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The enthalpies of formation of lanthanide compounds
III. $Ln_2O_3(cr)$

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Abstract

The enthalpies of formation of the lanthanide sesquioxides have been evaluated from the experimental data available in literature. All experimental results have been re-calculated to obtain a consistent set of data compatible with the assessed values for the lanthanide trihalides and the aqueous lanthanide trivalent ions, as reported previously. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The lanthanide sesquioxides form an interesting series of compounds, whose properties are of scientific as well as technological interest. They can occur in five different polymophic forms, of which three are stable at room temperature [1,2]. The hexagonal form is typical for the light lanthanide oxides La_2O_3 through Pm_2O_3. The monoclinic form has been identified as the stable room-temperature form for Sm_2O_3, Eu_2O_3 and Gd_2O_3, whereas Tb_2O_3 through Lu_2O_3 are cubic. However, the energy difference between these forms is small and in the middle of the lanthanide sesquioxide series different forms can co-exist at room temperature (see Table 1).

The study of their thermochemical properties dates back to the beginning of the 20th century, when the first combustion calorimetric experiments of lanthanum metal were performed by Muthmann and Weis [3]. At that time the separation chemistry was not yet sufficiently developed and the measurements up to the 1950s are in general made with materials of poor quality, especially when metals were employed. From 1950s onwards, the lanthanide metals became available in very pure form and the properties of their compounds were studied extensively. In their review of 1960, Spedding and Daane [4] gave an excellent description of the difficulties related to the production of pure materials. They also listed the enthalpies of formation of almost all lanthanide sesquioxides, principally based on the combustion calorimetric studies performed at Los Alamos Laboratory. These measurements will be discussed in the present paper in which we present a critical assessment of the standard molar enthalpies of formation of the lanthanide sequioxides, Ln_2O_3. This work is part of our study of the thermochemical properties of the lanthanide elements and their compounds. In previous papers, we have reported a consistent set of values for the enthalpies of

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formation of the trihalides $LnCl_3$, $LnBr_3$ and LnI_3 [5] and the aqueous trivalent ions [6], which are strongly linked to those of the sesquioxides.

Table 1
Structural properties of the lanthanide sesquioxides at room temperature and standard pressure [2][a]

Hexagonal $P\bar{3}m1$	Monoclinic C2/m	Cubic $Ia\bar{3}$
La_2O_3		
Ce_2O_3		
Pr_2O_3		
Nd_2O_3		
$\mathit{Pm_2O_3}$	Pm_2O_3	$\mathit{Pm_2O_3}$
	Sm_2O_3	$\mathit{Sm_2O_3}$
	Eu_2O_3	$\mathit{Eu_2O_3}$
	Gd_2O_3	$\mathit{Gd_2O_3}$
		Tb_2O_3
		Dy_2O_3
		Ho_2O_3
		Er_2O_3
		Tm_2O_3
		Yb_2O_3
		Lu_2O_3

[a] The metastable forms are shown in italics.

2. Methods

In general, two calorimetric techniques are used to determine the enthalpy of formation at 298.15 K of the lanthanide sesquioxides: enthalpy-of-solution calorimetry and combustion calorimetry. The derivation of the enthalpies of formation of the lanthanide sesquioxides from the solution calorimetry data was done using the following schemes of the thermochemical reactions. The principal scheme is based on the dissolution of the lanthanide metal as well as the lanthanide sesquioxide in hydrogen-saturated hydrochloric acid HCl(sln):

$2Ln(cr) + 6HCl\ (sln\ in\ 'A') = 2LnCl_3\ (sln\ in\ 'A') + 3H_2(g)$ $\Delta_r H^0$ (1)
$Ln_2O_3(cr) + 6HCl\ (sln\ in\ 'A') = 2LnCl_3\ (sln\ in\ 'A') + 6H_2O\ (sln\ in\ 'A')$ $\Delta_r H^0$ (2)
$3H_2(g) + 3/2O_2(g) + ('A') = 3H_2O\ (sln\ in\ 'A')$ $\Delta_r H^0$ (3)
$2Ln(cr) + 3/2O_2(g) = Ln_2O_3(cr)$ $\Delta_r H^0$ (4)

The standard molar enthalpy of formation of $Ln_2O_3(s)$ equals to $\Delta_r H^0$ (4), and can be calculated as:

$$\Delta_f H^0\ (Ln_2O_3,\ cr,\ 298.15\ K) = \Delta_r H^0(4) = \Delta_r H^0(1) - \Delta_r H^0(2) + \Delta_r H^0\ (3)$$

The enthalpy of solution of the lanthanide sesquioxide can also be obtained from a scheme based on the dissolution of the lanthanide trihalide:

$Ln_2O_3(cr) + 6HCl\ (sln\ in\ 'A') = 2LnCl_3\ (sln\ in 'A') + 3H_2O(sln)$ $\Delta_r H^0$ (2)
$2Ln(cr) + 3Cl_2(g) = 2LnCl_3(s)$ $\Delta_r H^0$ (5)
$2LnCl_3(cr) + (sln\ in\ 'A') = 2LnCl_3\ (sln\ in\ 'A')$ $\Delta_r H^0$ (6)
$3H_2(g) + 3Cl_2\ (standard\ state) + ('A') = 6HCl\ (sln\ in\ 'A')$ $\Delta_r H^0$ (3)
$3H_2(g) + 3/2O_2(g) + ('A') = 3H_2O\ (sln\ in\ 'A')$ $\Delta_r H^0$ (7)
$2Ln(cr) + 3/2O_2(g) = Ln_2O_3(cr)$ $\Delta_r H^0$ (4)

For this reaction sequence: $\Delta_f H^0(Ln_2O_3,\ cr,\ 298.15\ K) = \Delta_r H^0(4) = -\Delta_r H^0(2) + \Delta_r H^0(5) + \Delta_r H^0(6) - \Delta_r H^0(3) + \Delta_r H^0\ (7)$. It is evident that both schemes are in many cases interrelated and only in case the enthalpy of formation of the chloride is not based on the inverse scheme, this thermochemical cycle can be applied.

The enthalpies of solution of Ln(cr) and $Ln_2O_3(cr)$ are generally measured in HCl solutions (solvent 'A').

Therefore, the $1/3\Delta_r H^0$ (3) and $1/3\Delta_r H^0$ (7) represents the partial molar enthalpy of formation of H_2O(sln) from the elements in their standard states at 298.15 K in hydrochloric acid of the appropriate concentration. The values, $\Delta_f H^0$ (H_2O, sln in 'A'), were obtained from the enthalpy of formation of the infinitely dilute acid [7] and the relative apparent molar heat content of the HX solutions [8]. A listing of the values used can be found in part I of this series [5].

The experimental values for $\Delta_r H^0$ (1), the enthalpy of solution of the lanthanide metal, and $\Delta_r H^0$ (6), the enthalpy of solution of lanthanide trichloride, have been reviewed in detail in our assessment of the lanthanide trihalides [5] and the reader is referred to that publication for details. In this report only those data relevant to the present assessment will be discussed.

In the combustion calorimetric studies $\Delta_r H^0$ (4), the enthalpy of reaction of the metal with oxygen is measured directly. An additional method for the determination of the enthalpies of formation of the lanthanide sesquioxides involves a 'third-law' analysis of oxygen partial pressures above the sesquioxide as a function of the temperature. However, in view of the uncertainties related to this type of evaluation (phase definition, absolute entropy and heat capacity of the compounds), we decided to omit these measurements from this evaluation.

All data have been stored in a spreadsheet and have been processed simultaneously with those for the lanthanide trihalides $LnCl_3$, $LnBr_3$ and LnI_3 [5], and the aqueous lanthanide ions [6]. Uncertainty limits of the measurements, as listed in the tables, are always the values given in the original paper, because in many cases they could not be recalculated due to lack of information. As a consequence they might refer to one standard deviation of the mean, twice the standard deviation of the mean, or the 95% confidence interval, which is not always clear. When combining data from different sources to a selected value, a weighted mean is therefore considered not justified and the uncertainty limit of the selected (mean) value has been estimated.

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. Unless otherwise stated, the calorimetric measurements are reported for 298.15 K.

3. Results

3.1. La_2O_3(cr)

The values obtained for the standard enthalpy of formation of hexagonal lanthanum sesquioxide are summarized in Table 2. The early investigators reported a wide range of values which are mainly of historical interest due to the impurity levels of the samples used in those days. Huber and Holley [9] determined the enthalpy of formation by combustion of very pure sample of metal. This value has been confirmed by several authors using solution calorimetry [10,12].

These experiments are based on the dissolution reactions of La_2O_3(cr) and La(cr) in HCl(aq). However, the values for the enthalpy of solution of La(cr) show significant variation. For example, the enthalpy of solution in $1.0\ \mathrm{mol\ dm^{-3}}$ HCl(aq) measured by Fitzgibbon et al. [11], Gvelesiani and Yashvili [12] and Merli et al. [13] differ by maximum $3.6\ \mathrm{kJ\ mol^{-1}}$. We consider the results of Merli et al. [13] the most accurate since they made their measurements on a well-defined sample. Therefore, the results of the other studies have been recalculated using the values from this study, some obtained by inter- or extrapolation. The resulting enthalpies of formation are in excellent agreement with the combustion value. The selected value is the mean of the combustion value by Huber and Holley [9], and the recalculated values obtained from and the enthalpy of solution measurements Montgomery and Hubert [10], Fitzgibbon et al. [11], and Gvelesiani and Yashvili [12].

$$\Delta_f H^0(\mathrm{La_2O_3, cr, 298.15\,K}) \\ = -(1791.6 \pm 2.0)\,\mathrm{kJ\,mol^{-1}}$$

3.2. Ce_2O_3(cr)

Several combustion calorimetric studies of the enthalpy of formation of Ce_2O_3 have been reported, as shown in Table 3. Unlike the other actinide sequioxides they do not refer to the reaction $M(cr)+ 3/2O_2(g) = M_2O_3$, but to the reaction $Ce_2O_3(cr)+ 1/2O_2(g) = 2CeO_2(cr)$. The results for the enthalpy of reaction are discordant and when they are recombined with the assessed enthalpy of formation of CeO_2

Table 2
The enthalpy of formation of La_2O_3(cr) at 298.15 K[a]

References	Year	Method[b]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Muthmann and Weiss [3]	1904	C			−1857.7
Matignon [51]	1906	S			−1789.0
Kremers and Stevens [52]	1923	C			−1912.1
Moose and Parr [53]	1924	C			−1907.1
Beck [54]	1930	S (?)		−439.3	
Roth et al. [55]	1940	C			−2255 ± 17
Huber and Holley [9]	1953	C			−1793.1 ± 0.8
Wartenberg [56]	1959	S (0.1)		−468.6 ± 6.3	
Montgomery [10]	1959	S (0.51)	(−704.1 ± 1.2)[c]	−474.4 ± 1.6	−1791.3 ± 2.5
Fitzgibbon et al. [11]	1965	S (1.0)	−705.5 ± 1.3	−474.4 ± 0.4	−1794.2 ± 2.7
			(−704.4 ± 1.2)[13]		−1792.0 ± 2.7
		S (1.0)	−705.6 ± 1.3	−473.8 ± 0.4	−1794.8 ± 2.7
			(−704.4 ± 1.2)[13]		−1792.5 ± 2.7
Gvelesiani and Yashvili [12]	1967	S (1.0)	−708.0 ± 2.0	−475.3 ± 3.3	−1798.2 ± 5.2
			(−704.4 ± 1.2)[13]		−1791.0 ± 4.1
		S (1.5)	−708.8 ± 2.9	−475.3 ± 1.8	−1799.9 ± 6.1
			(−704.7 ± 1.2)[c]		−1791.7 ± 3.0
Oppermann et al. [57]	1997	S (4.0)	(−706.2 ± 1.1)[c]	−472.6 ± 0.3	−1798.2 ± 2.4
Selected value					−1791.6 ± 2.0

[a] ; ΔH_1^0 is the enthalpy of solution of La(cr), ΔH_2^0 of La_2O_3(cr) in HCl(aq).

[b] C: combustion calorimetry; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.

[c] Estimated/interpolated from the results of Merli et al. [13].

(see Appendix A), values varying from −1823.4 to −1790.2 kJ mol^{-1} are obtained. This variation may be due to: (i) differences in the O/M ratio of the starting material Ce_2O_3(cr); (ii) impurities in Ce_2O_3(cr) resulting from the fabrication by reduction of the dioxide (e.g. residual carbon has a big impact on the combustion values); and (iii) differences in the final state of the reaction product CeO_2 that is known to have a large range of substoichiometric compositions.

Huntelaar et al. [14] measured the enthalpy of solution of a well-defined sample of Ce_2O_3(cr) in 0.25 mol dm^{-3} HCl(aq) from which the enthalpy of formation is derived as $\Delta_f H^0(298.15\,\mathrm{K}) = -(1813.1 \pm 0.8)$ kJ mol^{-1}, using a reaction cycle based on the

Table 3
The enthalpy of formation of Ce_2O_3(cr) at 298.15 K[a]

References	Year	Method[b]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Kuznetsov et al. [58]	1960	C			−1823.4 ± 1.8[c]
Mah [59]	1961	C			−1790.2 ± 1.5[d]
Baker et al. [60]	1968	C			−1799.8 ± 1.7[e]
Huntelaar et al. [14]	2000	S (0.25)	(−699.2 ± 0.2) [15]	−442.7 ± 0.6	−1813.1 ± 0.8
					−1813.2 ± 3.2[f]
Putnam [16]	2000	H			−1809.2 ± 5.2
Selected value					−1813.0 ± 2.0

[a] ΔH_1^0 and ΔH_2^0 are the enthalpies of solution of Ce(cr) and Ce_2O_3(cr) in HCl(aq), respectively.

[b] C: combustion calorimetry; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}; H: high temperature oxide melt solution calorimetry.

[c] For the enthalpy of the reaction $Ce_2O_3(cr) + 1/2O_2(g) = 2CeO_2(cr)$, the following value was reported: −357.4 ± 1.1 kJ mol^{-1}.

[d] For the enthalpy of the reaction $Ce_2O_3(cr) + 1/2O_2(g) = 2CeO_2(cr)$, the following value was reported: −390.6 ± 0.4 kJ mol^{-1}.

[e] For the enthalpy of the reaction $Ce_2O_3(cr) + 1/2O_2(g) = 2CeO_2(cr)$, the following value was reported: −381.0 ± 0.7 kJ mol^{-1}.

[f] Cycle based on $CeCl_3$.

enthalpy of solution of Ce(cr) reported by Spedding and Miller [15]. The value $\Delta_f H^0(298.15\,\mathrm{K}) = -(1813.2 \pm 3.2)\,\mathrm{kJ\,mol^{-1}}$ is obtained when we use the enthalpy of solution of $CeCl_3$(cr) reported by Spedding and Miller [15] and our selected value for the enthalpy of formation of this compound [5]. Putnam et al. [16] measured the enthalpy of formation by high-temperature oxide-melt solution calorimetry. Recalculating their measurements with our selected value for the enthalpy of formation of CeO_2, we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(1813.2 \pm 5.2)\,\mathrm{kJ\,mol^{-1}}$. These results are preferred over the earlier high-temperature equilibrium studies for reasons given above. The recommended value for the standard enthalpy of formation of Ce_2O_3(cr) is the mean, weighted toward the simpler and more precise dissolution cycle.

$$\Delta_f H^0(298.15\,\mathrm{K}) = -(1813.2 \pm 5.2)\,\mathrm{kJ\,mol^{-1}}$$

3.3. Pr_2O_3(cr)

There are two solution calorimetric studies on the standard enthalpy of formation of hexagonal praseodymium sesquioxide; the results are presented in Table 4. The first value was reported by Stubblefield et al. [17] and based on the results of the determination of the enthalpy of reaction of Pr_2O_3(cr) with $6.0\,\mathrm{mol\,dm^{-3}}$ HNO_3(aq). When this value is combined with the literature value for the enthalpy of solution of the metal in the same medium [18], the value $-(1831.6 \pm 3.5)\,\mathrm{kJ\,mol^{-1}}$ is obtained. This approach is, however, not reliable since some of the hydrogen that is produced during dissolution of the metal, might reduce the nitric acid.

Fitzgibbon et al. [19] obtained the enthalpy of formation of Pr_2O_3(cr) by measuring the solution enthalpies of both Pr(cr) and Pr_2O_3(cr) in 2.0 mol

Table 4
The enthalpies of formation of Pr_2O_3(cr), Eu_2O_3(cr) and Gd_2O_3(cr) at 298.15 K[a]

References	Year	Method[b]	ΔH_1^0 ($\mathrm{kJ\,mol^{-1}}$)	ΔH_2^0 ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f H^0$ ($\mathrm{kJ\,mol^{-1}}$)
Pr_2O_3					
Stubblefield et al. [17]	1956	S (6.0)	$(-1020.9 \pm 3.4)^d$	-447.7 ± 0.8^c	-1831.6 ± 3.5
Fitzgibbon et al. [19]	1973	S (2.0)	-692.2 ± 1.3	-432.0 ± 1.4	-1809.9 ± 3.0
Selected value					-1809.9 ± 3.0
Eu_2O_3					
Huber et al. [31]	1964	C			-1648.1 ± 3.8
Yashvili and Gvelesiani [34]	1971	S (1.0)	-632.6 ± 3.8	-397.5 ± 3.8	-1725.5 ± 8.5
			$(-607 \pm 4)^e$		-1674.0 ± 8.9
Fitzgibbon et al. [32]	1972	C			-1651.0 ± 3.8
		S (4.0)	-605.2 ± 2.9	-416.8 ± 1.5	-1652.0 ± 6.0
		S (6.0)	(-589.9 ± 2.9) [33]	-415.2 ± 2.7	-1624.5 ± 6.4
			$(-603 \pm 4)^e$		-1650.7 ± 8.0
Hennig et al. [35]	1998	S (4.0)	(-583.0 ± 2.5) [36]	-338.3 ± 0.3	-1686.2 ± 5.0
					-1730.6 ± 5.8^f
Selected value					-1650.4 ± 4.0
Gd_2O_3					
Huber and Holley [37]	1955	C			-1819.7 ± 3.6
Spedding et al. [20]	1959	C			-1782.2
Yashvili and Gvelesiani [34]	1971	S (6.0)	-694.5 ± 1.7	-422.6 ± 1.3	-1826.3 ± 3.7
			(-694.9 ± 1.0) [13]		-1829.5 ± 2.6
					-1828.2 ± 3.6^g
Selected value					-1819.7 ± 3.6

[a] ΔH_1^0 and ΔH_2^0 are the enthalpies of solution of Ln(cr) and Ln_2O_3(cr) in HCl(aq), respectively.

[b] C: combustion calorimetry; S: solution calorimetry; values in parentheses give the concentration of the solvent in $\mathrm{mol\,dm^{-3}}$.

[c] The enthalpy of solution in HNO_3(aq).

[d] The enthalpy of solution of Pr in $6.0\,\mathrm{mol\,dm^{-3}}$ HNO_3(aq) [18].

[e] Estimated.

[f] Using ΔH_1^0 Baker et al. [32].

[g] Cycle based on $GdCl_3$ Merli et al. [13].

Table 5
The enthalpy of formation of Nd_2O_3(cr) at 298.15 K[a]

References	Year	Method[b]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Muthmann and Weiss [3]	1904	C			−1820
Matignon [61]	1907	S (0.5)		−441.4	
Huber and Holley [21]	1952	C			−1808.1 ± 1.0
Spedding et al. [15]	1952	C			−1798.2
					−1789.2
Fitzgibbon et al. [24]	1968	S (2.0)	(−691.7 ± 1.5)[c]	−434.0 ± 0.6	−1807.1 ± 3.1
		S (4.0)	(−693.6 ± 1.5) [25]	−438.3 ± 1.3	−1807.3 ± 2.2
Yashvili and Gvelesiani [34]	1971	S (1.0)	(−689.6 ± 2.0) [13]	−434.7 ± 2.1	−1799.6 ± 4.5
Morss et al. [62]	1989	S (6.0)	(−695.7 ± 1.8) [13]	−419.6 ± 6.0	−1831.7 ± 7.0
Popova and Monaenkova [22]	1989	S (2.19)	−686.8 ± 1.0	−434.2 ± 0.7	−1797.1 ± 2.1
			(−686.8 ± 1.0) [23]		−1805.1 ± 3.3
			(−691.9 ± 1.6) [23]		−1807.3 ± 4.1
Hennig and Oppermann [26]	1998	S (4.0)	(−691.7 ± 1.5)[c]	−419.5 ± 0.4	−1816.1 ± 1.9
Selected value					−1806.9 ± 3.0

[a] ΔH_1^0 and ΔH_2^0 are the enthalpies of solution of Nd(cr) and Nd_2O_3(cr) in HCl(aq), respectively.
[b] C: combustion calorimetry; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[c] Estimated by present authors from the data of Merli et al. [13].

dm^{-3} HCl(aq). Taking into the consideration the purity of the samples and the general quality of the determination, their measurements are selected here as the most reliable and best documented. From the results we calculate

$$\Delta_f H^0(Pr_2O_3, cr, 298.15\,K) = -(1809.9 \pm 3.0)\ kJ\,mol^{-1}$$

3.4. Nd_2O_3(cr)

The standard enthalpy of formation of hexagonal neodymium sesquioxide has been determined by solution as well as combustion calorimetry, as shown in Table 5. The early investigations are mainly of historical interest due to the poor quality of experimental techniques and samples used in those days. There are three combustion calorimetric measurements of the enthalpy of formation of Nd_2O_3(cr) [3,20,21]. Although the results are in reasonable agreement, the value of Huber and Holley [21], $\Delta_f H^0(298.15\,K) = -(1808.1 \pm 1.0)$ kJ mol^{-1}, is considered to be far more accurate since the starting materials were of rather high purity and the combustion was complete.

The value $\Delta_f H^0(298.15\,K) = -(1797.1 \pm 2.1)$ kJ mol^{-1}, based on results by Popova and Monaenkova [22] of the solution-calorimetric measurements of Nd(cr) and Nd_2O_3(cr) in 2.19 mol dm^{-3} HCl(aq), seem to be less accurate, since the sample of Nd(cr) was not analyzed for non-metallic impurities. The results obtained in the same laboratory [23] for the enthalpy of solution of a well-characterized sample of neodymium metal in 2.3 mol dm^{-3} HCl(aq) using the same equipment, are much more reliable. The latter value combined with the enthalpy of solution of Nd_2O_3(cr) in 2.19 mol dm^{-3} HCl(aq) from the previous study [22] yields: $\Delta_f H^0(298.15\,K) = -(1805.1 \pm 3.3)$ kJ mol^{-1}. The error arising from the difference in the molarities of the solvents used, has been ignored as it falls within the range of the experimental uncertainties. A concordant value $\Delta_f H^0(298.15\,K) = -(1807.3 \pm 4.1)$ kJ mol^{-1}, is obtained when the enthalpy of solution of Nd_2O_3 in 2.19 mol dm^{-3} HCl(aq) is combined with the enthalpy of solution of Nd(cr) in the same medium as interpolated from the results of Merli et al. [13], who determined the enthalpy of solution of high-purity Nd(cr) at 1.0, 3.0 and 6.0 mol dm^{-3} HCl(aq), respectively.

The derivation of the enthalpy of formation from other solution experiments (see Table 5) is difficult since none of the investigators has measured the enthalpy of solution of both Nd(cr) and Nd_2O_3(cr) in their calorimeter. The value of the enthalpy of solution of Nd_2O_3(cr) in 2.0 mol dm^{-3} HCl(aq) reported by Fitzgibbon et al. [24] is in perfect agreement with that obtained from the results by Popova and Monaenkova [22] in 2.19 mol dm^{-3} HCl(aq).

When this value is combined with a value for the the enthalpy of solution of Nd(cr) at 2.0 mol dm^{-3} interpolated from the results of Merli et al. [13], we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(1807.1 \pm 3.1)$ kJ mol^{-1}. The results of solution experiments in 4.0 mol dm^{-3} HCl(aq) obtained by Stuve [25] and Fitzgibbon et al. [24], can be combined directly since the molarity of the solvents was identical: $\Delta_f H^0(298.15\,\mathrm{K}) = -(1807.3 \pm 2.2)$ kJ mol^{-1}, being in agreement with the above mentioned calorimetric [22,23] and combustion [21] values. The same can be done for the solution experiments in 4.0 mol dm^{-3} HCl(aq) by Stuve [25] and Hennig and Oppermann [26], but the result, $\Delta_f H^0(298.15\,\mathrm{K}) = -(1816.1 \pm 1.9)$ kJ mol^{-1}, is significantly more negative.

The selected enthalpy of formation is the mean of the result of Huber and Holley [21] and the values obtained by combining the results of Stuve [25] and Fitzgibbon et al. [24], Popova and Monaenkova [22], Tiflova [23], Fitzgibbon et al. [24] and Merli et al. [13].

$$\Delta_f H^0(\mathrm{Nd_2O_3, cr, 298.15\,K}) = -(1806.9 \pm 3.0)\ \mathrm{kJ\,mol^{-1}}$$

3.5. Pm_2O_3(cr)

Experimental values for the standard molar enthalpy of formation of promethium sesquioxide are not available in the literature. The selected $\Delta_f H^0(298.15\,\mathrm{K})$ value has been estimated using the dependence of ($\Delta_f H^0$ (Ln_2O_3, cr) − $2\Delta_f H^0$ (Ln^{3+}, aq)) on the atomic radii of the trivalent lanthanides (see Fig. 2), and the assessed value of the enthalpy of formation of Pm^{3+}(aq). Pm_2O_3(cr) is a boundary compound of the domains of existence of the hexagonal and monoclinic rare earth sesquioxides, both crystal stuctures are acceptable for promethium sesquioxide with equal degree of probability [27]. Assuming a hexagonal crystal structure of Pm_2O_3(cr) to be the stable form, the enthalpy of formation was calculated as:

$$\Delta_f H^0(\mathrm{Pm_2O_3, cr,}) = -(1811 \pm 3.0)\ \mathrm{kJ\,mol^{-1}}$$

3.6. Sm_2O_3(cr)

The standard enthalpy of formation of monoclinic samarium sesquioxide has been determined by combustion as well as solution calorimetry. The values, presented in Table 6, show a large variation. The enthalpy of formation obtained by Spedding et al. [20] by the combustion calorimetric method, could be considered as a preliminary value only, due to lack of data for the nonmetallic impurities and incomplete combustion. In the first report on the enthalpy of formation of monoclinic Sm_2O_3(cr) by Huber et al. [28], the following value was obtained by oxygen-bomb combustion calorimetry: $\Delta_f H^0(298.15\,\mathrm{K}) = -(1815.4 \pm 2.0)$ kJ mol^{-1}. Later, determinations of this value carried out in the same laboratory [29] were conducted with samples of significantly higher quality. The values obtained by combustion as well as solution calorimetry, and carefully corrected for impurities, are in reasonable agreement (see Table 6).

Table 6
The enthalpy of formation of Sm_2O_3(cr) at 298.15 K[a]

References	Year	Method[b]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Huber et al. [28]	1955	C			−1815.4 ± 2.0
Montgomery and Hubert [10]	1959	S (0.48)		−408.8 ± 1.4[c]	
Spedding et al. [20]	1959	C			−1777.3
Gvelesiani and Yashvili [12]	1967	S (0.7)	−683.7 ± 5.4	−389.5 ± 0.4	−1835.4 ± 10.8
		S (1.0)	−682.6 ± 2.2	−391.2 ± 3.6	−1831.5 ± 5.7
Baker et al. [29]	1972	C			−1824.2 ± 2.6
		S (2.0)	−690.1 ± 1.3	−417.1 ± 1.2	−1820.8 ± 2.9
		S (3.99)	−689.5 ± 3.8	−406.7 ± 4.6	−1830.7 ± 8.9
Hennig and Oppermann [30]	1997	S (4.0)		−412.8 ± 0.5	−1824.6 ± 7.6[d]
Selected value					−1823.0 ± 4.0

[a] ΔH_1^0 and ΔH_2^0 are the enthalpies of solution of Sm(cr) and Sm_2O_3(cr) in HCl(aq), respectively.

[b] C: combustion calorimetry; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.

[c] Value used for $SmCl_3$.

[d] Using ΔH_1^0 from Baker et al. [29].

However, these results significantly deviate from the value derived from the work by Gvelesiani and Yashvili [12], who determined the enthalpy of formation by solution calorimetric measurements in 0.7 and 1.0 mol dm^{-3} HCl(aq). The authors did not report the analyses of the rare earth metal samples for nonmetallic impurities, and such impurities explain the difference in the results mentioned above.

Hennig and Oppermann [30] measured the enthalpy of solution of Sm_2O_3 in 4.0 mol dm^{-3} HCl(aq). The value obtained by combining their results with the enthalpy of solution of Sm(cr) in the same solvent, as reported by Baker et al. [29], is in good agreement with the results derived from the measurements by Baker et al. [29]. But, in view of the poor characterisation of the Sm_2O_3 sample and the fact that the measurements by Hennig and Opperman deviate significantly for most of the lanthanide sesquioxides (see La_2O_3, Nd_2O_3 and Eu_2O_3), this value is not taken into account for the selected value. This is the weighted mean of the three values derived from the work of Baker et al. [29].

$$\Delta_f H^0(\mathrm{Sm_2O_3, monoclinic, 298.15\,K}) = -(1823.0 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}$$

The enthalpy of formation of cubic Sm_2O_3 is derived from $\Delta_f H^0$ (Sm_2O_3, monoclinic) selected above, and $\Delta_{trs}H^0(\text{monoclinic/cubic}) = -(3.7 \pm 2.6)$ kJ mol^{-1} determined by Baker et al. [29] by solution calorimetry of the two forms in 2.0 kJ mol dm^{-3} HCl(aq). A similar experiment was made by Gvelesiani and Yashvili [12], who dissolved the monoclinic and forms in 1.0 mol dm^{-3} HCl(aq). Their results give $\Delta_{trs}H^0(\text{monoclinic/cubic}) = (5.5 \pm 4.0)$ kJ mol^{-1}. We here prefer the value of Baker et al. [29], which includes a carefull correction for the H_2O and CO_2 impurities that are always present in cubic Sm_2O_3. We thus obtain

$$\Delta_f H^0(\mathrm{Sm_2O_3, cubic, 298.15\,K}) = -(1826.8 \pm 4.8)\,\mathrm{kJ\,mol^{-1}}$$

3.7. *Eu_2O_3(cr)*

The standard enthalpy of formation of monoclinic europium sesquioxide has been determined by combustion as well as solution calorimetry, as shown in Table 4. The data measured by combustion calorimetry by Huber et al. [31] and Fitzgibbon et al. [32] have been carefully corrected for impurities and are in excellent agreement. Fitzgibbon et al. [32] also measured the enthalpy of formation by solution calorimetry. The value derived from the solution measurements of Eu(cr) and Eu_2O_3(cr) in 4.0 mol dm^{-3} HCl(aq), is in excellent agreement with the combustion values. Fitzgibbon et al. also measured the enthalpy of solution of Eu_2O_3(cr) in 6.0 mol dm^{-3} HCl(aq). This result can be combined with the enthalpy of solution of Eu(cr) in 6.0 mol dm^{-3} HCl(aq) reported by Stubblefield et al. [33], to give $\Delta_f H^0(298.15\,\mathrm{K}) = -(1624.5 \pm 6.0)$ kJ mol^{-1}. This value differs considerably from the three values by Holley and coworkers [31,32], which implies that the Eu(cr) solution data most probably are in error. Considering the systematic study of Merli et al. [13], who measured the enthalpies of solution of a number of lanthanide metal at 1.0, 3.0 and 6.0 mol dm^{-3} HCl(aq), the difference between 6.0 and 1.0 mol dm^{-3} HCl(aq) is in the order of 1–5 kJ mol^{-1}. We thus estimate the enthalpy of solution of Eu(cr) in 6.0 mol dm^{-3} HCl(aq) to be $-(603 \pm 4)$ kJ mol^{-1}. With this value, also the measurement in 6.0 mol dm^{-3} HCl(aq) by Fitzgibbon et al. is in good agreement.

These values deviate significantly from the value derived from the work by Yashvili and Gvelesiani [34], who measured the enthalpies of solution of Eu(cr) and Eu_2O_3(cr) in 1.0 mol dm^{-3} HCl(aq), leading $\Delta_f H^0(298.15\,\mathrm{K}) = -(1725.2 \pm 8.5)$ kJ mol^{-1}. Even when recalculated with an estimated enthalpy of solution of Eu(cr) in 1.0 mol dm^{-3} HCl(aq), $-(607 \pm 4)$ kJ mol^{-1} (see preceding paragraph), the resulting value is not in agreement with the work of Fitzgibbon et al. Also, the results derived from the measurements by Hennig and Oppermann [35] are significantly more negative (see Table 4). These authors measured the enthalpy of solution of Eu_2O_3(cr) in 4.0 mol dm^{-3} HCl(aq) which are combined with the enthalpy of solution of Eu(cr) in the same solvent, reported by Stuve [36] and Fitzgibbon et al. [29].

The selected value is the mean of the two combustion values and the solution value in 1.0 mol dm^{-3} by Holley and coworkers [31,32].

$$\Delta_f H^0(\mathrm{Eu_2O_3, monoclinic, 298.15\,K}) = -(1650.4 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}$$

The enthalpy of formation of cubic Eu_2O_3 is derived from $\Delta_f H^0$ (Eu_2O_3, monoclinic) selected above, and $\Delta_{trs} H^0$ (monoclinic/cubic) determined by Fitzgibbon et al. [32] by solution calorimetry in four different solvents as $-(11.13 \pm 1.17)$ kJ mol^{-1}. We thus obtain $\Delta_f H^0(298.15\,K) = -(1661.1 \pm 6.3)$ kJ mol^{-1}. The value derived for cubic Eu_2O_3 from the measurements of Stuve [36], $-(1618.9 \pm 4.0)$ kJ mol^{-1}, differs significantly from the selected value. When this value is recalculated using the enthalpy of solution of Eu_2O_3(cr) in 4.0 mol dm^{-3} HCl(aq) by Fitzgibbon et al. [32], we obtain $-(1663.3 \pm 5.9)$ kJ mol^{-1}, which is in excellent agreement with the other value. We select the mean of the two values.

$$\Delta_f H^0(Eu_2O_3, \text{cubic}, 298.15\,K) = -(1662.5 \pm 6.0)\,\text{kJ mol}^{-1}$$

3.8. *Gd_2O_3(cr)*

The standard enthalpy of formation of monoclinic gadolinium sesquioxide has been determined by solution calorimetry as well as combustion calorimetry (Table 4). The value reported by Spedding et al. [20] should be considered as a preliminary result due to incomplete combustion and lack of analytical characterization of the sample of Gd(cr) used in that study. A much more reliable combustion value has been obtained by Huber and Holley [37], using 97.05 mass% pure gadolinium metal, $\Delta_f H^0(298.15\,K) = -(1819.7 \pm 3.6)$ kJ mol^{-1}. Yashvili and Gvelesiani [34] determined the enthalpies of solution of Gd(cr) and Gd_2O_3(cr) in 6.0 mol dm^{-3} HCl(aq) and the value for the standard enthalpy of formation of gadolinium sesquioxide derived from these data is $\Delta_f H^0(298.15\,K) = -(1826.3 \pm 3.7)$ kJ mol^{-1}. When this value is recalculated using the more recent result for the enthalpy of solution of Gd(cr) in 6.0 mol dm^{-3} HCl(aq) by Merli et al. [13], a somewhat more negative value is obtained $\Delta_f H^0(298.15\,K) = -(1829.5 \pm 2.6)$ kJ mol^{-1}. An almost identical value, $\Delta_f H^0$ $(298.15\,K) = -(1828.2 \pm 3.6)$ kJ mol^{-1}, is obtained using a chloride cycle based on the enthalpy of solution of $GdCl_3$(cr) 6.0 mol dm^{-3} HCl(aq) and the selected enthalpy of formation of $GdCl_3$(cr) [5]. Though these values are in reasonable agreement with the value reported by Huber and Holley, they are considered significantly less accurate, especially in view of the difficulties of the (slow) dissolution of Gd_2O_3(cr) in HCl(aq). The value obtained by Huber and Holley [37] is thus selected here.

$$\Delta_f H^0(Gd_2O_3, \text{cr}, 298.15\,K) = -(1819.7 \pm 3.6)\,\text{kJ mol}^{-1}$$

3.9. *Tb_2O_3(cr)*

The standard enthalpy of formation of cubic terbium sesquioxide has been obtained by the solution calorimetry method, as shown in Table 7. The first value was reported by Stubblefield et al. [17] and is based on enthalpy-of-solution measurements of Tb_2O_3(cr) in 6.0 mol dm^{-3} HNO_3(aq). Using recent auxiliary data for the enthalpies of dilution of the constituents of the corresponding thermochemical reaction as well as the assessed value for the enthalpy of formation of Tb^{3+}(aq) [6], the following value for the enthalpy of formation of Tb_2O_3(cr) has been calculated, $\Delta_f H^0(298.15\,K) = -(1864.5 \pm 8.4)$ kJ mol^{-1}. The value thus obtained seems to be not reliable, since not all the auxiliary thermodynamic data important for that calculation, for example, the molar enthalpy of dilution of $Tb(NO_3)_3$(aq), are available in the literature with sufficient accuracy.

Fitzgibbon and Holley [38] measured the enthalpies of formation of several terbium oxides, $TbO_{1.510}$(cr), $TbO_{1.709}$(cr), $TbO_{1.817}$(cr), and $TbO_{1.975}$(cr), using a thermochemical cycle which involves the solution of terbium metal and the oxides in 1.0 mol dm^{-3} HCl(aq) and 6.0 mol dm^{-3} HNO(aq), respectively. Terbium metal was not dissolved in HNO_3(aq) for fear of reducing some of the acid, and the oxides were not dissolved in HCl(aq) in order to avoid oxidation of some of the HCl. In order to combine the results in the two solvents, the enthalpy of solution of terbium carbonate was measured in both solvents. The enthalpies of formation of the four aforesaid terbium oxides were found to fit a linear dependence against the composition of the oxide and the enthalpy of formation of stoichiometric Tb_2O_3(cr) has been determined by extrapolation of a plot of the measured values. The data by Fitzgibbon and Holley remain unchanged when recalculated by the present authors and the enthalpy of formation of Tb_2O_3(cr) thus obtained is

Table 7
The enthalpies of formation of Tb_2O_3(cr), Dy_2O_3(cr), Ho_2O_3(cr) and Er_2O_3(cr) at 298.15 K[a]

References	Year	Method[b]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Tb_2O_3					
Stubblefield et al. [17]	1956	S (1.0)[c]		-395.0 ± 2.5	-1864.5 ± 8.4
Fitzgibbon and Holley [38]	1968	S (1.0)[c]		-392.5 ± 5.0	-1865.2 ± 6.0
Selected value					-1865.2 ± 6.0
Dy_2O_3					
Huber et al. [40]	1956	C			-1865.2 ± 3.8
Huber et al. [39]	1971	C			-1862.9 ± 4.2
		S (4.0)	-695.3 ± 2.9	-385.1 ± 3.4	-1863.9 ± 6.7
Selected value					-1863.4 ± 5.0
Ho_2O_3					
Huber et al. [41]	1957	C			-1881.0 ± 5.0
Morss et al. [42]	1993	S (4.0)		-379.1 ± 5.2[d]	-1887.3 ± 9.5[e]
			(-710.5 ± 7.1) [43]		-1900.3 ± 15.1
					-1885.7 ± 7.3[f]
Selected value					-1883.3 ± 8.2
Er_2O_3					
Huber et al. [44]	1956	C			-1897.8 ± 3.8
Spedding et al. [20]	1959	C			-1762.8
Montgomery and Stuve [46]	1961	S (1.40)	(-705.6 ± 1.4) [45]	-370.6 ± 3.7	-1898.2 ± 4.6
Morss et al. [42]	1993	S (1.40)		-364.6 ± 1.9[d]	-1904.2 ± 3.4
Selected value					-1900.1 ± 6.5

[a] ΔH_1^0 and ΔH_2^0 are the enthalpies of solution of Ln(cr) and Ln_2O_3(cr) in HCl(aq), respectively.
[b] C: combustion calorimetry; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[c] Solvent was HNO_3(aq).
[d] Unceratinty recalculated.
[e] $\Delta H_1^0 = -704 \pm 4$ as suggested by Morss et al. [42].
[f] Cycle based on $HoCl_3$, as explained in the text.

$\Delta_f H^0(298.15\,K) = -(1865.2 \pm 6.0)$ kJ mol^{-1}. This value is selected here.

$$\Delta_f H^0(Tb_2O_3, cr, 298.15\,K) = -(1865.2 \pm 6.0)\,kJ\,mol^{-1}$$

3.10. Dy_2O_3(cr)

The standard enthalpy of formation of cubic dysprosium sesquioxide has been determined by combustion as well as solution calorimetry, as shown in Table 7. The values obtained by Holley and coworkers [39] by solution calorimetry and by oxygen bomb combustion calorimetry, are in perfect agreement. The results from the earlier publication by the same group [40] based on the combustion calorimetric measurements, seems to be less accurate, since the sample of dysprosium metal was less pure than that used in the later investigation. The dysprosium oxide formed, was composed of roughly equal proportions of cubic and monoclinic types of the sesquioxide.

The selected value is the mean of the two values by Holley and coworkers.

$$\Delta_f H^0(Dy_2O_3, cr, 298.15\,K) = -(1863.4 \pm 5.0)\,kJ\,mol^{-1}$$

3.11. Ho_2O_3(cr)

Huber et al. [41] determined the standard molar enthalpy of formation of cubic holmium sesquioxide by oxygen-bomb combustion calorimetric measurements. The value thus obtained, carefully corrected for impurities, is $\Delta_f H^0(298.15\,K) = -(1881.0 \pm 5.0)$ kJ mol^{-1}. Morss et al. [42] derived the enthalpy of formation of Ho_2O_3(cr) from solution calorimetric measurements of Ho_2O_3(cr) in 4.0 mol dm^{-3} HCl(aq), which were combined with an estimated enthalpy of solution of Ho(cr) in the same medium. The measurement of the latter quantity by Stuve [43] was rejected by Morss et al. A recalculation of the reaction cycle by Morss et al. (applying a different calculation of the uncertainty of their experimental data set) yields $\Delta_f H^0(298.15\,\mathrm{K}) = -(1887.3 \pm 9.5)$ kJ mol^{-1}. The enthalpy of solution of Ho_2O_3(cr) in 4.0 mol dm^{-3} HCl(aq) can also be combined with the enthalpy of solution of $HoCl_3$(cr) in the same medium by Stuve [43] and the selected enthalpy of formation of $HoCl_3$(cr) [5], to yield $\Delta_f H^0(298.15\,\mathrm{K}) = -(1885.7 \pm 7.3)$ kJ mol^{-1}. The selected value is the mean of the combustion calorimetric value by Huber et al. [41] and the value derived from the measurements by Morss et al. [42], using the chloride cycle.

$$\Delta_f H^0(\mathrm{Ho_2O_3, cr, 298.15\,K}) = -(1883.3 \pm 8.2)\,\mathrm{kJ\,mol^{-1}}$$

3.12. Er_2O_3(cr)

The standard enthalpy of formation of cubic erbium sesquioxide has been determined by combustion as well as solution calorimetry, as shown in Table 7. The results of oxygen bomb calorimetry measurements reported by Spedding et al. [20], must be considered as approximate only, since the erbium metal sample was not analyzed for the contamination of nonmetallic impurities. A much more precise value for the enthalpy of formation of Er_2O_3(cr) has been measured by the same method by Huber et al. [44], $\Delta_f H^0(298.15\,\mathrm{K}) = -(1897.8 \pm 3.8)$ kJ mol^{-1}. This value is in perfect agreement with the enthalpy of formation, $\Delta_f H^0(298.15\,\mathrm{K}) = -(1898.2 \pm 4.6)$ kJ mol^{-1}, obtained by combining the results of solution calorimetry measurements in ~1.4 mol dm^{-3} HCl(aq) of Er(cr) by Fuger and Morss [45] and of Er_2O_3(cr) by Montgomery and Stuve [46]. A somewhat more negative value, $\Delta_f H^0(298.15\,\mathrm{K}) = -(1904.2 \pm 3.4)$ kJ mol^{-1}, has been derived by combining the results of solution calorimetry measurements in ~1.4 mol dm^{-3} HCl(aq) of Er(cr) by Fuger and Morss [45] and of Er_2O_3(cr) by Morss et al. [42].

The mean of the three values for the enthalpy of formation of Er_2O_3(cr) is selected here.

$$\Delta_f H^0(\mathrm{Er_2O_3, cr, 298.15\,K}) = -(1900.1 \pm 6.5)\,\mathrm{kJ\,mol^{-1}}$$

3.13. Tm_2O_3(cr)

There is only one determination of the standard molar enthalpy of formation of cubic thulium sesquioxide carried, out by Huber et al. [47] using oxygen-bomb combustion calorimetric method. Two samples of Tm(cr) containing significantly different amount of impurities, were used in that study. For the two materials, the combustion varied from 88.67 to 99.67% of completion. The values for the enthalpy of formation of Tm_2O_3(cr) derived by Huber et al. from the measurements after correction for impurities, are $\Delta_f H^0(298.15\,\mathrm{K}) = -(1894.8 \pm 8.3)$ kJ mol^{-1} and $\Delta_f H^0(298.15\,\mathrm{K}) = -(1884.3 \pm 7.9)$ kJ mol^{-1} = $-(1884.3 \pm 7.9)$ kJ mol^{-1}. The selected value is the weighted mean of the two results.

$$\Delta_f H^0(\mathrm{Tm_2O_3, cr, 298.15\,K}) = -(1889.3 \pm 5.7)\,\mathrm{kJ\,mol^{-1}}$$

3.14. Yb_2O_3(cr)

A very limited number of data is available for the standard enthalpy of formation of cubic ytterbium sesquioxide. The only experimental value has been reported by Huber et al. [40], based on the results of oxygen-bomb combustion calorimetric measurements of 97.2 mass% pure Yb(cr) sample. The value thus obtained, and carefully corrected for impurities, is adopted here.

$$\Delta_f H^0(\mathrm{Yb_2O_3, cr, 298.15\,K}) = -(1814.5 \pm 6.0)\,\mathrm{kJ\,mol^{-1}}$$

The uncertainty is raised in view of experimental difficulties and estimated uncertainty of the correction for impurities.

3.15. Lu_2O_3(cr)

The only available experimental value for the standard enthalpy of formation of cubic lutetium sesquioxide has been determined by oxygen-bomb combustion calorimetry by Huber et al. [48]. Two well-analyzed samples of lutetium metal were used. For both materials, the combustion was not complete and varied from 93.6 to 99.5% of completion. For two sets of measurements, the following values for the enthalpy of formation of Lu_2O_3(cr) have been obtained by Huber et al. after correction for impurities: $\Delta_f H^0(298.15\,\mathrm{K}) = -(1891.8 \pm 14.2)$ kJ mol^{-1} and $\Delta_f H^0(298.15\,\mathrm{K}) = -(1870.9 \pm 9.1)$ kJ mol^{-1}, being almost within the range of combined error limits. The selected enthalpy of formation is the weighted mean of the two results.

$$\Delta_f H^0(\mathrm{Lu_2O_3, cr, 298.15\,K}) = -(1877.0 \pm 7.7)\,\mathrm{kJ\,mol^{-1}}$$

4. Discussion

The selected values for the enthalpy of formation of the lanthanide sesquioxides are summarised in Table 8 and plotted as a function of atomic number in Fig. 1. The general trend is not smooth since Eu_2O_3 and, to a lesser extend, Yb_2O_3 deviate significantly. This is a typical case for the lanthanide compounds, as observed also in the cases of the Ln(III) halides and ions [5,6], and can be related to the electronic configuration. In Eu and Yb metal the f shell of the lanthanide ions is half filled ($4f^7 6s^2$) or completely filled ($4f^{14} 6s^2$), respectively, leading to a divalent state for the metal. As a result, an extra step with an associated energy effect is needed for the divalent–trivalent transition, as can be understood from the Ln^{3+}(aq)–Ln(cr)–Ln(g)–Ln^{3+}(g) relationships constructed by Nugent et al. [49] and Morss [50].

Table 8
Summary of the selected enthalpies of formation of the lanthanide sesquioxides

Compound	$\Delta_f H^0$ (298.15 K) (kJ mol^{-1})
La_2O_3	-1791.6 ± 2.0
Ce_2O_3	-1813.0 ± 2.0
Pr_2O_3	-1809.9 ± 3.0
Nd_2O_3	-1806.9 ± 3.0
Pm_2O_3	-1811 ± 21
Sm_2O_3 (monoclinic)	-1823.0 ± 4.0
Sm_2O_3 (cubic)	-1826.8 ± 4.8
Eu_2O_3 (monoclinic)	-1650.4 ± 4.0
Eu_2O_3 (cubic)	-1662.5 ± 6.0
Gd_2O_3	-1819.7 ± 3.6
Tb_2O_3	-1865.2 ± 6.0
Dy_2O_3	-1863.4 ± 5.0
Ho_2O_3	-1883.3 ± 8.2
Er_2O_3	-1900.1 ± 6.5
Tm_2O_3	-1889.3 ± 5.7
Yb_2O_3	-1814.5 ± 6.0
Lu_2O_3	-1877.0 ± 7.7

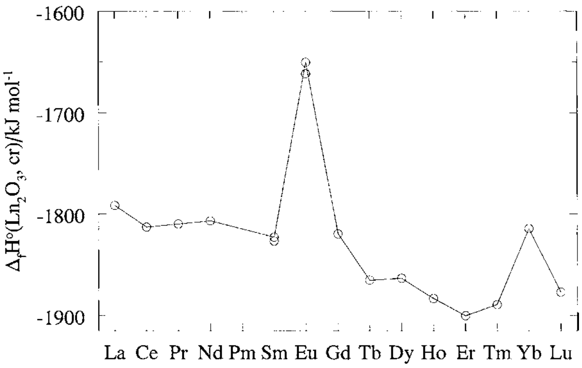

Fig. 1. The enthalpy of formation of the lanthanide sesquioxides.

In Fig. 2, the quantity $\Delta_f H^0$ (Ln_2O_3, cr) $-2\Delta_f H^0$ (Ln^{3+}, aq) is plotted as a function of the atomic radii of the trivalent lanthanide ion. It is clear that overall an approximate linear relation exists, as has been shown before by Morss [50]. This relation allows us to estimate the enthalpy of formation of Pm_2O_3, as is given the preceding section. Fig. 2 also shows that the data clearly fall into the three crystallographic classes that have been identified for the lanthanide sequioxides: hexagonal, monoclinic and cubic. When this figure is examined in more detail, it appears that within the group of monoclinic compounds (Sm_2O_3,

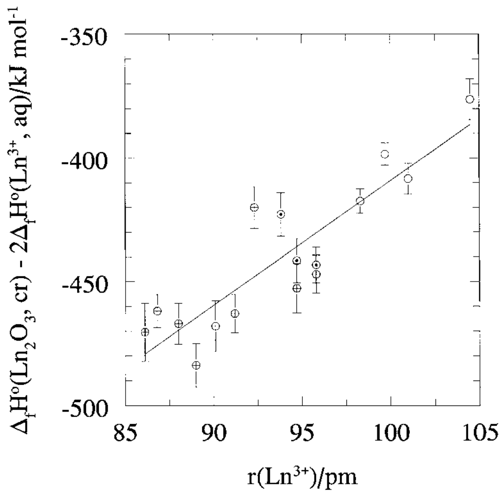

Fig. 2. The quantity $\Delta_f H^0$ (Ln_2O_3,cr) $-\Delta_f H^0$ (Ln^{3+}, aq) as a function of the ionic radius; (○), hexagonal; (⊙), monoclinic; (⊕), cubic crystal structure.

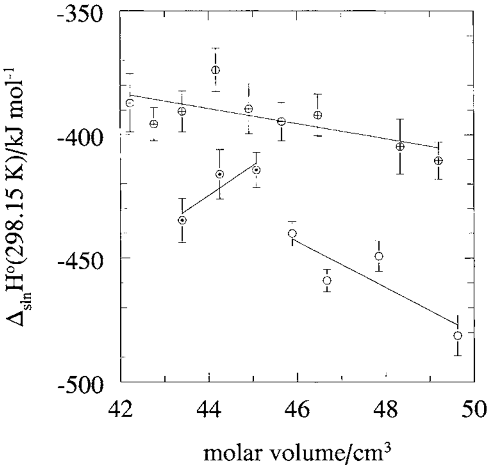

Fig. 3. The enthalpy of solution in water ($\Delta_{\text{sln}}H^0$) of the lanthanide sesquioxides as a function of their molar volume; (○), hexagonal; (⊙), monoclinic; (⊕), cubic crystal structure.

Eu_2O_3 and Gd_2O_3), the values follow a different trend. This becomes even more evident when the 'theoretical' enthalpy of solution in water ($\Delta_{\text{sln}}H^0$) is plotted as a function of the molar volume of the sesquioxide (Fig. 3), as suggested by Morss [50]. From this figure, it appears that ($\Delta_{\text{sln}}H^0$) follows different correlation for each crystallograpic class. Though the overall picture agrees with the one presented by Morss [50], we obtain a somewhat different trend for the monoclinic class, for which the recommended values from the present work show a much more pronounced dependence. This is mainly due to a significant different value for $\Delta_{\text{sln}}H^0$ of Gd_2O_3, which can be attributed to a different selected value for the enthalpy of formation of the Gd^{3+} ion, and, indirectly, to the use of a more recent value enthalpy of solution of Gd metal [13] in our work.

In general, the correlations presented in our in Figs. 2 and 3 are less convincing than in case of the lanthanide trihalides [5]. We attribute this to the less reliable data for the lanthanide sesquioxides. As noted already [5], the enthalpies of solution of a number of the lanthanide metals, of key importance in the solution cycles, are subjected to significant uncertainties and the number of reliable determinations on pure samples is limited. Also, the combustion calorimetry determinations rely heavily on the purity of the metal that is used as starting material. The set of combustion experiments of Holley and coworkers, which is unique in its quality and extensiveness, still is the main source of information for several of the heavy lanthanide sesquioxides. However, part of this work was done in the 1950s and involves significant corrections for impurities and incomplete combustion, especially in the case of Tm_2O_3, Yb_2O_3 and Lu_2O_3. Re-determinations of the enthalpies of formation of these compounds is therefore strongly recommended.

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Appendix A. The enthalpy of formation of CeO_2(cr)

A number of combustion calorimetric determination of the standard molar enthalpy of formation of CeO_2(cr) has been reported [3,9,53,63,64]. The results of early investigations [3,53,63] are mainly of historical interest due to a poor quality of materials and experimental techniques available at that time.

In 1953, Huber and Holley [9] determined the enthalpy of combustion of well-analyzed sample of cerium metal, giving $\Delta_f H^0(298.15\,\text{K}) = -(1088.6 \pm 1.4)\,\text{kJ mol}^{-1}$. This value, which was carefully corrected for impurities, is in excellent agreement with the result [64] of a later oxygen-bomb combustion calorimetric investigation carried out in the same laboratory, $\Delta_f H^0(298.15\,\text{K}) = -(1090.4 \pm 0.8)\,\text{kJ mol}^{-1}$. We have selected the latter value, because it is based on the results obtained in experiments with cerium metal sample of significantly higher purity.

$$\Delta_f H^0(\text{CeO}_2, \text{cr}, 298.15\,\text{K}) = -(1090.4 \pm 1.0)\,\text{kJ}\,\text{mol}^{-1}$$

The uncertainty being raised in view of the experimental difficulties and uncertainties in the calculated corrections for impurities.

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