically in terms of the electronegativities χ_A of the halogen ions

$$-\Delta H_{298}^{\ominus}\frac{\left[(-e^2/r_A)/(-418.4\ \text{kJ mol}^{-1})\right]^{1/2}}{(3e^2/r_C)} = a\chi_A + b$$

where a and b are empirical constants and the factor 3, e, r_C and r_A represent the valence of the cation, the electronic charge, the cation radius and the anion radius, respectively. The value of $ne^2/r_{(C\ \text{and/or}\ A)}$ corresponds to the electrostatic energy arising between the effective nuclear charge of the ion ne and an electron at a distance from its nucleus equal to its ionic radius $r_{(C\ \text{and/or}\ A)}$. The empirical constants a and b correlate with the sum of the first, second and third ionization potentials of the lanthanides giving three different trends: La–Eu(0–6f) series, Gd–Yb(7–13f) series and Lu(14f) series. This means that some other factors (e.g. polarizability of the ion) affect the heat of formation.

INTRODUCTION

Pauling's electronegativity was introduced as an attribute of an atom in a covalent compound. Therefore, his equation $0.208\sqrt{\Delta} = |\chi_X - \chi_Y|$ does not satisfactorily describe the relation between $\sqrt{\Delta}$ and $|\chi_X - \chi_Y|$ in an ionic compound. Ohashi [1–4] found that the ratio of the heat of formation to the potential energy $P_E = ne^2/r$ is an effective scale for correlating the heat of formation of the ionic compound with Pauling's electronegativity. This study examines the relation between the heats of formation of lanthanide trihalides LnX_3 and the electronegativities of the halogen and trivalent lanthanide ions concerned.

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RELATION BETWEEN HEATS OF FORMATION OF LANTHANIDE TRIHALIDES LnX_3 AND ELECTRONEGATIVITIES OF HALOGEN IONS

The electronegativities of the relevant Ln^{3+} and halogen ions obtained using Pauling's method are listed in Table 1, together with the ionic radii of Ln^{3+} r_C and X^- r_A in the octahedral site, the potential energy P_E and the ionization potential IP. The P_E values correspond to the electrostatic energy between the effective nuclear charge of the ion ne and an electron at a distance from the nucleus equal to the ionic radius r. If r is given in ångströms, P_E is evaluated using $N_A ne^2/r = 332(n/r)4.184$ kJ mol^{-1}, where N_A, n, e and r represent Avogadro's number, the valence, the electronic charge and the ionic radius, respectively. The heats of formation of the compounds LnX_3 (Ln = lanthanide, X = halogen) $-\Delta H^{\ominus}_{298}$(solid) are listed in Table 2. The values for the lanthanum trihalides LaX_3 are the refined values and not those referred to in ref. 3.

The scaled values $\langle -\Delta H \rangle$ are listed in Table 3, where $\langle -\Delta H \rangle = -\Delta H^{\ominus}_{298}[(-e^2/r_A)/(-418.4\ \text{KJ mol}^{-1})]^{1/2}/(3e^2/r_C)$. Figure 1 illustrates the relation between $\langle -\Delta H \rangle$ and χ_A. The solid lines in Fig. 1 connect data points for $\langle -\Delta H \rangle$. These lines are the result of a least-squares fit to the equation

$$-\Delta H^{\ominus}_{298}\frac{[(-e^2/r_A)/(-418.4\ \text{kJ mol}^{-1})]^{1/2}}{(3e^2/r_C)} = a\chi_A + b \qquad (1)$$

TABLE 1

Electronegativity χ [5], ionic radius r [6], potential energy ne^2/r, and ionization potential IP(I + II + III) [7] for lanthanide and halogen ions

Ion	χ	r (Å)	ne^2/r (kJ mol^{-1})	IP(I + II + III) (eV) [a]
La	1.1	1.032	4038.0	35.81 [7–9]
Ce		1.01	4126.0	36.52(8)
Pr		0.99	4209.4	37.59(8)
Nd		0.983	4239.3	38.40(31)
Pm		0.97	4296.1	38.77 [7–9]
Sm		0.958	4350.0	40.13(31)
Eu		0.947	4400.5	41.63(33)
Gd		0.938	4442.7	38.85(13)
Tb		0.923	4514.9	39.28(13)
Dy		0.912	4569.4	40.39(31)
Ho		0.901	4625.2	40.66(13)
Er		0.890	4682.3	40.77(13)
Tm		0.880	4735.5	41.91(13)
Yb		0.868	4801.0	43.45(3)
Lu	1.2	0.861	4840.0	40.29(40)
F	4.0	1.33	−1044.3	
Cl	3.0	1.81	−767.3	
Br	2.8	1.96	−708.8	
I	2.5	2.20	−631.4	

[a] Estimated uncertainties are in parentheses.

TABLE 2

Heat of formation $-\Delta H^{\ominus}_{298}(\mathrm{s})$ (kJ mol^{-1}) [10] for the compounds studied

Compound	LnF_3	$LnCl_3$	$LnBr_3$	LnI_3
La	1699	1073	907	667
Ce	1703	1058		650
Pr	1689	1059	891	654
Nd	1679	1042	873	639
Pm				
Sm	1669	1026	857	620
Eu	1571	936	779	
Gd	1699	1008	829	594
Tb	1707	1007		
Dy	1692	989	834	607
Ho	1698	995		623
Er	1694	995	839	613
Tm	1656	991		602
Yb	1570	960		
Lu	1701	986		548

where *a* and *b* are empirical constants. The values of these constants are listed in Table 3. Although its physical meaning is not clear, the empirical equation is useful in predicting the heat of formation.

TABLE 3

$\langle -\Delta H \rangle$ values for the compounds studied and the empirical constants *a* and *b* from eqn. (1) for the lanthanide halides

Compound	LnF_3	$LnCl_3$	$LnBr_3$	LnI_3	*a*	*b*
La	0.665	0.360	0.292	0.203	0.308	−0.568
Ce	0.652	0.347		0.194	0.306	−0.570
Pr	0.634	0.341	0.276	0.191	0.296	−0.550
Nd	0.626	0.333	0.268	0.185	0.295	−0.554
Pm						
Sm	0.606	0.320	0.256	0.175	0.289	−0.548
Eu	0.564	0.288	0.230		0.277	−0.545
Gd	0.604	0.307	0.243	0.164	0.296	−0.579
Tb	0.597	0.302				
Dy	0.585	0.293	0.238	0.163	0.284	−0.554
Ho	0.580	0.291		0.166	0.278	−0.535
Er	0.572	0.288	0.233	0.161	0.277	−0.537
Tm	0.553	0.284		0.156	0.265	−0.508
Yb	0.517	0.271				
Lu	0.555	0.276		0.139	0.278	−0.556

$\langle -\Delta H \rangle = -\Delta H^{\ominus}_{298}[(-e^2/r_A)/(-418.4\ \mathrm{kJ\ mol^{-1}})]^{1/2}/(3e^2/r_C)$.

RELATION BETWEEN HEATS OF FORMATION OF LANTHANIDE TRIHALIDES LnX_3 AND IONIZATION POTENTIALS OF LANTHANIDES

The empirical constants a and b from eqn. (1) are plotted against the sum of the first, second and third ionization potentials of the lanthanides in Fig. 2. There are three different trends: La–Eu(0–6f) series, Gd–Yb(7–13f) series and Lu(14f) series, Since the empirical constants for the Gd–Yb(7–13f) series have relatively large standard deviations, it is possible to consider that another scaled value (e.g. $\langle -\Delta H\rangle = -\Delta H^{\ominus}_{298}[(-e^2/r_A)/(-418.4\ \mathrm{kJ\ mol^{-1}})]^{1/4}/(3e^2/r_C))$ is suitable for the series. In any case, these facts indicate that some other factors (e.g. polarizability of the ion) affect the heat of formation.

In Gordy and Thomas's table [11], the electronegativities of Eu and Yb are ~ 1.1 on Pauling's scale, and are more electropositive than the other

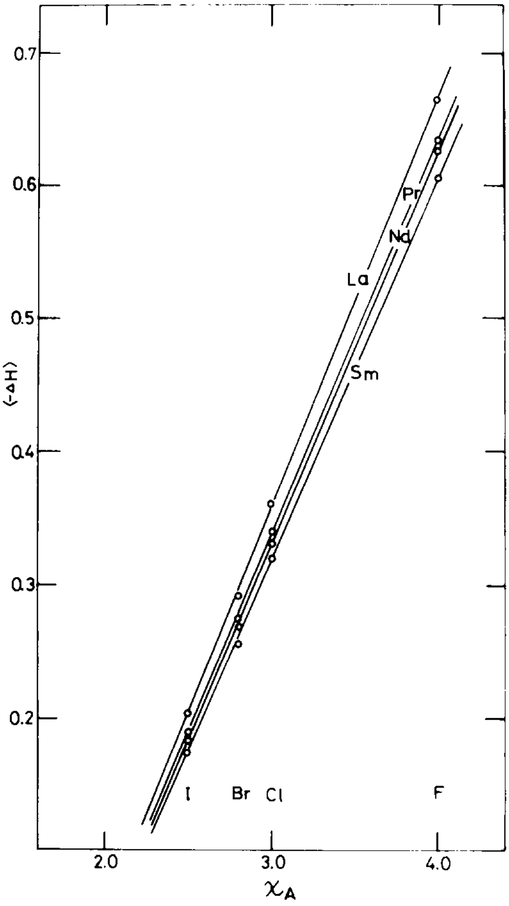

Fig. 1. $\langle -\Delta H\rangle$ for the LnX_3 halides (Ln = lanthanide) plotted against the electronegativities χ_A of the X^- ions.

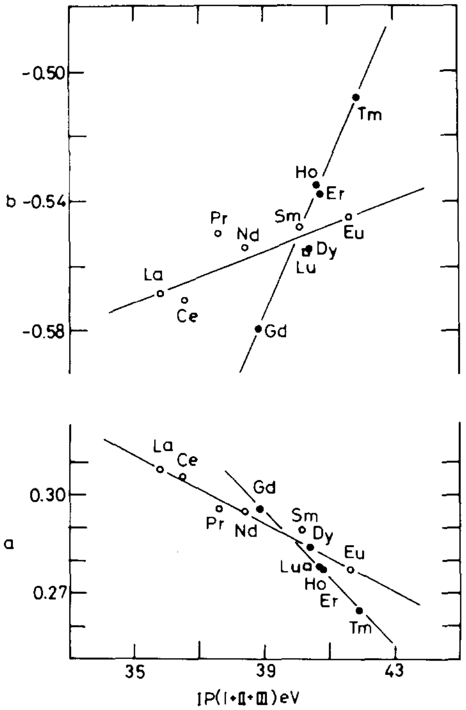

Fig. 2. Empirical constants a and b from eqn. (1) plotted against the sum of the first, second and third ionization potentials of the lanthanide atoms.

lanthanide ions. However, the correlations shown in Figs. 1 and 2 and the $\langle -\Delta H \rangle$ values listed in Table 2 indicate that the electronegativities of Ln^{3+}(0–6f) and Ln^{3+}(7–13f) ions should increase in the order La < Ce < Pr < Nd < Pm < Sm < Eu and Gd < Tb < Dy < Ho < Er < Tm < Yb, respectively.

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