Thermodynamics of Lanthanide Elements. Part 1. Enthalpies of Formation of Some Lanthanide Tribromides

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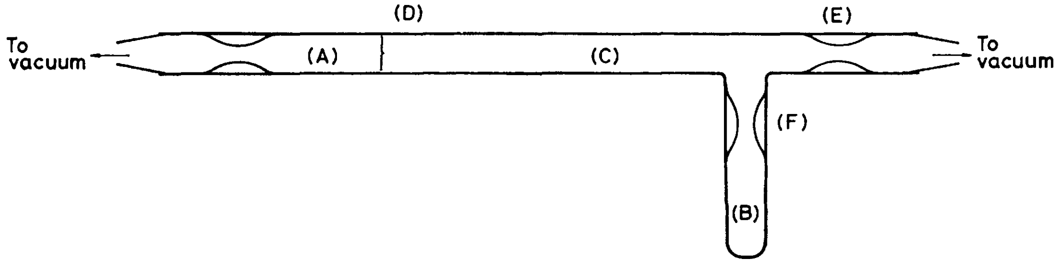
Enthalpies of solution have been measured for lanthanide tribromides (MBr_3; M = La, Pr, Nd, Sm, Gd, Dy, or Er) in 1.0, 10^{-1}, and 10^{-3} mol dm^{-3} hydrochloric acid. Combination of the resulting values with auxiliary thermodynamic data yields the following standard enthalpies of formation (in kJ mol^{-1}) at 298.15 ± 0.05 K: $LaBr_3$(s), −907.2 ± 1.7; $PrBr_3$(s), −891.4 ± 1.7; $NdBr_3$(s), −873.2 ± 1.7; $SmBr_3$(s), −857.3 ± 2.0; $GdBr_3$(s), −828.8 ± 2.4; $DyBr_3$(s), −834.1 ± 2.8; and $ErBr_3$(s), −835.8 ± 10.

SEVERAL experimental results on the enthalpies of formation of lanthanide trifluorides have been reported in recent years [1-13] and the wealth of existing data on the trichlorides, as well as the limited data available for the tri-iodides,[14,15] have been adequately assessed.[14,16] However, for the tribromides, the only experimental study has involved $EuBr_3$(s), for which the enthalpy of formation at 298.15 K is reported [17] to be -778.6 ± 12 kJ mol^{-1}. This value is based on a combination of the second-law enthalpy and Gibbs energy for the decomposition (i) with the enthalpies and Gibbs energies of

$$2\,EuBr_3(s) \rightleftharpoons 2\,EuBr_2(s) + Br_2(g) \qquad \text{(i)}$$

formation of the solid dibromide and gaseous bromine. During an investigation of the preparation of trivalent lanthanide and actinide oxide halides, MOX (X = Cl, Br, or I), high-purity samples of several lanthanide tribromides were prepared as starting materials.[18] In view of the paucity of experimental thermodynamic data on these compounds the opportunity was taken to measure their enthalpies of solution in hydrochloric acid solutions of varying molarity and to combine the results with ancillary thermodynamic data to obtain the enthalpies of formation. The results will ultimately be correlated with similar data, yet to be obtained, on lanthanide oxide bromides. In addition, when reliable experimental results are available for lanthanide dibromides, correlation with the present results will provide an understanding of the relative ease of preparation of such compounds and serve as a guide for the preparation of actinide dihalides.



Apparatus used for the preparation of lanthanide tribromides

EXPERIMENTAL

Instruments and Operating Procedure.—The microcalorimeter has been described [19] and details of calibration runs have been published.[20,21]

The tribromides were handled in a dry oxygen-free atmosphere (nitrogen). In every case the atmosphere of the boxes used during the filling and weighing of the sample holders contained less than 10 p.p.m. water vapour (Alnor Dewpoint meter, Casella, London) and less than 10 p.p.m. oxygen (potential drop across a ZrO_2 membrane).[22] Samples were weighed with a Cahn (Paramount, California) model Gram electric microbalance with an ultimate sensitivity of 0.1 μg. Sample weights were reduced to weights *in vacuo*.

Materials and Reagents.—**CAUTION:** The anhydrous tribromides were prepared (in duplicate or triplicate) by direct combination of the elements using, initially, an apparatus similar to that described [23] for the preparation of $PaBr_5$, which was essentially a silica tube with a side-arm into which bromine could be pipetted in a dry-atmosphere box. However, in one instance, a small amount of liquid bromine ran along the length of tube and on contact with the small particles of Pr metal (*ca*. 0.5 g) there was a violent explosion, resulting in complete destruction of the vessel. Subsequent brominations were therefore performed using the modified vessel shown in the Figure. With this the metal was sealed *in vacuo* in section (A) following which bromine was introduced into side-arm (B) and degassed in the usual manner. Sections (B) and (C) were then evacuated with the bromine frozen in liquid nitrogen and the tube sealed at (E), following which the break seal (D) was broken

TABLE 1

Analytical results (%) with calculated values given in parentheses

Compound	Br	M
$LaBr_3$	63.35 (63.3)	36.65 (36.7)
$PrBr_3$	62.85 (63.0)	37.0 (37.0)
$NdBr_3$	62.45 (62.45)	37.6 (37.55)
$SmBr_3$	61.45 (61.45)	38.5 (38.55)
$GdBr_3$	60.35 (60.4)	39.65 (39.6)
$DyBr_3$	59.55 (59.6)	40.3 (40.4)
$ErBr_3$	58.9 (58.9)	41.1 (41.1)

TABLE 2

Enthalpies of solution of lanthanide tribromides in aqueous hydrochloric acid at 298.15 ± 0.05 K

Compound	Preparation no.	Expt. no.	Weight of sample (mg)	Concentration of compound in solution (10^3 mol dm^{-3})	Enthalpy effect (J)	ΔH_1/ kJ mol^{-1}
$LaBr_3$						
	In 1 mol dm^{-3} HCl					
	(I)	1	5.318	1.652	2.2247	−158.4
	(I)	2	8.054	2.503	3.3763	−158.7
	(I)	3	4.978	1.547	2.0842	−158.5
					Average	−158.5 ± 0.4
	In 0.1 mol dm^{-3} HCl					
	(I)	1	6.186	1.922	2.6664	−163.2
	(I)	2	4.623	1.436	2.0028	−164.0
	(I)	3	7.875	2.447	3.4056	−163.7
	(II)	4	8.867	2.755	3.8445	−164.2
	(II)	5	5.313	1.651	2.2957	−163.6
					Average	−163.7 ± 0.5
	In 10^{-3} mol dm^{-3} HCl					
	(II)	1	4.006	1.245	1.7687	−167.2
	(II)	2	7.230	2.247	3.1816	−166.6
	(II)	3	6.950	2.160	3.0547	−166.4
	(II)	4	6.871	2.135	3.0007	−165.3
					Average	−166.4 ± 1.3
$PrBr_3$						
	In 1 mol dm^{-3} HCl					
	(II)	1	6.877	2.126	3.1030	−171.7
	(II)	2	5.217	1.613	2.3453	−171.1
	(II)	3	7.198	2.225	3.2571	−172.2
					Average	−171.7 ± 1.4
	In 0.1 mol dm^{-3} HCl					
	(I)	1	7.747	2.394	3.5843	−176.1
	(I)	2	8.214	2.539	3.8173	−176.9
	(I)	3	7.034	2.174	3.2616	−176.5
	(II)	4	4.846	1.498	2.2394	−175.9
	(II)	5	4.149	1.282	1.9171	−175.9
					Average	—176.3 ± 0.5
	In 10^{-3} mol dm^{-3} HCl					
	(I)	1	6.259	1.935	2.9272	−178.0
	(I)	2	5.743	1.775	2.6598	−176.3
	(I)	3	9.163	2.832	4.3199	−179.4
	(II)	4	6.205	1.918	2.9270	−179.6
	(II)	5	6.560	2.028	3.0269	−175.6
					Average	−177.8 ± 2.2
$NdBr_3$						
	In 0.1 mol dm^{-3} HCl					
	(I)	1	6.082	1.864	2.9287	−184.9
	(I)	2	5.248	1.608	2.5248	−184.7
	(I)	3	4.871	1.493	2.3458	−184.9
	(II)	4	4.939	1.513	2.3692	−184.2
	(II)	5	6.331	1.940	3.0275	−183.6
	(II)	6	5.520	1.691	2.6372	−183.4
	(III)	7	6.645	2.036	3.2113	−185.6
					Average	−184.5 ± 0.7
	In 10^{-3} mol dm^{-3} HCl					
	(II)	1	4.026	1.234	1.9630	−187.2
	(II)	2	5.762	1.766	2.8098	−187.2
	(II)	3	7.077	2.168	3.4483	−187.1
	(II)	4	5.464	1.674	2.6573	−186.7
	(III)	5	6.648	2.037	3.2367	−186.9
	(III)	6	8.651	2.651	4.2261	−187.6
					Average	−187.1 ± 0.3
$SmBr_3$						
	In 1 mol dm^{-3} HCl					
	(III)	1	6.704	2.022	3.2654	−190.0
	(III)	2	5.822	1.756	2.8617	−191.8
					Average	−190.9 ± 2.4 *

TABLE 2 (*Continued*)

Compound	Preparation no.	Expt. no.	Weight of sample (mg)	Concentration of compound in solution (10^3 mol dm^{-3})	Enthalpy effect (J)	ΔH_1/ kJ mol^{-1}
	In 0.1 mol dm^{-3} HCl					
	(I)	1	5.817	1.754	2.9324	−196.7
	(I)	2	6.864	2.070	3.4270	−194.8
	(II)	3	6.130	1.849	3.0619	−194.9
	(II)	4	6.884	2.076	3.4350	−194.7
	(III)	5	6.886	2.077	3.4621	−196.1
					Average	−195.4 ± 1.1
	In 10^{-3} mol dm^{-3} HCl					
	(I)	1	5.730	1.728	2.8645	−195.0
	(I)	2	6.825	2.058	3.4560	−197.5
	(I)	3	9.187	2.771	4.6743	−198.5
	(II)	4	2.301	0.6939	1.1703	−198.4
	(III)	5	5.952	1.795	2.9661	−194.4
					Average	−196.8 ± 2.4
$GdBr_3$	In 1 mol dm^{-3} HCl					
	(I)	1	6.061	1.796	3.2825	−215.0
	(I)	2	4.708	1.395	2.5535	−215.3
	(I)	3	8.037	2.382	4.3361	−214.2
					Average	−214.8 ± 1.4
	In 0.1 mol dm^{-3} HCl					
	(I)	1	6.761	2.004	3.7557	−220.5
	(I)	2	7.603	2.253	4.2330	−221.0
	(I)	3	7.273	2.155	4.0313	−220.0
	(II)	4	3.654	1.083	2.0139	−218.8
	(II)	5	4.493	1.332	2.4826	−218.3
					Average	−219.9 ± 1.1
	In 10^{-3} mol dm^{-3} HCl					
	(II)	1	2.787	0.8260	1.5453	−220.1
$DyBr_3$	In 1 mol dm^{-3} HCl					
	(I)	1	3.311	0.9685	1.8015	−218.8
	(I)	2	2.739	0.8012	1.4907	−218.9
	(I)	3	6.789	1.986	3.6963	−219.0
					Average	−218.9 ± 0.3
	In 0.1 mol dm^{-3} HCl					
	(I)	1	5.418	1.585	3.0168	−224.0
	(I)	2	8.065	2.359	4.5150	−225.2
	(I)	3	5.243	1.534	2.9121	−223.4
	(II)	4	3.637	1.064	2.0059	−221.8
	(II)	5	1.518	0.4440	0.8360	−221.5
					Average	−223.2 ± 1.8
	In 10^{-3} mol dm^{-3} HCl					
	(II)	1	3.119	0.9123	1.7601	−227.0
$ErBr_3$	In 1 mol dm^{-3} HCl					
	(I)	1	8.411	2.431	4.6725	−226.1
	(I)	2	6.630	1.917	3.6729	−225.5
	(I)	3	8.506	2.459	4.7296	−226.3
					Average	−226.0 ± 1.0
	In 0.1 mol dm^{-3} HCl					
	(I)	1	6.233	1.802	3.5511	−231.9
	(I)	2	5.268	1.523	2.9786	−230.1
	(I)	3	6.425	1.857	3.6691	−232.4
	(II)	4	4.387	1.268	2.4909	−231.1
	(II)	5	6.018	1.740	3.3740	−228.2
					Average	−230.7 ± 2.1

[*] The uncertainty limit of ±11.4 based on the 95% confidence interval is unrepresentative, therefore the uncertainty limit obtained with $SmBr_3$ in 10^{-3} mol dm^{-3} HCl was used.

before the bromine had liquefied. The brominations proceeded readily at 500 °C, after which excess of bromine was condensed into (B) which was sealed at (F). The products were sublimed at 900—1 000 °C; they were resublimed immediately before the calorimetric runs.

The lanthanide metals (Rare Earth Products Ltd., >99.99% purity) were provided by Mr. J. T. Dalton (Chem. Div., A.E.R.E., Harwell). Commercially available bromine (B.D.H. Ltd.) was used without purification other than degassing as described above. The reaction vessels were heated (*ca.* 500 °C) under a continuously pumping vacuum prior to use and transported to an inert-atmosphere box without exposure of the inner walls to the atmosphere.

Merck-titrated 1.000 and 0.100 mol dm^{-3} hydrochloric acid solutions were used. The 10^{-3} mol dm^{-3} HCl solution was obtained by dilution of the latter.

Analysis.—The tribromides were dissolved in 2 mol dm^{-3} HNO_3 and bromide precipitated and weighed as the silver salt. The lanthanide elements were then precipitated by addition of an aqueous ammonia–acetone mixture. After filtration and ignition (700 °C) they were weighed as the sesquioxide (La, Nd, Sm, Gd, Dy, or Er) or higher oxide (Pr_6O_{11}). The results are listed in Table 1. Analytical data pertaining to one preparation only (I) of each compound are listed, since results for the analyses of the other preparations were not significantly different. *X*-Ray powder photographs of the products contained no extraneous lines.

Units and Limits of Error.—The joule (J) is used throughout as the energy unit. All literature data originally reported in calories were recalculated using the conversion factor 1 cal (thermochemical) = 4.184 J. The ^{12}C scale of atomic weights [24] was used to calculate molecular weights. All the calorimetric measurements are reported for 298.15 ± 0.05 K.

Uncertainty limits on the mean of several identical measurements and representing the consistency of the measurements are based on the 95% confidence interval [25] except where stated (*cf.* Table 2). When combining the new results with data from other sources no attempt has been made to retain this limit; the error stated by the author has been accepted. The errors quoted for the calculated enthalpies of formation have been obtained from the errors on the individual terms of the thermodynamic cycle used, according to a standard procedure.[26] Unless otherwise specified, auxiliary data recommended by CODATA or values consistent with the CODATA selection have been employed.[27, 28]

RESULTS AND DISCUSSION

Table 2 shows the results obtained for the dissolution of the lanthanide tribromides (MBr_3; M = La, Pr, Nd, Sm, Gd, Dy, or Er) in 1.0, 10^{-1}, and 10^{-3} mol dm^{-3} hydrochloric acid. The reactions can be represented by equation (1), in which b/a = 54.4, 553, and 55 500 for

$$MBr_3(s) + a\,HCl,\ b\,H_2O \longrightarrow MBr_3,\ a\,HCl,\ b\,H_2O;\quad \Delta H_1 \qquad (1)$$

1.0, 10^{-1}, and 10^{-3} mol dm^{-3} HCl, respectively, with *a* ranging from *ca.* 400 to 1 200, 40 to 200, and 0.4 to 1.4 for the three different solutions.

TABLE 3

Enthalpies of formation (kJ mol^{-1}) of the trivalent M^{3+} ions

M	ΔH_f (M^{3+}, 1 mol dm^{-3} HCl) *	ΔH_f (M^{3+}, 0.1 mol dm^{-3} HCl) *	ΔH_f (M^{3+}, 10^{-3} mol dm^{-3} HCl) *	$\Delta H_f^{\ominus}$ (M^{3+}, aq) (ref. 16)
La	−708.1 ± 1.7	−708.5 ± 1.6	−708.5 ± 1.6	−709.4 ± 1.6
Ce				−700.4 ± 2.1
Pr	−704.9 ± 1.7	−705.3 ± 1.6	−705.3 ± 1.6	−706.2 ± 1.6
Nd		−695.7 ± 1.7	−695.7 ± 1.7	−696.6 ± 1.7
Pm				
Sm	−689.8 ± 1.7	−690.2 ± 1.7	−690.2 ± 1.7	−691.1 ± 1.7
Eu				−605.6 ± 2.3
Gd	−685.7 ± 2.1	−686.1 ± 2.1		−687.0 ± 2.1
Tb				−698 ± 6
Dy	−694.8 ± 2.8	−695.1 ± 2.8		−695.9 ± 2.8
Ho				−707 ± 8
Er	−703.6 ± 10	−704.1 ± 10		−705 ± 10
Tm				−705.2 ± 3.0
Yb				−674.5 ± 3.0
Lu				−702.6 ± 2.6

* Values corrected for M^{3+} concentration in each medium (see text). One decimal place figure has been retained throughout to preserve the internal consistency of our calculations.

The enthalpies of formation of the tribromides, according to reaction (2), can be calculated by use of relationships (1), (3), and (4), which, upon combination, yield equation (5).

$$M(s,\alpha) + \tfrac{3}{2}\,Br_2(l) \longrightarrow MBr_3(c);\quad \Delta H_2 = \Delta H_f^{\ominus}(MBr_3,s) \qquad (2)$$

$$\tfrac{3}{2}\,Br_2(l) + \tfrac{3}{2}\,H_2(g) + MCl_3,(a-3)\,HCl,\ b\,H_2O \longrightarrow MBr_3,\ a\,HCl,\ b\,H_2O;\quad \Delta H_3 \qquad (3)$$

$$M(s,\alpha) + a\,HCl,\ b\,H_2O \longrightarrow MCl_3,\ (a-3)\,HCl,\ b\,H_2O + \tfrac{3}{2}\,H_2\,(g);\quad \Delta H_4 \qquad (4)$$

$$\Delta H_f^{\ominus}(MBr_3,\,s) = \Delta H_3 + \Delta H_4 - \Delta H_1 \qquad (5)$$

$\tfrac{1}{3}\,\Delta H_3$ represents the partial molar enthalpy of formation of hydrobromic acid from the elements in their standard states at 298 K, in hydrochloric acid of the appropriate concentration, *viz.* 1.0, 10^{-1}, or 10^{-3} mol dm^{-3}. The values, H_f(HBr, 1.0 mol dm^{-3} HCl) = −119.37 ± 0.04 kJ mol^{-1}, H_f(HBr, 10^{-1} mol dm^{-3} HCl) = −120.80 ± 0.04 kJ mol^{-1}, and H_f(HBr, 10^{-3}

TABLE 4

Enthalpies of formation (kJ mol^{-1}) * of the tribromides at 298.15 ± 0.05 K

Compound	From 1 mol dm^{-3} HCl data	From 0.1 mol dm^{-3} HCl data	From 10^{-3} mol dm^{-3} HCl data	Recommended value
$LaBr_3$	-907.7 ± 1.8	-907.2 ± 1.7	-906.4 ± 2.1	-907.2 ± 1.7
$PrBr_3$	-891.3 ± 2.2	-891.4 ± 1.7	-891.8 ± 2.7	-891.4 ± 1.7
$NdBr_3$		-873.6 ± 1.8	-872.9 ± 1.7	-873.2 ± 1.7
$SmBr_3$	-857.0 ± 2.9	-857.2 ± 2.0	-857.7 ± 2.9	-857.3 ± 2.0
$GdBr_3$	-829.0 ± 2.5	-828.6 ± 2.4		-828.8 ± 2.4
$DyBr_3$	-834.0 ± 2.8	-834.3 ± 3.3		-834.1 ± 2.8
$ErBr_3$	-835.7 ± 10	-835.8 ± 10		-835.8 ± 10

* One decimal place figure has been retained throughout to preserve the internal consistency of our calculations.

mol dm^{-3} HCl) = **-121.42 ± 0.04 kJ mol^{-1}** * were, as is usual, obtained from the enthalpy of formation of the infinitely dilute acid and the relative apparent molar heat content of the hydrobromic acid solutions.[28,29] The customary assumption was made that the apparent enthalpy of formation of hydrobromic acid is the same in hydrochloric acid as in hydrobromic acid of the same molality, neglecting the influence of the lanthanide ion.

ΔH_4 corresponds to the enthalpy of formation of the trivalent cation in the acid of the appropriate concentration. The values employed (Table 3) are derived from those selected by Morss [16] for $\Delta H_f^\ominus(M^{3+}, aq)$ using a small correction for the non-infinite dilution of the cation.[14] This correction ranged from 0.6 to 0.9 kJ mol^{-1} depending on the average M^{3+} concentration used in each series of experiments in a given [HCl]. The enthalpy of formation of the cations in 1 mol dm^{-3} HCl was taken as 0.4 kJ mol^{-1} less negative than that in 0.1 mol dm^{-3} HCl by analogy with the accepted variation of the enthalpies of solution of $PuCl_3$ [30] and $AmCl_3$ [31] with acid concentration. This correction is smaller than the accepted uncertainty limits on each $\Delta H_f^\ominus(M^{3+}, aq)$ value.

The resulting enthalpies of formation are listed in Table 4. They differ appreciably from previous estimates [32,33] for the enthalpies of formation of lanthanide tribromides suggesting that such values for the compounds not included in the current investigation should be treated with caution.

The trend in the enthalpy of solution of the tribromides throughout the lanthanide series is quite apparent from the results in Table 2. Interpolation of these data as a function of the lanthanide ionic radii [34] gives for $EuBr_3(s)$ a value which yields for this compound an enthalpy of formation at least 10 kJ mol^{-1} less negative than that reported by Haschke [17] (-778.6 ± 12 kJ mol^{-1}), thus being marginally within the uncertainty limits given by this author. We hope to improve this situation during an investigation of the enthalpies of formation of europium-(II) and -(III) bromides and iodides.

We thank Mr. F. Watelet for assistance in the operation of the calorimeter, and express our appreciation to the Institut Interuniversitaire des Sciences Nucléaires (Brussels) for support of the Laboratory of Radiochemistry (Liège). This work was also supported by a Euratom grant to C. H. during his period of attachment to Harwell from the University of Liège.

[9/223 *Received, 12th February,* 1979]

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* In 10^{-3} mol dm^{-3} HCl, the dissolution of the salt yields a bromide concentration two to seven times that of the chloride, the average concentration being *ca.* 6×10^{-3} mol dm^{-3} Br^-. Therefore, for that medium, we have used for $\frac{1}{3}\,\Delta H_3$ the best approximation, which is the integral enthalpy of formation of hydrobromic acid at an overall halide concentration of *ca.* 7×10^{-3} mol dm^{-3} minus the integral enthalpy of dilution of hydrohalic acid from 10^{-3} mol dm^{-3} to infinite dilution.

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