Thermodynamics of Lanthanide Elements. Part 2.[1] Enthalpies of Formation of Erbium Trichloride and of the Aqueous Erbium(3+) Ion

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Enthalpies of solution of high-purity erbium metal and erbium trichloride in dilute hydrochloric acid media lead to the following standard enthalpies of formation (in kJ mol^{-1}) at 298.15 ± 0.10 K: $ErCl_3$(s), −994.5 ± 1.7; and Er^{3+}(aq), −708.1 ± 1.8.

In general the thermodynamic properties of lanthanide oxides and chlorides are well established but the thermochemistry of many other classes of lanthanide compounds is poorly characterized. A programme on lanthanide thermochemistry has recently been initiated with a series of determinations of the enthalpies of formation of several lanthanide tribromides.[1] During that study it became clear that basic thermochemical data for some of the lanthanides have unacceptably high uncertainty limits. In particular, to calculate the enthalpies of formation of lanthanide tribromides, enthalpies of formation of the trichlorides and of the aqueous trivalent lanthanides were used; however, in some instances, as in the case of erbium, the latter data have assessed uncertainties [2] so large that they may mask significant trends in the tribromide enthalpies of formation.

A more general need for accurate values of the enthalpies of formation of lanthanide aqueous ions arises from correlations between the energies of the gaseous atoms and their aqueous ions. Nugent *et al.*[3] introduced a function P(M) which showed regular behaviour when the enthalpy difference between the trivalent gaseous atoms (electronic configuration f^nds^2) and the trivalent aqueous ions was correlated against the number of *f* electrons. Johansson [4] has refined the P(M) function by correcting it for *f–d* coupling; the deviations between his refined P(M) values and the predicted linear plot against the number of electrons are of the order of the experimental uncertainties in some of the enthalpies of formation. Since calculations of this sort are useful in understanding the behaviour of the lanthanides and in predicting the behaviour of the heavy actinides, it is important to have accurate enthalpies of formation of aqueous lanthanide ions.

The first thermochemical investigation involving erbium metal of significant purity was that of Spedding and Flynn [5] who dissolved both Er metal and $ErCl_3$ in 1.47 mol kg^{-1} HCl. Using their enthalpies of reaction and, from currently accepted data,[6,7] the value of -163.52 ± 0.10 kJ mol^{-1} for the partial molar enthalpy of formation of hydrochloric acid in its 1.47 mol kg^{-1} aqueous solution, we calculate $\Delta H_f^\ominus(ErCl_3, s) = -958.6$ kJ mol^{-1}. Spedding and Flynn [8] also measured the enthalpy of solution of $ErCl_3$ in water, from which we calculate $\Delta H_f^\ominus(Er^{3+}, aq) = -665.7$ kJ mol^{-1}, using $\Delta H_f^\ominus(HCl, aq) = -157.08 \pm 0.09$ kJ mol^{-1}. When compared with those for other lanthanide trichlorides and aqueous ions, both of these enthalpies of formation appear abnormally small (*i.e.* not sufficiently exothermic).

More recently, Montgomery and Stuve [9] redetermined the enthalpy of formation of $ErCl_3$(s) by measuring the enthalpies of solution of $ErCl_3$ and Er_2O_3 in 1.43 mol kg^{-1} HCl, and combining these data with the enthalpy of combustion of Er_2O_3. From their measurements, the latest value for the enthalpy of combustion of Er_2O_3,[10,11] and auxiliary thermochemical data we calculate $\Delta H_f^\ominus(ErCl_3, s) = -997$ kJ mol^{-1}. Since they also measured the enthalpies of solution of $ErCl_3$ in water, we calculate from their data $\Delta H_f^\ominus(Er^{3+}, aq) = -711$ kJ mol^{-1}.

The discrepancies between the results of Spedding and Flynn and those of Montgomery and Stuve led Morss [2] to assign large uncertainty limits (± 10 kJ mol^{-1}) to assessed values of $\Delta H_f^\ominus(ErCl_3, s)$ and $\Delta H_f^\ominus(Er^{3+}, aq)$. In view of these discrepancies, and since the uncertainty limits are larger than those assigned to the other lanthanides, new measurements have been made on Er metal and $ErCl_3$.

EXPERIMENTAL

Instruments and Operating Procedure.—The calorimeter used was a LKB (Bromma, Sweden) model 8700–1 batch instrument with a glass vessel (100 cm^3), and equipped with a Hewlett-Packard (San Diego, California) model 7131 A/B strip chart recorder. The performance of the instrument was checked by measuring the enthalpy of solution of tris [tris(hydroxymethyl)aminomethane], U.S. National Bureau of Standards, Standard Reference Material No. 724a, in 0.100 mol dm^{-3} HCl solution, to obtain a concentration of *ca.* 5 g l^{-1} tris. The resultant enthalpy effect of -29.738 ± 0.022 kJ mol^{-1} (five measurements, uncertainty limits based on the 95% confidence interval) compares favourably with the N.B.S. recommended value [12] for the same batch, -29.769 ± 0.029 kJ mol^{-1}.

Samples were weighed on a Cahn (Paramount, California) model GRAM electric balance. Sample weights were reduced to weights *in vacuo*. Polycrystalline pieces of $ErCl_3$ were handled in a nitrogen-filled dry-box with moisture content below 10 p.p.m. as measured with an Alnor (Casella, London) dew-point meter. The samples were weighed directly in the LKB calorimetric ampoules before being sealed under dry nitrogen with polypropylene plugs protected by melted beeswax. Since a microscopic observation revealed, as expected, no surface tarnish of the erbium metal samples upon standing for a few days in air, freshly cut and scraped pieces of the metal were weighed in air and similarly sealed in the LKB ampoules.

Materials and Reagents.—Polycrystalline erbium metal was supplied by Rare Earth Products Ltd. (Widnes). Analytical data (*X*-ray fluorescence and spark-source spectrographic techniques) for the sample, batch BM 222, provided by the supplier were (in p.p.m.): Dy, Ho, and Tm, 100; Mg and Si, 1; Ca <1. Combustion and vacuum-fusion analysis gave the following results for light elements (in p.p.m.): O, 55; C, 45; N <10; H, 4.

Erbium trichloride was prepared from 99.9% Er_2O_3 (Labelcomat, Brussels) by dissolving 3.0 g in the minimum volume of hot 6 mol dm^{-3} HCl solution, evaporating the solution almost to dryness, and dehydrating the hydrated trichloride by heating it in a stream of dry HCl(g).[13] The product was transferred in the dry-box into a quartz tube and sublimed at 950 °C under vacuum (better than 10^{-5} mmHg),* the sublimate subsequently being melted in a side arm of the quartz tube. Upon cooling the polycrystalline trichloride detached spontaneously as a single cylindrical piece from the quartz walls. The quartz showed no trace of etching at the end of this operation. Samples of sublimed $ErCl_3$ dissolved completely in water. Chloride, 38.82 ± 0.11% (based on the 95% confidence interval for five samples from two different preparations), was determined by potentiometric titration with Ag[NO_3] (calc. for $ErCl_3$: 38.87% Cl). An *X*-ray Debye–Scherrer pattern of the sublimed $ErCl_3$ was in perfect agreement with the pattern calculated for the known structure[14] (monoclinic, space group C^3_{2h}–$C2/m$) and the lattice dimensions obtained from this pattern, $a = 6.813(15)$, $b = 11.804(24)$, $c = 6.398(10)$ Å, and $\beta = 110.76(13)°$ using the lattice-parameter refinement program LCR-2,[15] were identical within their uncertainty limits with the literature values,[14] $a = 6.80$, $b = 11.79$, $c = 6.39$ Å, and $\beta = 110.7°$.

The concentration of the hydrochloric acid used for the calorimetric dissolution of Er(s) and $ErCl_3$(s) was established by titration as 1.428 ± 0.005 mol dm^{-3}. Merck-titrated 0.100 mol dm^{-3} HCl solution was used to obtain by dilution the 10^{-3} mol dm^{-3} HCl used in the calorimetric dissolution of $ErCl_3$(s).

Units and Limits of Errors.—The joule (J) is used throughout as the energy unit and literature data originally reported in calories have been recalculated using the conversion factor 1 cal (thermochemical) = 4.184 J. The ^{12}C scale of atomic weights was used to calculate molecular weights. Uncertainty limits on the mean of several identical measurements are based on the 95% confidence interval. All calorimetric measurements are reported for 298.15 ± 0.10 K. Unless otherwise specified, auxiliary data recommended by CODATA[6] have been used.

RESULTS AND DISCUSSION

Tables 1 and 2 show the results obtained for the enthalpies of solution of erbium metal in 1.428 mol dm^{-3} HCl and those of $ErCl_3$ in 1.428 and 0.001 mol

$$Er(s) + \{aHCl,\ bH_2O\} \longrightarrow \{ErCl_3,\ (a-3)HCl,\ bH_2O\} + \tfrac{3}{2}H_2\ (g);\ \Delta H_1 \qquad (1)$$

$$ErCl_3(s) + \{aHCl,\ bH_2O\} \longrightarrow \{ErCl_3,\ aHCl,\ bH_2O\};\ \Delta H_2 \qquad (2)$$

dm^{-3} HCl, respectively. These data are summarized by equations (1) and (2), with $b/a = 37.75$ and $a =$ *ca.* 480 in 1.428 mol dm^{-3} HCl and $b/a = 55\ 500$ and $a =$ *ca.* 0.40 in 10^{-3} mol dm^{-3} HCl respectively.

TABLE 1

Enthalpy of solution of erbium metal in 1.428 mol dm^{-3} hydrochloric acid at 298.15 ± 0.10 K

Expt. no.	Wt. of sample mg	Concentration of erbium in solution 10^3 mol dm^{-3}	Enthalpy effect J	ΔH_1 * kJ mol^{-1}
1	52.84	3.159	222.05	−704.8
2	56.75	3.393	239.00	−706.3
3	57.65	3.447	242.69	−706.0
4	59.74	3.572	250.14	−702.3
5	52.99	3.168	223.46	−707.3
6	59.78	3.574	252.32	−707.9
7	51.62	3.086	216.89	−704.7
			average	−705.6 ±1.7

* Includes a correction of 1.93 kJ (mol Er)$^{-1}$ for the vaporization of the solvent by the evolved hydrogen.

The enthalpy of formation of $ErCl_3$(s), according to reaction (3), is calculated from the data in 1.428 mol

$$Er(s) + \tfrac{3}{2}Cl_2(g) \longrightarrow ErCl_3(s);\ \Delta H_3 = \Delta H_f^{\ominus}(ErCl_3,s) \qquad (3)$$

dm^{-3} HCl by use of relationships (1)—(4) which upon combination yield equation (A). $\tfrac{1}{3}\ \Delta H_4$ represents the

$$\tfrac{3}{2}H_2(g) + \tfrac{3}{2}Cl_2(g) + \{ErCl_3,\ (a-3)HCl,\ bH_2O\} \longrightarrow \{ErCl_3,\ aHCl,\ bH_2O\};\ \Delta H_4 \qquad (4)$$

$$\Delta H_3 = \Delta H_f^{\ominus}(ErCl_3,s) = \Delta H_1 - \Delta H_2 + \Delta H_4 \qquad (A)$$

partial molar enthalpy of formation of hydrochloric acid in HCl of the appropriate concentration from the elements in their standard state at 298 K, neglecting the influence of the low erbium concentration ($<4 \times 10^{-3}$ mol dm^{-3}). This value, H_f(HCl, 1.428 mol dm^{-3} HCl) = −163.52 ± 0.10 kJ mol^{-1}, is obtained as usual

TABLE 2

Enthalpies of solution of erbium trichloride in hydrochloric acid at 298.15 ± 0.10 K

Prep. no.	Expt. no.	Wt. of sample mg	Concentration of erbium in solution 10^3 mol dm^{-3}	Enthalpy effect J	ΔH_2 kJ mol^{-1}
(*a*) In 1.428 mol dm^{-3} HCl					
I	1	75.29	2.752	55.511	−201.7
I	2	77.75	2.842	57.427	−202.1
I	3	69.25	2.531	51.079	−201.8
I	4	79.07	2.890	58.220	−201.5
II	5	72.51	2.650	51.270	−201.3
II	6	71.15	2.600	52.523	−202.0
II	7	76.97	2.813	56.743	−201.7
				average	−201.7 ±0.3
(*b*) In 10^{-3} mol dm^{-3} HCl					
II	1	68.85	2.516	53.673	−213.3
II	2	61.95	2.264	48.441	−214.0
II	3	76.17	2.784	59.492	−213.7
II	4	80.43	2.939	62.658	−213.2
II	5	77.49	2.832	60.396	−213.3
II	6	72.80	2.661	56.777	−213.4
				average	−213.5 ±0.3

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

from the enthalpy of formation of the infinitely dilute acid[6] and the relative apparent molar heat content of the 1.428 mol dm^{-3} hydrochloric acid.[7] We thus obtain $\Delta H_f^\ominus(\mathrm{ErCl_3,s}) = -994.5 \pm 1.7$ kJ mol^{-1}.

In order to calculate $\Delta H_f^\ominus(\mathrm{Er^{3+}, aq})$ we have converted the enthalpies of solution of $\mathrm{ErCl_3(s)}$ in 10^{-3} mol dm^{-3} HCl (Table 2) into values at infinite dilution using the enthalpies of dilution given by Spedding *et al.*[16] For individual solutions this correction ranges from -1.26 to -1.37 kJ mol^{-1}, the absolute uncertainty on these corrections being estimated as ± 0.1 kJ mol^{-1}. The resulting enthalpy of solution of $\mathrm{ErCl_3}$ in water at infinite dilution [relationship (1) with $a = 0$ and $b = \infty$] is -214.8 ± 0.3 kJ mol^{-1}. With the above new value for $\Delta H_f^\ominus(\mathrm{ErCl_3,s})$ and $\Delta H_f^\ominus(\mathrm{HCl, aq}) = -167.08 \pm 0.09$ kJ mol^{-1}, equation (A) now yields for an infinitely dilute solution, $\Delta H_f^\ominus(\mathrm{Er^{3+}, aq}) = -708.1 \pm 1.8$ kJ mol^{-1}.

The thermochemical results of Spedding and Flynn[5] for $\mathrm{LaCl_3}$, $\mathrm{PrCl_3}$, and $\mathrm{GdCl_3}$ are consistent with more recent measurements, but their results for $\mathrm{ErCl_3}$ and $\mathrm{YCl_3}$ are significantly less exothermic than more recent data. Although their metal samples are described as ' found, by spectrographic analysis, to be free of other rare earths and all common elements ' they were prepared by calcium reduction of unsublimed trichloride and it is likely[17] that they contained oxygen since the calcium ' was sieved to remove the undersize particles and loose calcium oxide power '.[18] In addition, contamination of the products, erbium in particular, by other light elements which could not be detected by spectrographic analysis cannot be ruled out.

Recent thermochemical assessments by Schumm *et al.*,[11] Morss,[2] and Glushko *et al.*[19] give -998.7, -995 ± 10, and -992.4 ± 2.5 kJ mol^{-1}, respectively, for $\Delta H_f^\ominus(\mathrm{ErCl_3,s})$ and -705.4, -705 ± 10, and -705.8 ± 2.9 kJ mol^{-1} for $\Delta H_f^\ominus(\mathrm{Er^{3+}, aq})$. These assessments justifiably gave higher weight to the more recent result of Montgomery and Stuve[9] than to the earlier measurements of Spedding and Flynn.[5] The values obtained from the current investigation, $\Delta H_f^\ominus(\mathrm{ErCl_3, s}) = -994.5 \pm 1.7$ kJ mol^{-1} and $\Delta H_f^\ominus(\mathrm{Er^{3+}, aq}) = -708.1 \pm 1.8$ kJ mol^{-1}, reinforce these assessments and significantly decrease their uncertainty limits.

The assessed uncertainties[2] on the enthalpies of formation of the trichloride and aqueous ion of yttrium are, respectively, as large as and larger than those for erbium. Rather larger uncertainties are also given[2] for similar species of terbium and holmium. The thermochemistry of these elements will therefore be the subject of our future investigations.

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