Inorganica Chimica Acta, 65 (1982) L53–L55

Lanthanide Thermodynamic Predictions. Part III. Enthalpies of Formation of Lanthanide(IV) Compounds

STEVEN BRATSCH* and HERBERT B. SILBER

Earth and Physical Sciences, The University of Texas at San Antonio (UTSA), San Antonio, Tex. 78285, U.S.A.

Received March 4, 1982

Ionic models have often been utilized to predict thermodynamic properties of many types of cations [1]. For the formation of a lanthanide species, LnX, the Born-Haber cycle is:

$$\Delta H^\circ_f(\mathrm{LnX}) = \Delta H^\circ_f(\mathrm{Ln}^{n+}, g) + \Delta H^\circ_f(\mathrm{X}^{n-}, g) - \Delta H^\circ_{\mathrm{lattice}}(\mathrm{LnX}) \qquad (1)$$

We assume the lattice energy is a function of the sum of the ionic radii within a particular ligand series, given by:

$$\Delta H^\circ_{\mathrm{lattice}}(\mathrm{LnX}) = \frac{A}{r_{\mathrm{Ln}^{n+}} + r_{\mathrm{X}^{n+}}} + k_2 \qquad (2)$$

Here A and k_2 are constants. For a series using one ligand, ΔH°_f (X^{n-}, g) is a constant. Combining all of the constant terms together, yields

$$\Delta H^\circ_f(\mathrm{LnX}) = Q_n + \frac{A}{r_{\mathrm{Ln}^{n+}} + r_{\mathrm{X}^{n-}}} + B \qquad (3)$$

where Q_n is the sum of the lanthanide ionization energies plus the sublimation energy [2]. A graph of ΔH°_f (LnX) – Q_n as a function of the inverse of the ionic radii sum is a straight line yielding the empirical constants A and B. For the plus three lanthanides, the La, Gd and Lu compounds are used to establish the series constants. For the plus-two series, Ba^{2+}, Sr^{2+} and Ca^{2+}, or Ba^{2+}, Eu^{2+} and Yb^{2+} can be utilized to determine the constants [3]. Figure 1 is a plot of the calculated ΔH°_f for the lanthanide(III) bromides [3] compared to experimental results [4], and the excellent agreement confirms the validity of this technique. We will extend this technique to the lanthanide(IV) compounds using Ce(IV) and Zr(IV) as the standards to calculate A and B for each ligand series. Hf(IV) is a good standard except for the observation that the second and third ionization potentials are not well characterized [11].

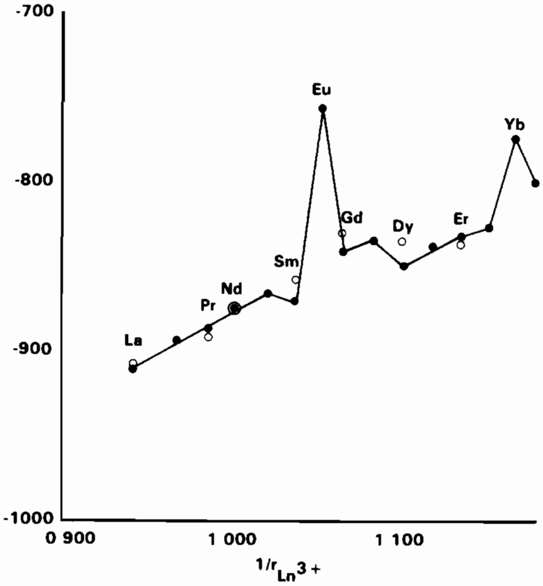

Fig. 1. The enthalpy of formation of the lanthanide(III) bromides. Key: ● Calculated using eqn. (3) from reference [3]. ○ Experimental from reference [4].

The determination of the ionic radius for a plus-four ion is complicated by the existence of ligand Pπ to Zr(IV) dπ bonding, often observable as a shortening of the metal ligand bond [12]. Our estimate of the Zr(IV) ionic radius is the mean of that from the longest Zr–I bond (3.030 Å) in ZrI_4 [13] and the two Zr–O bond lengths in $Zr(PhCOCH_2COPh)_4$ (2.153 and 2.192) [14]. Our average value for Zr(IV) is (0.84 ± 0.02) Å.

The ionic radii of the lanthanide(IV) ions have been estimated by Morss [5], and these are summarized in Table I. We have developed an alternative method of estimating the ionic radii of the plus-two lanthanides which included a break at f^7 similar to the 'gadolinium break' [2]. For the plus-four lanthanide ions a similar break is expected near Tb(IV), and we have developed the following two equations to estimate the lanthanide(IV) radii.

$$r_{M^{4+}} = 3.78/(q + 14) + 0.700 \text{ Å (Ce through Tb)} \qquad (4)$$

$$r_{M^{4+}} = 4.20/(9 + 14) + 0.680 \text{ Å (Tb through Hf)} \qquad (5)$$

The number of 4f electrons is given by the symbol q. The results from these empirical two equations are similar to the estimates given by Morss. They are summarized in Table I and are used in all subsequent calculations. Using eqn. (3), and known compounds,

---

*Author to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

TABLE I. Enthalpy of Formation Data for Lanthanide(III) Compounds.

Ln(IV)	$r_{Ln^{4+}}$, (A) [5]	$r_{Ln^{4+}}$, (A) Eqns. (4) and (5)	L_4 (ev)	Q_4 (KJ/mol)	ΔH_f° (LnO_2)[a] (KJ/mol)	$\Delta H_{decomp.}$ oxides (KJ/mol)	ΔH_f° (LnF_4)[b] (KJ/mol)	$\Delta H_{decomp.}$ fluorides (KJ/mol)	ΔH_f° ($LnCl_4$)[b] (KJ/mol)	$\Delta H_{decomp.}$ chloride (KJ/mol)
Ce	0.97	0.970	36.758[6]	7491	−1089	+190	−1910[7]	+181	−1020[13]	−38
Pr	0.96	0.952	38.98 [7]	7745	−912	+3	−1732	+10	−837	−214
Nd	0.945	0.936	40.41 [8]	7923	−804	−102	−1622	−94	−724	−315
Pm	0.93	0.922	41.1 [9]	8023	−766		−1583		−680	−352
Sm	0.915	0.910	41.4 [10]	8070	−773	−141	−1589	−134	−682	−355
Eu	0.90	0.899	42.6 [9]	8323	−569	−263	−1385	−228	−475	−448
Gd	0.89	0.889	44.0 [9]	8393	−545	−369	−1359	343	−447	−560
Tb	0.88	0.880	39.79 [8]	8018	−961	+29	−1775	+74	−859	−132
Dy	0.872	0.871	41.47 [8]	8189	−832	−100	−1645	−77	−726	−276
Ho	0.865	0.863	42.5 [9]	8324	−735	−206	−1547	−168	−625	−368
Er	0.857	0.855	42.65 [8]	8366	−730	−219	−1542	−173	−617	−375
Tm	0.849	0.848	42.69 [8]	8395	−734	−211	−1545	−170	−618	−374
Yb	0.841	0.842	43.74 [8]	8568	−590	−318	−1401	−265	−471	−471
Lu	0.835	0.836	45.19 [7]	8698	−489	−450	−1299		−367	−606
Hf	0.83	0.830	33.33[11]	8163[11]			−1930[12]			
Zr	0.84	0.840	34.34	8067[12]	−1101[12]		−1911[12]		−981[12]	
$r_{x^{n-}}$, A					1.38		1.33		1.81	
A, KJ-A/mol					−23,600		−22,160		−30,430	
B, KJ/mol					1463		+234		2435	

[a] Ce, Tb, and Zr are used to determine A and B. [b] Ce and Zr are used to determine A and B.

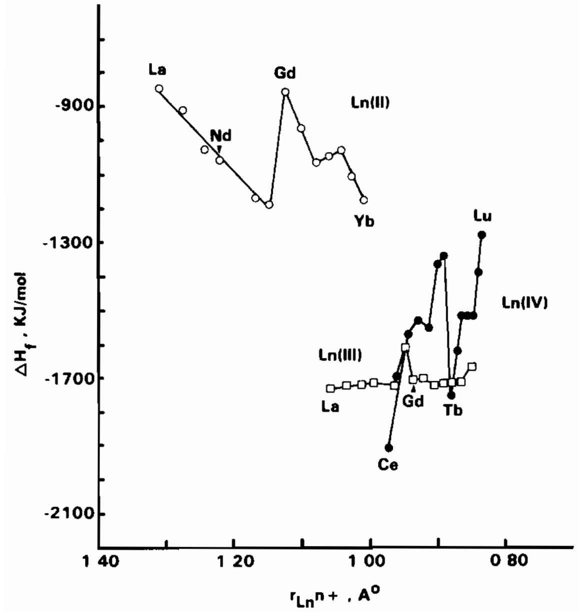

Fig. 2. The enthalpies of formation of lanthanide fluorides. Key: ○ Lanthanide(II) from reference [3]. □ Lanthanide(III) from reference [2]. ● Lanthanide(IV) from this paper.

the constants A and B have been determined for the lanthanide(IV) oxides, fluorides and chlorides. In order to predict the stabilities of the plus-four lanthanides, their decomposition compared to the plus-three lanthanides must be determined by a reaction of the type:

$$LnCl_4(s) \rightleftharpoons LnCl_3(s) + \tfrac{1}{2}Cl_2(g) \qquad (6)$$

These values, symbolized as ΔH_{decomp}, are also summarized in Table I using previously determined enthalpy of formation values for the plus-three lanthanides [2, 3]. The entropy for reaction (6) is positive and therefore ΔH_{decomp} must be positive for decomposition not to occur. We predict that CeO_2, TbO_2 and CeF_4 should be stable and all are known compounds. Other compounds which may be prepared include PrO_2, $PrCl_4$ and $CeCl_4$, but all should decompose in time. PrF_4 complexes to Lif or NaF is known with compositions such as Na_3PrF_7, Na_2PrF_6, etc., indicating that additional contributions are necessary to stabilize this species [17]. The predicted enthalpies for Pr compounds seems not quite low enough. Two possible reasons for this include the strong possibility that the fourth ionization potential is too high and needs to be remeasured and ligand field effects may be important for the higher oxidation state lanthanides. The other plus-four lanthanide oxided, fluorides and chlorides should be unstable. The data for the LnF_2, LnF_3 and LnF_4 compounds are summarized in Fig. 2.

Acknowledgement

One of us (HBS) gratefully acknowledges the support of the Robert A. Welch Foundation of Houston, Texas through Grant AX-659.

References

1 C. S. G. Phillips and R. J. P. Williams, 'Inorganic Chemistry. I. Principles and Non-metals', Oxford University Press, New York (1965), pp. 142–187.
2 S. Bratsch and H. B. Silber, *Polyhderon,* in press.
3 S. Bratsch and H. B. Silber, 'The Rare Earths in Modern Science and Technology', Vol. 3, ed. by G. J. McCarthy, J. J. Rhyne and H. B. Silber, Plenum Publishing Corp., N.Y. (1982), in press.
4 C. Hurtgen, D. Brown and J. Fuger, *J. Chem. Soc. Dalton,* 70 (1980).
5 L. R. Morss, *Chem. Rev., 76,* 827 (1976).
6 D. A. Johnson, *J. Chem. Soc. (A),* 1525 (1969).
7 D. A. Johnson, *Adv. Inorg. Chem. Radiochem., 20,* 1 (1977).
8 D. A. Johnson, *J. Chem. Soc. Dalton,* 1671 (1974).
9 L. J. Nugent, *Int. Rev. Sci, 2,* 7 (1975).
10 D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc., 76,* 5237 (1954).
11 W. C. Martin, L. Hagen, J. Reader and J. Sugar, *J. Phys Chem. Ref. Data, 3,* 771 (1974).
12 R. C. Fay, *Coord Chem. Rev., 37,* 41 (1981).
13 B. Krebs, G. Herkel and M. Dartmann, *Acta Crystallogr., B35,* 274 (1979).
14 H. K. Chun, W. L. Steffar and R. C. Fay, *Inorg. Chem., 18,* 2458 (1979).
15 'Selected Values of Chemical Thermodynamic Properties', N. B. S. Tech. Notes 270-3-7, Washington, D.C. (1973).
16 S. Bratsch, work in progress.
17 D. Brown, 'Halides of the Lanthanides and Actinides', Wiley-Interscience, N.Y. (1968), pp. 59–78.