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The enthalpies of formation of lanthanide compounds I. $LnCl_3$(cr), $LnBr_3$(cr) and LnI_3(cr)

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Abstract

The enthalpies of formation of the lanthanide trichlorides, tribromides and tri-iodides have been evaluated from the experimental data available in literature. All experimental results have been re-calculated using a consistent set of the most recent auxiliary data. On the basis of the results obtained, recommended values are given in those cases where sufficient data are available. When this is not the case, the recommended values are obtained from estimations using empirical correlations based on the variation of the ionic radii or the atomic number. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The 15 elements that are known as the rare earths or lanthanides, are scientifically interesting because they form compounds in which the physical and chemical properties only change gradually. In these compounds, the lanthanides occur mainly as trivalent ions, although both tetravalent and divalent compounds have been prepared as well. In the solid state, the +2 oxidation state is obtained in a few halides and oxides. The +4 oxidation state is best known for a few oxide compounds.

The anhydrous trihalides form a group with important practical applications. For instance, the chlorides are of high relevance to the pyrochemical reprocessing of nuclear waste, the bromides and iodides as additives in high-pressure discharge lamps. They are known for all the rare earth elements. An exception forms the tri-iodide of europium which is known to be unstable. Whereas the anhydrous fluorides are stable in air at room temperature and non-hygroscopic, the anhydrous trichlorides, tribromides, and tri-iodides are extremely sensitive to air and moisture. As a consequence, they are difficult to prepare in a very pure form. However, the growing interest in these materials since 1950, and the need for pure compounds for thermophysical and thermodynamic measurements, has given the impetus for the better separation and preparative methods developed by Spedding and Daane [1], and Gschneider and Capellen [2]. A review of the various methods has been given by Haschke [3].

The improvement of the preparative methods made it possible to synthesize and re-investigate the thermochemical properties of many of these compounds. Comprehensive reviews covering the period up to 1975 and the period up to 1992 have been presented by Morss [4,5]. In addition, several sets of estimated values for the enthalpies of formation of solid rare

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earth metal trihalides are available [6–8]. The most recent one, presented by Struck and Baglio [9], listed enthalpy of formation values published in the literature, accompanied by Born–Haber cycle estimations for all lanthanide trihalides.

Although the thermodynamic data for the lanthanide compounds have been carefully reviewed, assessed and tabulated by the different authors, the values for many compounds, in particular, the enthalpies of formation of tribromides and tri-iodides of the rare earth metals, are rather contradictory, and often based on estimations. Since experimental results for some of these compounds have become available only recently, the present review was made to solve the contradictions in the existing values for the enthalpies of formation of lanthanide compounds and to assess a consistent set of the values of the highest accuracy.

2. Methods

In this assessment the enthalpies of formation at 298.15 K of the anhydrous lanthanide chlorides, bromides and iodides will be considered. This quantity is generally derived from enthalpy of solution measurements but occasionally other techniques have been used also.

The derivation of the enthalpies of formation of the rare earth metal halides from the solution calorimetric data was done using the following schemes of the thermochemical reactions. The first scheme is based on the dissolution of the lanthanide metal as well as the lanthanide trihalide in (hydrogen-saturated) hydrochloric acid HCl(sln):

$$\begin{array}{lr}
\mathrm{Ln(cr)} + 3\mathrm{HCl(sln\ in\ ``A")} = \mathrm{LnCl_3(sln\ in\ ``A")} + \frac{3}{2}\mathrm{H_2(g)} & \Delta_r H^0(1) \\
\mathrm{LnX_3(cr)} + 3\mathrm{HCl(sln\ in\ ``A")} = \mathrm{LnX_3(sln\ in\ ``A")} + 3\mathrm{HX(sln\ in\ ``A")} & \Delta_r H^0(2) \\
\frac{3}{2}\mathrm{H_2(g)} + \frac{3}{2}\mathrm{X_2(standard\ state)} + \mathrm{(``A")} = 3\mathrm{HX(sln\ in\ ``A")} & \Delta_r H^0(3) \\
\hline
\mathrm{Ln(cr)} + \frac{3}{2}\mathrm{X_2(standard\ state)} = \mathrm{LnX_3(cr)} & \Delta_r H^0(4)
\end{array}$$

The standard molar enthalpy of formation of LnX_3(cr) equals to $\Delta_r H^0(4)$, and can be calculated as $\Delta_f H^0(\mathrm{LnX_3},\ \mathrm{s},\ 298.15\ \mathrm{K}) = \Delta_r H^0(4) = \Delta_r H^0(1) - \Delta_r H^0(2) + \Delta_r H^0(3)$. The value $\Delta_r H^0(3)$ is the partial molar enthalpy of formation of HX(sln) at the concentration given, and is calculated from the enthalpy of formation of the infinitely dilute acid [10], the enthalpy of formation of the HX solutions [11] and the densities of the HX solutions at 298.15 K [12], neglecting the influence of the lanthanide ion. The values used in the present calculations are given in Table 1. In case X represents the same halide ion in LnX_3 and HX(sln), e.g. $LnCl_3$ in HCl(aq), this calculation refers to the binary system H_2O–HX and is straightforward. But in case X represents different halide ions, e.g. LnI_3 in HCl(aq), the situation becomes more complex as we have to deal with the ternary system H_2O–HCl–HX. In that case, it is assumed that the apparent enthalpy of formation of HX in HCl solutions is the same as in HX solutions of the same molality.

Table 1
The partial molar enthalpy of formation of HX(aq) at 298.15 K

Molarity (mol dm^{-3})	Molality (mol kg^{-1})	$\overline{H}$(HX) (kJ mol^{-1})	$\overline{H}$(H_2O) (kJ mol^{-1})
HCl(aq)			
6.00	6.85	−153.42	−286.64
4.00	4.36	−158.35	−286.14
2.00	2.09	−162.52	−285.90
1.50	1.55	−163.43	−285.87
1.00	1.02	−164.37	−285.85
0.50	0.51	−165.29	−286.84
0.25	0.25	−165.84	−286.83
0.10	0.10	−166.27	−286.83
0	0	−167.08	−286.83
HBr(aq)			
6.00	7.06	−109.18	−286.63
4.00	4.44	−114.26	−286.11
1.00	1.03	−119.37	−285.84
0.25	0.25	−120.41	−286.83
0.10	0.10	−120.70	−286.83
0	0	−121.41	−286.83
HI(aq)			
4.00	4.73	−50.44	−286.11
1.00	1.03	−55.37	−285.84
0.25	0.25	−56.04	−286.83
0.10	0.10	−56.20	−286.83
0	0	−56.78	−286.83

The second scheme involves the enthalpy of solution of the lanthanide sesquioxide and the lanthanide trihalide:

$\mathrm{Ln(cr)}+\frac{3}{4}\mathrm{O_2(g)} = \frac{1}{2}\mathrm{Ln_2O_3(cr)}$ $\Delta_rH^0(5)$

$\frac{1}{2}\mathrm{Ln_2O_3(cr)} + 3\mathrm{HX(sln\ in\ ``A")} = \mathrm{LnX_3(sln\ in\ ``A")} + \frac{3}{2}\mathrm{H_2O(sln)}$ $\Delta_rH^0(6)$

$\mathrm{LnX_3(cr)} + \mathrm{(sln\ in\ ``A")} = \mathrm{LnX_3(sln\ in\ ``A")}$ $\Delta_rH^0(2)$

$\frac{3}{2}\mathrm{H_2(g)} + \frac{3}{2}\mathrm{X_2(standard\ state)} + \mathrm{(``A")} = 3\mathrm{HX(sln\ in\ ``A")}$ $\Delta_rH^0(3)$

$\frac{3}{2}\mathrm{H_2(g)} + \frac{3}{4}\mathrm{O_2(g)} + \mathrm{(``A")} = \frac{3}{2}\mathrm{H_2O(sln\ in\ ``A")}$ $\Delta_rH^0(7)$

$\mathrm{Ln(cr)} + \frac{3}{2}\mathrm{X_2(standard\ state)} = \mathrm{LnX_3(cr)}$ $\Delta_rH^0(4)$

For this reaction sequence: $\Delta_fH^0(\mathrm{LnX_3}, \mathrm{Cr}, 298.15\ \mathrm{K}) = \Delta_rH^0(4) = \Delta_rH^0(5) + \Delta_rH^0(6) + \Delta_rH^0(3) - \Delta_rH^0(7) - \Delta_rH^0(2)$, where $\Delta_rH^0(7)$ is the partial enthalpy of formation of $\mathrm{H_2O(sln)}$ in hydrochloric acid. Only in case the enthalpy of formation of the sequioxide is based on the combustion of the lanthanide metal, the two schemes are really independent.

In the present study data are evaluated from the literature between 1940 and 2000, which means that, for example, the studies by Matignon [13], Sieverts and Gotta [14], and Biltz and Pieper [15] are not dealt with. All data have been stored in a spreadsheet and have been processed simultaneously with those for the aqueous ions and the lanthanide oxides [16]. 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. Auxiliary data recommended by CODATA or values consistent with the CODATA selection [10] have been employed.

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. Lanthanum

3.1.1. $\mathrm{LaCl_3(cr)}$

Values for the standard enthalpy of formation of $\mathrm{LaCl_3(cr)}$ published in the literature, are listed in Table 2. Bommer and Hohmann [17,18] dissolved La(cr) and $\mathrm{LaCl_3(cr)}$ in 0.1 mol dm^{-3} HCl(aq), yielding for the enthalpy of formation $\Delta_fH^0(298.15\ \mathrm{K}) = -(1105.1 \pm 2.6)\ \mathrm{kJ\ mol^{-1}}$, which differs significantly from the other values for the standard enthalpy of formation of $\mathrm{LaCl_3}$ obtained by solution calorimetry. It has been emphasized by Spedding and Miller [19] that impurities, especially of potassium, in the sample of the rare-earth metal used by Bommer and Hohmann, might be responsible for the difference. Nevertheless, by combining the value of the enthalpy of solution of $\mathrm{LaCl_3(cr)}$ reported by Bommer and Hohmann [17], with the enthalpy of solution of La(cr) in 0.27 mol dm^{-3} HCl(aq) obtained by Spedding and Flynn [20], we derive for the standard molar enthalpy of formation of $\mathrm{LaCl_3(cr)}$ the value $-(1070.3 \pm 2.7)$ kJ mol^{-1}. The uncertainty of the value has been increased due to the difference in the molarities of the solvents used in these studies. The latter value is in good agreement with the more accurate value based on solution measurements of La(cr) and $\mathrm{LaCl_3(cr)}$ in 1.0 mol dm^{-3} HCl(aq) by Fitzgibbon et al. [21], and Cordfunke and Booij [22], respectively. An almost identical value is obtained when the more recent value for the enthalpy of solution of La(cr) in 1.0 mol dm^{-3} HCl(aq) by Merli et al. [23] is used. The value by Morss [24] for the enthalpy of solution of La(cr) in 1.0 mol dm^{-3} HCl(aq) is in good agreement with the results of Fitzgibbon et al. and Merli et al., but is considered less accurate as it has been made on small quantities.

Montgomery [25] and Oppermann et al. [26] measured the enthalpies of solution of $\mathrm{La_2O_3(cr)}$ and $\mathrm{LaCl_3(cr)}$ in HCl(aq). When combined with the value for $\Delta_fH^0(\mathrm{La_2O_3}, \mathrm{cr}, 298.15\ \mathrm{K})$ [27], as derived by combustion calorimetry (which in this case is preferred to the selected value [16] to assure an independent reaction cycle), we obtain $\Delta_fH^0(298.15\ \mathrm{K}) = -(1070.2 \pm 0.7)\ \mathrm{kJ\ mol^{-1}}$ from the results of Montgomery [25] and $\Delta_fH^0(298.15\ \mathrm{K}) = -(1065.9 \pm 0.6)\ \mathrm{kJ\ mol^{-1}}$ from the results of Oppermann et al.

Table 2
The enthalpy of formation of LaX_3(cr) at 298.15 K and the enthalpies of solution of La(cr) and LaX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$LaCl_3$					
Bommer and Hohmann [17,18][b]	1941	S (0.1)	−738.5 ± 2.6	−132.2 ± 0.1	−1105.1 ± 2.6
					−1072.2 ± 2.7[c]
Lohr and Cunningham [39]	1951	S (1.5)	−695.0 ± 5.9		
Spedding and Flynn [20]	1954	S (0.27)	−705.7 ± 0.2	−130.3 ± 0.7	−1073.0 ± 0.9
Montgomery [25]	1959	S (0.51)		−129.7 ± 0.4	−1070.2 ± 0.7[d]
					−1070.3 ± 1.6[e]
Fitzgibbon et al. [21]	1965	S (1.0)	−705.5 ± 1.3		
Gvelesiani and Yashvili [55]	1967	S (1.0)	−708.0 ± 2.0		
		S (1.5)	−708.8 ± 1.4		
Morrs [24]	1969	S (1.0)	−703.3 ± 3.8		
Laptev et al. [28]	1990	E			−1066.9 ± 1.1
Cordfunke and Booij [22]	1994	S (1.0)		−126.4 ± 0.5	−1072.3 ± 1.5[f]
					−1071.1 ± 1.4[g]
Oppermann et al. [26]	1997	S (4.0)		−111.8 ± 0.4	−1065.9 ± 0.6[d]
					−1069.4 ± 1.3[e]
Merli et al. [23]	1998	S (1.0)	−704.4 ± 1.2		
		S (6.0)	−707.8 ± 1.2		
Selected value					−1071.6 ± 1.5
$LaBr_3$					
Hurtgen et al. [31]	1980	S (1.0)		−158.5 ± 0.2	−905.1 ± 1.4[f]
					−904.0 ± 1.2[g]
		S (0.1)		−163.7 ± 0.4	−902.3 ± 0.7[c]
Oppermann et al. [26]	1997	S (4.0)		−146.1 ± 0.4[h]	−902.8 ± 1.2[d]
Selected value					−904.4 ± 1.5
LaI_3					
Honmann and Bommer [33]	1941	S (0.1)	−738.5 ± 2.6	−200.6 ± 0.7	−706.5 ± 2.7
					−671.9 ± 1.7[c]
Furkaliouk et al. [34]	1995	S (1.0)			−667.9 ± 1.6
				−196.6 ± 1.1[i]	−673.9 ± 1.6[f]
Oppermann et al. [26]	1997	S (4.0)		−167.5 ± 0.4[j]	−689.4 ± 1.1[d]
Selected value					−673.9 ± 2.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[b] The measurements were carried out at 293–294 K and corrected to 298.15 K.
[c] Using ΔH_1^0 from Spedding and Flynn [20].
[d] Cycle based on $\Delta_f H^0(La_2O_3(cr))$.
[e] Using ΔH_1^0 extra- or interpolated from the results of Merli et al. [23].
[f] Using ΔH_1^0 from Merli et al. [23].
[g] Using ΔH_1^0 from Fitzgibbon et al. [21].
[h] In HBr(aq).
[i] Derived from Furkaliouk et al. [34].
[j] In HI(aq).

[26]. When the enthalpies of solution of $LaCl_3$(cr) in HCl(aq) reported in these studies, are combined with the enthalpies of solution of La(cr) in the same media, inter- or extrapolated from the measurements of Merli et al. [23], we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(1070.3 \pm 1.6)$ and $-(1069.4 \pm 1.3)$ kJ mol^{-1}, respectively. The former value agrees well with that derived from the oxide cycle, the latter is somewhat more negative which indicate that the lanthanum oxide samples may have contained some impurities.

Laptev et al. [28] measured the electrochemical cell:

$$(\mathrm{Pt})\mathrm{La}, \mathrm{LaCl_3}/\mathrm{BaCl_2}/\mathrm{MgCl_2}, \mathrm{Mg}(\mathrm{Pt}).$$

Recalculating their results with auxiliary data for Mg from Cox et al. [10] and $MgCl_2$ from Glushko et al. [29], and the thermodynamic functions of $LaCl_3$(cr) given by Pankratz [30], we obtain $\Delta_r H^0(298.15\,K) = -(200.8 \pm 0.9)\,kJ\,mol^{-1}$ by third-law, giving $\Delta_f H^0(298.15\,K) = -(1066.9 \pm 1.1)\,kJ\,mol^{-1}$, somewhat lower than the calorimetric results.

The mean of values derived from the results of Montgomery [25], Spedding and Flynn [20], and Cordfunke and Booij [22], the latter in combination with the results of Fitzgibbon et al. [21] and Merli et al. [23], is selected here, the overall uncertainty being estimated by the present authors:

$$\Delta_f H^0(LaCl_3, cr, 298.15\,K) = -(1071.6 \pm 1.5)\,kJ\,mol^{-1}.$$

3.1.2. $LaBr_3$(cr)

The existing literature data for the standard enthalpy of formation of $LaBr_3$(cr) are listed in Table 2. Hurtgen et al. [31] measured the enthalpy of solution of a well-analyzed sample of $LaBr_3$(cr) in 1.0, 0.1, and 0.001 $mol\,dm^{-3}$ HCl(aq). The enthalpy of solution [31] of $LaBr_3$(cr) in 1.0 $mol\,dm^{-3}$ HCl(aq) can be combined directly with the results of Fitzgibbon et al. [21] for the solution enthalpy of La(cr) in the same medium since the purity of the samples in both studies was high and the molarity of the solvents was identical. This yields $\Delta_f H^0(298.15\,K) = -(905.1 \pm 1.4)\,kJ\,mol^{-1}$. An almost identical value, $\Delta_f H^0(298.15\,K) = -(904.0 \pm 1.4)\,kJ\,mol^{-1}$, is obtained when the more recent value for the enthalpy of solution of La(cr) in 1.0 $mol\,dm^{-3}$ HCl(aq) by Merli et al. [23] is used.

When combining the enthalpy of solution of $LaBr_3$(cr) in 0.1 $mol\,dm^{-3}$ HCl(aq) reported by Hurtgen [31] with the value obtained by von Wartenberg [32] for the enthalpy of solution of La_2O_3(cr) in 0.1 $mol\,dm^{-3}$ HCl(aq), $-(468.6 \pm 6.3)\,kJ\,mol^{-1}$, the value $-(902.3 \pm 6.6)\,kJ\,mol^{-1}$ for the enthalpy of formation of $LaBr_3$(cr) is calculated. The impurities of the lanthanum oxide sample used by von Wartenberg might have been responsible for the less negative value of enthalpy of formation.

Oppermann et al. [26] measured the enthalpies of the solution of La_2O_3(cr) and $LaBr_3$(cr) in 4.0 $mol\,dm^{-3}$ HBr(aq). From their results we obtain $\Delta_f H^0(298.15\,K) = -(902.8 \pm 1.2)\,kJ\,mol^{-1}$, when recalculated with the selected enthalpy of formation of La_2O_3(cr) [16]. This value agrees well with that of the oxide cycle in HCl(aq) based on the results of Hurtgen [31] and von Wartenberg [32], but is somewhat lower than results of the metal cycle, as was the case for $LaCl_3$(cr).

The selected value is the mean of the results of Hurtgen et al. [31], and Fitzgibbon et al. [21] and Merli et al. [23] for the solution measurements in 1.0 $mol\,dm^{-3}$ HCl(aq):

$$\Delta_f H^0(LaBr_3, cr, 298.15\,K) = -(904.4 \pm 1.5)\,kJ\,mol^{-1}.$$

3.1.3. LaI_3(cr)

Values for the standard enthalpy of formation of LaI_3(cr) reported by different authors are listed in Table 2. The value derived from the measurements by Hohmann and Bommer [33] is $-(706.5 \pm 2.7)\,kJ\,mol^{-1}$, which was obtained by solution calorimetry. As already noted, the lanthanum metal sample used by Hohmann and Bommer contained a significant amount of impurities. When the enthalpy of solution of LaI_3(cr) reported by Hohmann and Bommer [33], is combined with an estimated enthalpy of solution of La(cr) in 0.1 $mol\,dm^{-3}$ HCl based on measurements by Spedding and Flynn [20] (see Table 2), we obtain $\Delta_f H^0(298.15\,K) = -(671.9 \pm 0.9)\,kJ\,mol^{-1}$.

The latter value is in reasonable agreement with the results of Furkaliouk et al. [34] who dissolved a mixture of LaI_3 +KCl in 1.0 $mol\,dm^{-3}$ HCl(aq). When their result is combined with the enthalpy of solution of La_2O_3 in the same solvent, we obtained for the enthalpy of formation $\Delta_f H^0(298.15\,K) = -(667.9 \pm 1.5)\,kJ\,mol^{-1}$. When we deduce the enthalpy of solution of pure LaI_3 in 1.0 HCl(aq) from these measurements, we obtain $\Delta_{sln} H^0(298.15\,K) = -(196.6 \pm 1.1)\,kJ\,mol^{-1}$, which yields $\Delta_f H^0(298.15\,K) = -(673.9 \pm 1.6)\,kJ\,mol^{-1}$ when combined with the enthalpy of solution of La(cr) in the same solvent, measured by Merli et al. [23].

Oppermann et al. [26] measured the enthalpies of the solution of La_2O_3(cr) and LaI_3(cr) in 4.0 $mol\,dm^{-3}$ HI(aq). From their results we obtain $\Delta_f H^0(298.15\,K) = -(689.4 \pm 1.1)\,kJ\,mol^{-1}$, when recalculated with the selected enthalpy of formation of La_2O_3(cr) [16]. This value is significantly more negative than those derived from the work of

Furkaliouk et al. [34]. The reason for this is not clear, in absence of chemical analyses of the samples used by Oppermann et al. [26].

We select the value derived from the combined measurements of Furkaliouk et al. [34] and Merli et al. [23]:

$$\Delta_f H^0(\mathrm{LaI_3, cr, 298.15\,K}) = -(673.9 \pm 2.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.2. Cerium

3.2.1. $CeCl_3(cr)$

Values for the standard enthalpy of formation of $CeCl_3$(cr) are summarized in Table 3. All values have been recalculated using recent auxiliary values. The emf measurements by Laptev et al. [35] have been recalculated using the thermodynamic functions of $CeCl_3$ given by Pankratz [30]. The results deviate significantly from the calorimetric values. The result derived from the measurements by Bommer and Hohmann [17] differs by about 30 kJ mol^{-1} from the other values obtained by solution calorimetry, probably due to the substantial amount of potassium impurity in the sample of Ce(cr) used. Nevertheless, when the value of the enthalpy of solution of $CeCl_3$(cr) obtained by Bommer and Hohmann [17] is combined with the enthalpy of solution of Ce(cr) reported by Spedding and Miller [19], the value $\Delta_f H^0(298.15\,\mathrm{K}) = -(1061.1 \pm 0.8)$ kJ mol^{-1} is obtained. The latter value is in good agreement with results of other solution calorimetry studies.

The value, $\Delta_f H^0(298.15\,\mathrm{K}) = -(1059.6 \pm 0.5)$ kJ mol^{-1}, obtained from the results of Spedding and Miller [19] for the enthalpies of solution of Ce(cr) and $CeCl_3$(cr) in 0.24 mol dm^{-3} HCl(aq), is in good agreement with the value derived from the result of Montgomery [36], $\Delta_f H^0(298.15\,\mathrm{K}) = -(1058.9 \pm 0.7)$ kJ mol^{-1}, based on the measurements of well-characterized samples of Ce(cr) and $CeCl_3$(cr) in 1.5 mol dm^{-3} HCl(aq). However, the results of the

Table 3
The enthalpy of formation of CeX_3(cr) at 298.15 K and the enthalpies of solution of Ce(cr) and CeX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$CeCl_3$					
Bommer and Hohman [17,18]	1941	S (0.1)	−726.8 ± 2.9	−136.8 ± 0.7	−1088.8 ± 3.0
					−1061.1 ± 0.8[b]
Spedding and Miller [19]	1952	S (0.24)	−699.2 ± 0.2	−137.1 ± 0.4	−1059.6 ± 0.5
		S (0.37)		−134.2 ± 0.9	
Montgomery [36]	1962	S (1.5)	−690.9 ± 0.6	−129.4 ± 0.3	−1058.9 ± 0.7
Laptev et al. [28]	1990	E			−1029.2 ± 0.7
Cordfunke and Booij [22]	1994	S (0.24)		−136.24 ± 0.48	−1060.5 ± 0.6
Selected value					−1059.7 ± 1.5
$CeBr_3$					
Furkaliouk and Cordfunke [37]	1996	S (0.25)		−168.87 ± 0.38	−891.5 ± 0.8[b]
					−891.4 ± 1.0[c]
					−890.7 ± 1.7[d]
Selected value					−891.2 ± 1.5
CeI_3					
Hohmann and Bommer [33]	1941	S (0.1)	−726.8 ± 2.9	−205.0	−690.4 ± 2.9
				−206.8	−662.8
Furkaliouk et al. [37]	1995	S (1.0)			−669.4 ± 0.9
			−200.9 ± 0.9		−667.3 ± 1.0[b]
					−666.4 ± 1.9[c]
Selected value					−666.8 ± 3.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.

[b] Using ΔH_1^0 from Spedding and Flynn [20].

[c] Recalculation of the reaction cycle in [22] based on KCl/KBr.

[d] Chloride cycle using $\Delta H_1^0(CeCl_3)$ from Corrdfunke and Booji [22].

chemical analysis for the non-metallic impurities of the Ce(cr) sample used by Spedding and Miller [19] were not reported. The values for the enthalpies of solution of $CeCl_3$(cr) in 0.24 and 1.5 mol dm^{-3}, obtained by Spedding and Miller [19] and Montgomery [36], respectively, are in reasonable agreement with each other, taking into consideration the presumed dependence of the enthalpy of solution of rare earth chlorides on the molarity of the solvent. Cordfunke and Booij [22] remeasured the enthalpy of solution of $CeCl_3$(cr) in 0.24 mol dm^{-3} HCl(aq) using a high-purity sample. Combining this value with the value of the enthalpy of solution of Ce(cr) reported by Spedding and Miller [19], $\Delta_f H^0(298.15\,\mathrm{K}) = -(1060.5 \pm 0.6)$ kJ mol^{-1} is obtained. This value is in excellent agreement with the value derived from the measurements by Spedding and Miller [19], and Montgomery [36].

The selected value is the mean from the results of Montgomery [36] and the combination of those of Spedding and Miller [19] for the dissolution of the metal and Cordfunke and Booij [22] for the dissolution of $CeCl_3$. The uncertainty of the selected value is estimated as ±1.5 kJ mol^{-1}:

$$\Delta_f H^0(\mathrm{CeCl_3, cr, 298.15\,K}) = -(1059.7 \pm 1.5)\,\mathrm{kJ\,mol^{-1}}.$$

3.2.2. $CeBr_3$(cr)

The only available value for the enthalpy of formation of $CeBr_3$(cr) has been reported by Furkaliouk and Cordfunke [37], who measured the solution enthalpy of a well-characterized sample of $CeBr_3$ (cr) in 0.25 mol dm^{-3} HCl(aq). The authors derived $\Delta_f H^0(298.15\,\mathrm{K}) = -(891.4 \pm 1.5)$ kJ mol^{-1}, by combining their result with the enthalpies of solution of KCl and KBr in the same medium and with the enthalpy of solution of Ce(cr) in HCl(aq) of the same molarity reported by Spedding and Miller [19]. Combining the enthalpy of solution of $CeBr_3$(cr) directly with the enthalpy of solution of Ce(cr) in HCl(aq) reported by Spedding and Miller [19], yields $\Delta_f H^0(298.15\,\mathrm{K}) = -(891.5 \pm 0.8)$ kJ mol^{-1}. Using a reaction cycle based on the assessed enthalpy of formation of $CeCl_3$, using the enthalpy of solution of $CeCl_3$ reported by Cordfunke and Booij [22], we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(890.7 \pm 1.7)$ kJ mol^{-1}. The mean of the three values is adopted here, the uncertainty being estimated:

$$\Delta_f H^0(\mathrm{CeBr_3, cr, 298.15\,K}) = -(891.2 \pm 1.5)\,\mathrm{kJ\,mol^{-1}}.$$

3.2.3. CeI_3(cr)

The first value for the enthalpy of formation of CeI_3(cr) was reported by Hohmann and Bommer [33] (see Table 3) and is based on enthalpy of solution measurements of Ce(cr) in 0.1 mol dm^{-3} HCl(aq) and CeI_3(cr) in water. The value derived from these results, $\Delta_f H^0(298.15\,\mathrm{K}) = -(690.4 \pm 2.9)$ kJ mol^{-1}, is ∼20 kJ mol^{-1} more negative than the recently reported value by Furkaliouk et al. [34], probably due to impurities in the rare earth metal used by Bommer and Hohmann [18]. Furkaliouk et al. [34] combined the experimental results for the enthalpy of solution of a high purity CeI_3(cr) sample (mixed with KCl at a molar K/Ce ratio of about 3) in 0.25 mol dm^{-3} HCl(aq) with the value reported by Spedding and Miller [19] for the solution enthalpy of Ce(cr) in HCl(aq) of the same molarity. This cycle yields $-(669.3 \pm 1.5)$ kJ mol^{-1} for the enthalpy of formation of CeI_3. From the results of Furkaliouk et al. we calculate for the enthalpy of solution of CeI_3 in 0.25 mol dm^{-3} HCl(aq) $\Delta_{sln}H^0 = -(200.0 \pm 0.9)$ kJ mol^{-1}. This value yields $\Delta_f H^0(298.15\,\mathrm{K}) = -(667.3 \pm 1.0)$ kJ mol^{-1} when combined with the enthalpy of solution of cerium metal [19], and $-(666.4 \pm 1.9)$ kJ mol^{-1} when combined with the enthalpy of solution of $CeCl_3$ in the same medium. The mean of the latter values is selected here:

$$\Delta_f H^0(\mathrm{CeI_3, cr, 298.15\,K}) = -(666.8 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.3. Praseodymium

3.3.1. $PrCl_3$(cr)

The measurements of the enthalpy of formation of $PrCl_3$(cr) are summarized in Table 4. The results have been recalculated using recent auxiliary data. The thermodynamic functions given by Pankratz [30] have been used for the recalculation of the results of emf measurements by Laptev et al. [28].

The value, $\Delta_f H^0(298.15\,\mathrm{K}) = -(1081.1 \pm 2.5)$ kJ mol^{-1}, derived from the results by Bommer and Hohmann [17,18], seems to be in error by about 20 kJ mol^{-1}, probably due to a significant amount

Table 4
The enthalpy of formation of PrX_3(cr) at 298.15 K and the enthalpies of solution of Pr(cr) and PrX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$PrCl_3$					
Bommer and Hohmann [17,18][b]	1941	S (0.1)	−723.4 ± 1.1	−141.8 ± 2.2	−1081.1 ± 2.5
					−1061.8[b]
Lohr and Cunningham [39]	1951	S (1.5)	−687.9 ± 9.6		
Spedding and Flynn [20]	1954	S (0.25)	−704.1	−142.2 ± 0.6	−1059.4
		S (1.47)	−692.8	−125.6 ± 0.9	−1057.7
					−1052.6 ± 9.6[c]
Stubblefield [40]	1969	S (1.0)	−687.9 ± 3.4		
Fitzgibbon et al. [38]	1973	S (2.0)	−692.2 ± 1.3		
Laptev et al. [28]	1990	E			−1035.9 ± 1.1
Selected value					−1058.6 ± 1.5
$PrBr_3$					
Hurtgen et al. [31]	1980	S (1.0)		−171.7 ± 0.7	−874.3 ± 3.4[d]
		S (0.25)		−174.8 ± 0.6[e]	−890.5 ± 4.0[b]
		S (0.1)		−176.3 ± 0.4	−889.9[f]
Selected value					−890.5 ± 4.0
PrI_3					
Hohmann and Bommer [33][g]	1941	S (0.1)	−723.4 ± 1.1	−208.9 ± 0.1	−683.1 ± 1.1
					−664.7 ± 2.0[b]
Selected value					−664.7 ± 5.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.

[b] Using ΔH_1^0 from Spedding and Flynn [20].

[c] Using ΔH_1^0 from Lohr and Cunningham [39].

[d] Using ΔH_1^0 from Stubblefield [40].

[e] Estimated by interpolation.

[f] Using ΔH_1^0 from Bommer and Hohmann [17].

[g] The measurements were carried out at 293 K.

of potassium impurity in the rare earth metal sample used in that study, as it was emphasized by Spedding and Miller [19]. A more reliable enthalpy of formation has been calculated by combining the value for the solution enthalpy of $PrCl_3$(cr) obtained by Bommer and Hohmann [18] with the enthalpy of solution of Pr(cr) in 0.27 mol dm^{-3} HCl(aq), as measured by Spedding and Flynn [20]: $\Delta_f H^0(298.15\,\mathrm{K}) = -1061.8\,\mathrm{kJ\,mol^{-1}}$. This value is in good agreement with the values obtained from the results of Spedding and Flynn [20] based on the results of two sets of solution calorimetric measurements of both Pr(cr) and $PrCl_3$(cr) in 0.25 and 1.47 mol dm^{-3} HCl(aq), respectively. In a later study by Fitzgibbon et al. [38] the enthalpy of solution of a well-characterized sample of Pr(cr) in 2.0 mol dm^{-3} HCl(aq) was measured, being consistent with the single result by Spedding and Flynn [20] obtained in 1.47 mol dm^{-3} HCl(aq), see Table 4. One more value for the enthalpy of formation, $\Delta_f H^0(298.15\,\mathrm{K}) = -(1052.6 \pm 9.6)\,\mathrm{kJ\,mol^{-1}}$ has been derived from the experimental data by Lohr and Cunningham [39] for the enthalpy of solution of praseodymium metal in 1.5 mol dm^{-3} HCl(aq) and the enthalpy of solution of $PrCl_3$(cr) in 1.47 mol dm^{-3} HCl(aq) by Spedding and Flynn [20].

The value calculated from the results of Laptev et al. [28], $\Delta_f H^0(298.15\,\mathrm{K}) = -(1035.9 \pm 1.1)\,\mathrm{kJ\,mol^{-1}}$, differs substantially from the aforesaid values. Probably, an undetected side reaction in the cell was responsible for such a deviation. It should be noted that the results for the enthalpies of formation of $LaCl_3$(cr) and $CeCl_3$(cr) also measured by these authors [28,35], show a poor agreement with the more accurate enthalpy of solution data (see Tables 2 and 3).

The selected enthalpy of formation is the mean of the values derived from the results by Spedding and

Flynn [20], obtained in 0.27 and 1.47 mol dm^{-3} HCl(aq):

$$\Delta_f H^0(\mathrm{PrCl_3, cr, 298.15\,K}) = -(1058.6 \pm 1.5)\,\mathrm{kJ\,mol^{-1}}.$$

The uncertainty of the value has been increased in view of a limited number of measurements of solution of praseodymium metal carried out by the authors [20].

3.3.2. $PrBr_3$(cr)

The thermochemical data used for the evaluation of the standard enthalpy of formation of $PrBr_3$(cr) are listed in Table 4. The only experimental result has been published by Hurtgen et al. [31], who determined the solution enthalpies of $PrBr_3$(cr) in 1.0, 0.1, and 0.001 mol dm^{-3} HCl(aq). Combining the result obtained in 1.0 mol dm^{-3} HCl(aq) with the solution enthalpy of preaseodymium metal measured in the same medium by Stubblefield [40], yields for the enthalpy of formation, $\Delta_f H^0(298.15\,\mathrm{K}) = -(874.3 \pm 3.4)$ kJ mol^{-1}. Taken into consideration that the Pr(cr) sample used for that study was poorly characterized, this value seems not to be reliable. The value $\Delta_f H^0(298.15\,\mathrm{K}) = -890.5$ kJ mol^{-1} has been derived from the single result by Spedding and Flynn [20] for the solution enthalpy of Pr(cr) in 0.25 mol dm^{-3} HCl(aq) and the enthalpy of solution of $PrBr_3$(cr) in the same medium, $\Delta_{sln}H^0 = -(174.8 \pm 0.6)$ kJ mol^{-1}, estimated by interpolation of the results of Hurtgen et al. [31] measured in HCl solutions of different molarity. The accuracy of the thus obtained enthalpy of formation has been adopted as $\pm$4.0 kJ mol^{-1} in view of an insufficient number of solution measurements carried out by Spedding et al. [20].

The selected enthalpy of formation of $PrBr_3$(cr) is the value derived from the results of Hurtgen et al. [31], and Spedding and Flynn [20] for 0.25 mol dm^{-3} HCl(aq):

$$\Delta_f H^0(\mathrm{PrBr_3, cr, 298.15\,K}) = -(890.5 \pm 4.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.3.3. PrI_3(cr)

The standard enthalpy of formation of PrI_3(cr) is poorly known. The only available experimental enthalpy of formation has been reported by Hohmann and Bommer [33], based on the calorimetric determination of the solution enthalpies of both Pr(cr) and PrI_3(cr) in 0.1 mol dm^{-3} HCl(aq) (see Table 4). It was emphasized earlier [20] that a significant contamination of potassium impurity in the rare earth metal samples used by the authors might have produced too negative values for the obtained solution enthalpies. For that reason the enthalpy of formation derived from these results seems much less accurate than the value, $\Delta_f H^0(298.15\,\mathrm{K}) = -664.7$ kJ mol^{-1}, calculated by combining the value for the enthalpy of solution of PrI_3(cr) in 0.1 mol dm^{-3} HCl(aq) with the enthalpy of solution of Pr(cr) in the same medium, $\Delta_{sln}H^0 = -705.0$ kJ mol^{-1}, being estimated from the single result by Spedding and Flynn [20] for the solution enthalpy of Pr(cr) in 0.25 mol dm^{-3} HCl(aq).

The selected enthalpy of formation of PrI_3(cr) is

$$\Delta_f H^0(\mathrm{PrI_3, cr, 298.15\,K}) = -(664.7 \pm 5.0)\,\mathrm{kJ\,mol^{-1}}.$$

The uncertainty has been estimated taking into account the accuracy of the extrapolation procedure and the doubtful quality of the PrI_3(cr) sample.

3.4. Neodymium

3.4.1. $NdCl_3$(cr)

The available data on the standard enthalpy of formation of $NdCl_3$(cr) are summarized in Table 5. The results of the different solution-calorimetric studies show a large scatter. The value derived from the measurements reported by Bommer and Hohmann [17,18] should be considered as an approximate value because of the poor quality of the samples and the insufficient analytical characterization. The concordant results by Spedding and Miller [19], Polyachenok and Novikov [41] obtained by measuring the enthalpies of solution of both Nd(cr) and $NdCl_3$(cr) in 0.25 and 0.2 mol dm^{-3} HCl(aq), respectively, seem also to be not accurate enough since the concentration of non-metallic impurities in neodymium metal samples applied in these studies, is not known.

The first investigation of the enthalpy of formation of $NdCl_3$(cr) made on a specimen of Nd(cr) of appreciable purity, was carried out by Stuve [42] in 4.0 mol dm^{-3} HCl(aq). The result obtained, $\Delta_f H^0(298.15\,\mathrm{K}) = -(1041.3 \pm 1.0)$ kJ mol^{-1}, differs significantly from the earlier values. Corroborative evidence for

Table 5
The enthalpy of formation of NdX_3(cr) at 298.15 K and the enthalpies of solution of Nd(cr) and NdX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$NdCl_3$					
Bommer and Hohmann [17,18]	1941	$S\ (0.1)^{b}$	-717.1 ± 4.3	-150.2 ± 0.2	-1065.7 ± 4.3
			-688.0 ± 2.5^{c}		-1036.6 ± 2.5
Spedding and Miller [19]	1952	S (0.25)	-680.3 ± 0.8	-148.7 ± 0.4	-1029.0 ± 0.9
Polyachenok and Novikov [41]	1963	S (0.2)	-685.8 ± 5.4	-154.8 ± 0.8	-1028.9 ± 5.5
Stuve [42]	1965	S (4.0)	-693.6 ± 0.9	-127.3 ± 0.3	-1041.3 ± 1.0
Popova and Monaenkova [93]	1989	S (2.19)	-686.8 ± 1.0		
Tiflova [75]	1990	S (2.3)	-690.8 ± 1.6	-140.0 ± 0.6	-1036.6 ± 1.7
Cordfunke et al. [46]	1995	S (2.3)		-137.1 ± 0.5	-1039.5 ± 1.7^{d}
			-692.8 ± 2.0^{c}		-1041.5 ± 2.1^{e}
		S (4.0)		-128.3 ± 0.3	-1040.3 ± 1.0^{f}
			-695.1 ± 2.0^{c}		-1041.8 ± 2.0^{e}
Merli et al. [23]	1998	S (1.0)	-689.6 ± 2.0		
		S (3.0)	-693.9 ± 1.3		
		S (6.0)	-695.7 ± 1.8		
Hennig and Oppermann [47]	1998	S (4.0)		-127.5 ± 0.3	-1037.1 ± 0.6^{g}
					-1042.6 ± 2.0^{e}
Selected value					-1040.9 ± 1.0
$NdBr_3$					
Hurtgen et al. [31]	1980	S (0.1)	-688.0 ± 2.5^{c}	-184.5 ± 0.6	-865.6 ± 2.6
Hennig and Oppermann [48]	1999	$S\ (4.0)^{c}$		-169.9 ± 0.2	-862.3 ± 3.1^{g}
Selected value					-864.0 ± 3.0
NdI_3					
Hohmann and Bommer [33]	1941	$S\ (0.1)^{b}$	-717.1 ± 4.3	-215.7 ± 0.2	-670.0 ± 4.3
			-688.0 ± 2.5^{c}		-640.9 ± 2.5
Hennig and Oppermann [49]	2000	$S\ (4.0)^{h}$		-201.8 ± 0.6	-637.4 ± 1.6^{h}
Selected value					-639.2 ± 4.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[b] The measurements were carried out at 293 K.
[c] Value estimated by the present authors.
[d] Using ΔH_1^0 from Tiflova [75].
[e] Using ΔH_1^0 (interpolated) from Merli et al. [23].
[f] Using ΔH_1^0 from Stuva [42].
[g] In HBr(aq); cycle based on $\Delta_f H^0(Nd_2O_3(cr))$.
[h] In HI(aq); cycle based on $\Delta_f H^0(Nd_2O_3(cr))$.

the correctness of Stuve's value comes from the study of the enthalpy of formation of Nd_2O_3 by Fitzgibbon et al. [43]. The enthalpy of formation of Nd_2O_3 derived by combining the results of these authors with Stuve's value for the enthalpy of solution of Nd(cr), $-(1807.2 \pm 2.2)$ kJ mol^{-1}, is in excellent agreement with the value obtained independently by combustion calorimetry, $-(1808.1 \pm 1.0)$ kJ mol^{-1} [44].

In a later study, Tiflova [45] determined the enthalpy of formation by similar calorimetric measurements of Nd(cr) and $NdCl_3$(cr) in 2.3 mol dm^{-3} HCl(aq). The value derived from these results, $\Delta_f H^0(298.15\,K) = -(1036.6 \pm 1.7)$ kJ mol^{-1}, is not in good agreement with that derived from the work of Stuve. Cordfunke et al. [46] remeasured the enthalpies of solution of high-purity sample of $NdCl_3$(cr) in 2.3 and 4.0 mol dm^{-3} HCl(aq). When their results are combined with the enthalpies of solution of Nd(cr) in corresponding solvents [42,45], the enthalpies of formation are $\Delta_f H^0(298.15\,K) = -(1039.5 \pm 1.7)$ and $-(1040.3 \pm 2.1)$ kJ mol^{-1}, respectively. Somewhat more negative values, $-(1041.5 \pm 2.1)$ and $-(1041.8 \pm 2.0)$ kJ mol^{-1}, respectively, are obtained when the enthalpies of solution of the metals obtained by interpolation of the measurements of Merli et al. [23] are used. It is therefore likely that undetected impurities, most probably oxychloride, in the sample of neodymium trichloride used by Tiflova, might have been responsible for the difference with the results given above.

Hennig and Oppermann [47] determined the enthalpies of solution of $NdCl_3(cr)$ and Nd_2O_3 in 4.0 mol dm^{-3} HCl(aq). From these results we calculate $\Delta_f H^0(298.15\,K) = -(1037.1 \pm 0.6)$ kJ mol^{-1}, using the enthalpy of formation of Nd_2O_3 [16] as derived by combustion calorimetry [44] (which in this case is preferred to the selected value [16] to assure an independent reaction cycle). When the enthalpy of solution of $NdCl_3(cr)$ in HCl(aq) is combined with the enthalpy of solution of Nd(cr) in the same medium, interpolated from the measurements of Merli et al. [23], we obtain $\Delta_f H^0(298.15\,K) = -(1042.6 \pm 2.0)$ kJ mol^{-1}.

The mean of the results derived from the measurements by Stuve [42] and Cordfunke et al. [46] for $NdCl_3(cr)$, and Stuve [42] and Merli et al. [23] for Nd(cr) is selected here:

$$\Delta_f H^0(NdCl_3, cr, 298.15\,K) = -(1040.9 \pm 1.0)\,kJ\,mol^{-1}.$$

3.4.2. NdBr$_3$(cr)

Hurtgen et al. [31] determined the solution enthalpies of high-purity sample of $NdBr_3(cr)$ in 0.1 and 0.001 mol dm^{-3} HCl(aq). By combining the result of Hurtgen et al. for $NdBr_3(cr)$ in 0.1 mol dm^{-3} HCl(aq) with an estimated enthalpy of solution of Nd(cr) in 0.1 mol dm^{-3} HCl(aq), $\Delta_{sln}H^0 = -(688.0 \pm 2.5)$ kJ mol^{-1}, based on measurements by Merli et al. [23], we obtain for the enthalpy of formation of $NdBr_3$, $\Delta_f H^0(298.15\,K) = -(865.6 \pm 2.6)$ kJ mol^{-1}.

Hennig and Oppermann [48] determined the enthalpies of solution of $NdBr_3(cr)$ and $Nd_2O_3(cr)$ in 4.0 mol dm^{-3} HBr(aq). From these results we calculate $\Delta_f H^0(298.15\,K) = -(862.3 \pm 1.5)$ kJ mol^{-1}, using the assessed enthalpy of formation of Nd_2O_3 [16].

The selected value is the mean of these two results:

$$\Delta_f H^0(NdBr_3, cr, 298.15\,K) = -(864.0 \pm 3.0)\,kJ\,mol^{-1}$$

3.4.3. NdI$_3$(cr)

The literature data on the enthalpy of formation of $NdI_3(cr)$ are listed in Table 5. The first result based on the solution-calorimetric measurements by Matignon [13], is mainly of historical interest due to difficulties in separating the rare earth elements from each other and by the preparation of pure substances in those days. An other experimental result has been reported by Hohmann and Bommer [33] who measured the enthalpies of solution of Nd(cr) and $NdI_3(cr)$ in 0.1–0.05 mol dm^{-3} HCl(aq) at 293 K. From these results the value $\Delta_f H^0(298.15\,K) = -(670.0 \pm 4.3)$ kJ mol^{-1} is derived. As emphasized earlier, the rare earth metal samples used in that study might have been heavily contaminated by potassium metal resulting in too exothermic values. This is evident when the enthalpy of solution of NdI_3 reported by Hohmann and Bommer [33] is combined with the enthalpy of solution of Nd(cr) in dilute HCl(aq) estimated from measurements by Merli et al. [23], from which we obtain $\Delta_f H^0(298.15\,K) = -(640.9 \pm 2.5)$ kJ mol^{-1}.

Hennig and Oppermann [49] determined the enthalpies of solution of $NdI_3(cr)$ and $Nd_2O_3(cr)$ in 4.0 mol dm^{-3} HI(aq). From these results we calculate $\Delta_f H^0(298.15\,K) = -(637.4 \pm 1.6)$ kJ mol^{-1}, using the assessed enthalpy of formation of Nd_2O_3 [16].

The selected value is the mean of these two results:

$$\Delta_f H^0(NdI_3, cr, 298.15\,K) = -(639.2 \pm 4.0)\,kJ\,mol^{-1}.$$

This value should be considered as a tentative values in view of the insufficient analytical characterization of the samples used in these studies. For that reason the uncertainty has been raised.

3.5. Promethium

3.5.1. PmCl$_3$(cr)

Since experimental values for the standard molar enthalpy of formation of promethium trichloride are not available in the literature, the $\Delta_f H^0(PmCl_3$, cr, 298.15 K) value was estimated using the dependence of $\{\Delta_f H^0(LnCl_3, cr) - \Delta_f H^0(Ln^{3+}, aq)\}$, obtained for the rare earth trichlorides of the hexagonal crystal structure (see Section 4), as well as the assessed value for the enthalpy of formation of the aqueous promethium +3 ion, $\Delta_f H^0(\mathrm{Pm}^{3+}$, aq, 298.15 K$) = -(693 \pm 10)$ kJ mol^{-1} [16]. This gives

$$\Delta_f H^0(\mathrm{PmCl_3, cr, 298.15\,K}) = -(1030 \pm 10)\,\mathrm{kJ\,mol^{-1}}.$$

An almost identical value is obtained by taking the average of the neighboring trichlorides in the lanthanide series, $\Delta_f H^0(298.15\,\mathrm{K}) = -1032$ kJ mol^{-1}.

3.5.2. $PmBr_3(cr)$

The value for the standard enthalpy of formation of promethium tribromide has been estimated using the dependence of $\{\Delta_f H^0(\mathrm{LnBr_3, cr}) - \Delta_f H^0(\mathrm{Ln^{3+}, aq})\}$ on the ionic radii of the lanthanides (see Section 4), and the assessed value for the enthalpy of formation of Pm^{3+}(aq) [16]. Promethium tribromide has an orthorhombic crystal structure, but the accuracy of the results obtained for the rare earth tribromides does not show with certainty a significant difference between the hexagonal, orthorhombic and rhombohedral compounds. Thus, the enthalpy of formation of $\mathrm{PmBr_3}$(cr) has been calculated assuming the same slope of the dependence $\{\Delta_f H^0(\mathrm{LnBr_3, cr}) - \Delta_f H^0(\mathrm{Ln^{3+}, aq})\}$ for all rare earth tribromides:

$$\Delta_f H^0(\mathrm{PmBr_3, cr, 298.15\,K}) = -(858 \pm 10)\,\mathrm{kJ\,mol^{-1}}.$$

An almost identical value is obtained by taking the average of the neighboring tribromides in the lanthanide series, $\Delta_f H^0(298.15\,\mathrm{K}) = -859$ kJ mol^{-1}.

3.5.3. $PmI_3(cr)$

Experimental values for the standard molar enthalpy of formation of promethium tri-iodide as well as any information about the crystal structure of that compound, are not available in the literature. The selected $\Delta_f H^0(298.15\,\mathrm{K})$ value has been estimated using the dependence of $\{\Delta_r H^0(\mathrm{LnI_3, cr}) - \Delta_r H^0(\mathrm{Ln^{3+}, aq})\}$ on the atomic radii of the trivalent lanthanides (see Section 4), and the assessed value of the enthalpy of formation of Pm^{3+}(aq) [16]. Since $\mathrm{PmI_3}$(cr) is a boundary compound in the domains of existence of the rhombic and rhombohedral tri-iodides, both crystal structures are acceptable for promethium tri-iodide with equal degree of probability. At the same time, the accuracy of the results obtained for the rare earth tri-iodides does not show with certainty a significant difference between the hexagonal, orthorhombic and rhombohedral compounds. Thus, the enthalpy of formation of $\mathrm{PmI_3}$(cr) has been calculated assuming the same slope of the dependence $\{\Delta_f H^0(\mathrm{LnI_3, cr}) - \Delta_f H^0(\mathrm{Ln^{3+}, aq})\}$ for all rare earth tri-iodides:

$$\Delta_f H^0(\mathrm{PmI_3, cr, 298.15\,K}) = -(634 \pm 10)\,\mathrm{kJ\,mol^{-1}}.$$

An almost identical value is obtained by taking the average of the neighboring tri-iodides in the lanthanide series, $\Delta_f H^0(298.15\,\mathrm{K}) = -629$ kJ mol^{-1}.

3.6. Samarium

3.6.1. $SmCl_3(cr)$

Values for the standard enthalpy of formation of $\mathrm{SmCl_3}$(cr) are listed in Table 6. When the measurements of Montgomery and Hubert [50] for the enthalpies of solution of $\mathrm{Sm_2O_3}$(cr) and $\mathrm{SmCl_3}$(cr) in 0.48 mol dm^{-3} HCl(aq) are combined with the molar enthalpy of formation of $\mathrm{Sm_2O_3}$ measured by combustion calorimetry [51], the value $\Delta_f H^0(298.15\,\mathrm{K}) = -(1025.1 \pm 1.8)$ kJ mol^{-1} is obtained. The derivation of the enthalpy of formation from the other solution experiments is complex, since none of the investigators measured both the enthalpy of solution of Sm(cr) and $\mathrm{SmCl_3}$(cr). Nevertheless, the solution enthalpies obtained by Morss and Fahey [52] for $\mathrm{SmCl_3}$(cr) in 2.0 mol dm^{-3} HCl(aq), and by Baker et al. [51] for Sm(cr) in the same medium, can be combined. The result $\Delta_f H^0(298.15\,\mathrm{K}) = -(1025.8 \pm 1.3)$ kJ mol^{-1} is in reasonable agreement with the value derived from the results of Montgomery and Hubert. Another value for the enthalpy of formation of $\mathrm{SmCl_3}$(cr) can be derived by combining the enthalpy of $\mathrm{SmCl_3}$(cr) in 0.05 mol dm^{-3} HCl(aq) obtained by Bommer and Hohmann [18], and the solution enthalpy of samarium metal in 0.05 mol dm^{-3} $\mathrm{HClO_4}$(aq) reported by Khanaev et al. [53]. The assumption was made that the enthalpies of solution of Sm(cr) in HCl(aq) and in $\mathrm{HClO_4}$(aq) are equal, taking into consideration the negligible heat effect caused by complexing of Sm^{3+}(aq) in this concentration. The value thus obtained, $\Delta_f H^0(298.15\,\mathrm{K}) = -(1025.9 \pm 1.7)$ kJ mol^{-1}, is in agreement with the results mentioned above.

Hennig and Oppermann [54] determined the enthalpies of solution of $\mathrm{SmCl_3}$(cr) and $\mathrm{Sm_2O_3}$ in 4.0 mol dm^{-3} HCl(aq). From these results we calculate $\Delta_f H^0(298.15\,\mathrm{K}) = -(1025.1 \pm 1.4)$ kJ mol^{-1}, using the enthalpy of formation of $\mathrm{Nd_2O_3}$ [16] as

Table 6
The enthalpy of formation of SmX_3(cr) at 298.15 K and the enthalpies of solution of Sm(cr) and SmX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$SmCl_3$					
Bommer and Hohmann [18]	1941	S (0.05)[b]		−163.2 ± 0.2	−1025.9 ± 1.7[c]
Machlan et al. [60]	1955	S (6.0)		−123.4 ± 0.8	
Montgomery and Hubert [50]	1959	S (0.48)		−158.5 ± 1.0	−1025.1 ± 1.8[d]
Gvelesiani and Yashvilli [55]	1967	S (0.7)	−683.7 ± 5.4		
		S (1.0)	−682.6 ± 2.4		
Baker et al. [51]	1972	S (2.0)	−690.1 ± 1.3		
		S (3.99)	−689.5 ± 3.8		
Morss and Fahey [52]	1976	S (2.0)		−151.9	−1025.8 ± 1.3[e]
Khanaev et al. [53]	1987	S (0.05)[f]	−689.6 ± 1.7		
Hennig and Oppermann [54]	1997	S (4.0)		−139.2 ± 0.2	−1025.1 ± 1.4[d]
					−1025.3 ± 3.8[e]
Selected value					−1025.3 ± 2.0
$SmBr_3$					
Hurtgen et al. [31]	1980	S (1.0)		−190.2 ± 0.9	−850.5 ± 2.6[g]
			−689.0 ± 2.0[h]		−856.9 ± 2.2
		S (0.1)		−195.4 ± 0.8	−856.3 ± 2.1[c]
Selected value					−853.4 ± 3.0
SmI_3					
Hohmann and Bommer [33]	1941	S (0.05)		−237.0 ± 0.7	−621.5 ± 1.8[c]
Selected value					−621.5 ± 4.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[b] The measurements were carried out at 293 K.
[c] Using ΔH_1^0 from Khanaev et al. [53].
[d] Cycle based on $\Delta_f H^0(Sm_2O_3(cr))$.
[e] Using ΔH_1^0 from Baker et al. [51].
[f] The measurements were carried out in $HClO_4$(aq).
[g] Using ΔH_1^0 from Gvelesiani and Yashvilli [55].
[h] Estimated by present authors.

derived by combustion calorimetry [51] (which in this case is preferred to the selected value [16] to assure an independent reaction cycle). When the enthalpy of solution of $SmCl_3$(cr) in HCl(aq) is combined with the enthalpy of solution of Nd(cr) in the same medium [51], we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(1025.3 \pm 3.8)$ kJ mol^{-1}, in excellent agreement.

The selected value is the mean of the values derived from the combined results of Montgomery and Hubert [50] and Baker et al. [51] for the oxide cycle, and the combined results of Morss and Fahey [52] and Baker et al. [51] for the metal cycle, and the values derived from the oxide and metal cycle based on the results of Hennig and Oppermann [54]:

$$\Delta_f H^0(\mathrm{SmCl_3, cr, 298.15\,K}) = -(1025.3 \pm 2.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.6.2. $SmBr_3$(cr)

The only experimental enthalpy of formation of $SmBr_3$(cr) has been reported by Hurtgen et al. [31] and is based on the results of solution calorimetric measurements of $SmBr_3$(cr) in 1.0 and 0.1 mol dm^{-3} HCl(aq) (see Table 6). Combining the results of Hurtgen et al. for the enthalpy of solution of $SmBr_3$(cr) in 1.0 mol dm^{-3} HCl(aq) with the value reported by Gvelesiani and Yashvili [55] for Sm(cr) in the same medium, $\Delta_f H^0(298.15\,\mathrm{K}) = -(850.5 \pm 2.6)$ kJ mol^{-1} has been derived. The accuracy of this value is uncertain because the samarium metal sample used by Gvelesiani and Yashvili was not analyzed for non-metallic impurities. If we estimate the enthalpy of solution of Sm(cr) in 1.0 mol dm^{-3} HCl(aq) as $\Delta_{sln} H^0 = -(689.0 \pm 2.0)$ kJ mol^{-1} from the result of Baker et al. [51], taking into account the general trend that the enthalpy of solution slightly decreases with increasing molarity of the solvent (see Section 4), we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(856.9 \pm 2.2)$ kJ mol^{-1}.

No results are available in the literature for the enthalpy of solution of Sm(cr) in 0.1 mol dm^{-3} HCl(aq). The only value for the enthalpy of solution of Sm(cr) in dilute acid solution is that obtained by Khanaev et al. [53], in 0.06 mol dm^{-3} $HClO_4$(aq). The latter value being combined with the result of Hurtgen et al. [31] for $SmBr_3$(cr) in 0.1 mol dm^{-3} HCl(aq), yields the molar enthalpy of formation, $\Delta_f H^0(298.15\,\mathrm{K}) = -(856.3 \pm 2.1)$ kJ mol^{-1}, which is in reasonable agreement with the aforesaid result.

The selected value is based on the value derived from the measurements of Hurtgen et al. [31], combined with the estimated enthalpy of solution of the metal, the uncertainty being raised to 3.0 kJ mol^{-1}:

$$\Delta_f H^0(\mathrm{SmBr_3, cr, 298.15\,K}) = -(853.4 \pm 3.0)\ \mathrm{kJ\,mol^{-1}}.$$

3.6.3. SmI_3(cr)

A very limited amount of literature data is available for the enthalpy of formation of SmI_3(cr). The only experimental result on the enthalpy of solution of SmI_3(cr) was reported by Hohmann and Bommer [33], who carried out two measurements in ~0.05 mol dm^{-3} HCl(aq) at 293 K: $\Delta_{sln}H^0(293\,\mathrm{K}) = -(233.5 \pm 0.7)$ kJ mol^{-1}. Assuming the same temperature dependence of the solution enthalpies of SmI_3(cr) and $SmCl_3$(cr), the reported enthalpy of solution of SmI_3(cr) corrected to 298.15 K, $\Delta_{sln}H^0(298.15\,\mathrm{K}) = -(237.0 \pm 0.7)$ kJ mol^{-1}, yields $\Delta_f H^0(298.15\,\mathrm{K}) = -(621.5 \pm 1.8)$ kJ mol^{-1} for the enthalpy of formation of SmI_3(cr) when combined with the value for the enthalpy of solution of Sm(cr) in dilute perchloric acid, reported by Khanaev et al. [53]. This is also the selected value. The uncertainty is raised in view of insufficient purity of the SmI_3(cr) sample used by Bommer and Hohmann.

$$\Delta_f H^0(\mathrm{SmI_3, cr, 298.15\,K}) = -(621.5 \pm 4.0)\ \mathrm{kJ\,mol^{-1}}.$$

3.7. Europium

3.7.1. $EuCl_3$(cr)

The first value of the standard enthalpy of formation of $EuCl_3$(cr) was reported by Stuve [56], who measured the enthalpies of solution of both Eu(cr) and $EuCl_3$(cr) in 4.0 mol dm^{-3} HCl(aq) (see Table 7). From his results the value $\Delta_f H^0(298.15\,\mathrm{K}) = -(914.5 \pm 2.5)$ kJ mol^{-1} is obtained. In a later study Fitzgibbon et al. [57] determined the enthalpy of solution of europium metal in the same medium, using a europium metal sample of significantly higher purity. When their value is combined with Stuve's value for the solution enthalpy of $EuCl_3$(cr), we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(936.6 \pm 2.9)$ kJ mol^{-1}. Almost the same value has been calculated from the results of Stuve [56] for the enthalpies of solution of $Eu_2O_3(\mathrm{cr}, \gamma)$ and $EuCl_3$(cr) in 4.0 mol dm^{-3} HCl(aq), and the enthalpy of formation of cubic europium sesquioxide derived by combustion calorimetry by Fitzgibbon et al. [57].

Bommer and Hohmann [17] and Burnett and Cunningham [58,59] measured the enthalpies of solution of $EuCl_3$(cr) and Eu(cr) in 0.1 mol dm^{-3} HCl(aq), respectively. However, the HCl solution used by Burnett and Cunningham was saturated with oxygen gas. According to Burnett and Cunningham the reaction sequence in this medium is

$$\mathrm{Eu(cr) + 2HCl(aq) = EuCl_2(aq) + H_2(g)}$$

$$\mathrm{EuCl_2(aq) + HCl(aq) + \tfrac{1}{4}O_2(g) = EuCl_3(aq) + \tfrac{1}{2}H_2O(sln)}$$

which is clearly different from the reaction given in the scheme in Section 2. When this reaction is used for the reaction scheme, the value $\Delta_f H^0(298.15\,\mathrm{K}) = -(872.3 \pm 2.9)$ kJ mol^{-1} is obtained, which is significantly different from the value derived from the work of Stuve. An explanation for the difference might be the fact that the competing reaction

$$\mathrm{EuCl_2(aq) + HCl(aq) = EuCl_3(aq) + \tfrac{1}{2}H_2(sln)}$$

for the oxidation of Eu^{2+} may occur. If this reaction would dominate, we obtain the value $\Delta_f H^0(298.15\,\mathrm{K}) = -(1015.2 \pm 2.9)$ kJ mol^{-1}. It thus seems likely that some effect cannot be excluded.

The value $\Delta_f H^0(298.15\,\mathrm{K}) = -(920.8 \pm 2.6)$ kJ mol^{-1}, obtained by combining the results of Machlan et al. [60] and Stubblefield et al. [61] for the enthalpies of solution of $EuCl_3$(cr) and Eu(cr) in 6 mol dm^{-3} HCl, respectively, also deviates considerably.

Hennig et al. [62] determined the enthalpies of solution of $EuCl_3$(cr) and Eu_2O_3 in 4.0 mol dm^{-3}

Table 7
The enthalpy of formation of EuX_3(cr) at 298.15 K and the enthalpies of solution of Eu(cr) and EuX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$EuCl_3$					
Bommer and Hohmann [18]	1941	S (0.1)		-172.2 ± 0.2[b]	-872.3 ± 2.9[c] -1015.2 ± 2.9[c,d]
Machlan et al. [60]	1955	S (6.0)		-129.3 ± 0.8	-920.8 ± 2.6[e]
Burnett and Cunningham [58,59]	1964	S (0.1)	-688.6 ± 2.9		
Stuve [56]	1965	S (4.0)	-583.0 ± 2.5[f]	-143.6 ± 0.4	-914.5 ± 2.5 -936.6 ± 2.9[g] -936.1 ± 2.1[h]
Stubblefield et al. [61]	1965	S (6.0)	-589.9 ± 2.9		
Fitzgibbon et al. [57]	1972	S (4.0)	-605.2 ± 2.9		
Hennig et al. [62]	1998	S (4.0)		-146.9 ± 0.2	-893.6 ± 2.1[h] -911.2 ± 2.5[i] -933.4 ± 2.9[g]
Selected value					-935.4 ± 3.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[b] The measurements were carried out at 293 K.
[c] Using ΔH_1^0 from Burnett and Cunningham [58].
[d] Using ΔH_1^0 from Burnett and Cunningham [58] neglecting the effect of oxygen in the HCl(aq) solution.
[e] Using ΔH_1^0 from Stubblefield et al. [61].
[f] Two sets of measurements with different samples of Eu(cr).
[g] Using ΔH_1^0 from Fitzgibbon et al. [57].
[h] Cycle based on $\Delta_f H^0(Eu_2O_3(cr))$.
[i] Using ΔH_1^0 from Stuve [56].

HCl(aq) from which we calculate $\Delta_f H^0(298.15\,K) = -(893.6 \pm 2.1)$ kJ mol^{-1}, using the enthalpy of formation of Eu_2O_3 [16] as derived by combustion calorimetry [57] (which in this case is preferred to the selected value [16] to assure an independent reaction cycle). This value is significantly lower than the ones given in the previous paragraphs. This is observed more often for the values derived from the results of these authors, and is likely due deviations in the enthalpies of solution of the oxides. Therefore, the enthalpy of solution of $EuCl_3$(cr) in HCl(aq) is also combined with the enthalpy of solution of Eu(cr) in the same medium as reported by Fitzgibbon et al. [57], giving $\Delta_f H^0(298.15\,K) = -(933.4 \pm 2.9)$ kJ mol^{-1}.

The selected enthalpy of formation is the mean of the two concordant values derived from the results by Stuve [56] from the oxide cycle and the metal cycle, the latter in combination with the enthalpy of solutions of Eu(cr) by Fitzgibbon et al. [57], and value derived from the metal cycle with the results of Hennig et al. [62] and Fitzgibbon et al. [57]:

$$\Delta_f H^0(EuCl_3, cr, 298.15\,K) = -(935.4 \pm 3.0)\ kJ\,mol^{-1}.$$

3.7.2. $EuBr_3$(cr)

The standard molar enthalpy of formation of $EuBr_3$(cr) is poorly known. The only experimental determination of the enthalpy of formation was carried out by Haschke [63], who studied the incongruent vaporization of $EuBr_3$(cr) according to the reaction

$$2EuBr_3(cr) = 2EuBr_2(cr) + Br_2(g)$$

The equilibrium vapor pressures were measured by a spectrophotometric procedure in the temperature range 502–623 K. Haschke obtained for the enthalpy of reaction at 298.15 K, $\Delta_r H^0(298.15\,K) = (99.0 \pm 1.3)$ kJ mol^{-1} by second-law method and $\Delta_r H^0(298.15\,K) = (112.7 \pm 1.0)$ kJ mol^{-1} by third-law method. When these values are combined with the standard enthalpy of formation of $EuBr_2$(cr), $\Delta_f H^0(298.15\,K) = -(720 \pm 33)$ kJ mol^{-1}, as assessed by Rard [64] from the results of vaporization studies of $EuBr_2$(cr) by Haschke et al. [65,66], and the enthalpy of formation of for Br_2(g) [10], the enthalpy of formation of $EuBr_3$(cr) is obtained as $\Delta_f H^0(298.15\,K) = -(754 \pm 33)$ and $-(761 \pm 33)$ kJ mol^{-1}, respectively. As this analysis is subjected to considerable uncertainties (especially the entropies and heat capacities of the solid europium bromides), the enthalpy of formation of $EuBr_3$ has also been estimated from the general trend in the lanthanide bromide series (see Section 4). The value $\Delta_f H^0(298.15\,K) = -(759 \pm 10)$ kJ mol^{-1} is thus obtained, which is in excellent agreement with the experimental values. This value is selected here.

$$\Delta_f H^0(\mathrm{EuBr_3, cr, 298.15\,K}) = -(759 \pm 10)\,\mathrm{kJ\,mol^{-1}}.$$

3.7.3. EuI_3(cr)

EuI_3(cr) is thermodynamically unstable. Experimental values for its standard molar enthalpy of formation are, therefore, not available. The estimated value (see Section 4) obtained from the dependence of $\{\Delta_r H^0(\mathrm{LnI_3, cr}) - \Delta_r H^0(\mathrm{Ln^{3+}, aq})\}$ on the atomic radii of the trivalent lanthanides (see Section 4), is:

$$\Delta_f H^0(\mathrm{EuI_3, cr, 298.15\,K}) = -(538 \pm 10)\,\mathrm{kJ\,mol^{-1}}.$$

3.8. Gadolinium

3.8.1. $GdCl_3$(cr)

Values for the standard enthalpy of formation of $GdCl_3$(cr) are summarized in Table 8. The emf measurements by Laptev et al. [67] have been recalculated using the thermodynamic functions of $GdCl_3$ given by Pankratz [30]. The results obtained by the different

Table 8
The enthalpy of formation of GdX_3(cr) at 298.15 K and the enthalpies of solution of Gd(cr) and GdX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$GdCl_3$					
Bommer and Hohmann [17,18][b]	1941	S (0.1)	−706.3 ± 2.3[b]	−177.4 ± 0.2	−1027.7 ± 2.3
					−1005.0 ± 1.3[c]
Spedding and Flynn [20]	1954	S (0.27)	−683.6 ± 1.3	−174.1 ± 0.7	−1006.9 ± 1.5
Daire [94]	1968	S (1.0)	−682.8 ± 1.3		
Yashvili and Gvelesiani [95]	1971	S (6.0)	−694.5 ± 1.7		
Tiflova et al. [68]	1989	S (2.19)	−684.9 ± 0.4	−165.3 ± 0.2	−1006.1 ± 0.5
			−695.2 ± 1.5[d]		−1016.3 ± 1.5
Furkaliouk et al. [69]	1992	S (1.0)	−683.7 ± 0.7		
Laptev et al. [67]	1993	E			−1009.8 ± 1.1
Merli et al. [23]	1998	S (1.0)	−694.9 ± 1.0	−170.5 ± 0.7	−1017.5 ± 1.3
		S (6.0)	−696.1 ± 1.1		
		S (6.1)		−136.4 ± 0.7	−1018.9 ± 1.3
Selected value					−1018.2 ± 1.5
$GdBr_3$					
Hurtgen et al. [31]	1980	S (1.0)		−214.8 ± 0.7	−827.0 ± 1.6[c]
					−838.2 ± 1.8[e]
		S (0.27)		−218.4 ± 1.1[f]	−826.3 ± 2.0[c]
		S (0.1)		−219.9 ± 1.1	
Selected value					−838.2 ± 2.0
GdI_3					
Hohmann and Bommer [33]	1941	S (0.1)	−706.3 ± 2.3[b]	−256.0 ± 2.5[g]	−618.9 ± 3.4
Furkaliouk et al. [69]	1992	S (1.0)	−688.2 ± 0.8	−236.9 ± 0.3	−612.9 ± 0.9
					−624.1 ± 1.1[e]
Selected value					−624.1 ± 3.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.

[b] The measurements were carried out at 293 K.

[c] Using ΔH_1^0 from Spedding and Flynn [20].

[d] ΔH_1^0 estimated from the results of Merli et al. [23].

[e] Using ΔH_1^0 from Merli et al. [23].

[f] ΔH_2^0 interpolated from the results of Hurtgen et al. [31].

[g] The value corrected to 298.15 K.

investigators are in reasonable agreement, with the exception of the experimental value reported by Bommer and Hohmann [17,18], who measured the enthalpies of solution of Gd(cr) and $GdCl_3$(cr) in $\sim$0.1 mol dm^{-3} HCl(aq). The discordant value for the enthalpy of formation of $GdCl_3$(cr) derived from that work, could be caused by high contamination of potassium impurity in the sample of rare earth metal used by the authors.

The first thermochemical investigation involving gadolinium metal of sufficient purity was that of Spedding and Flynn [20], who dissolved both Gd(cr) and $GdCl_3$(cr) in 0.27 mol dm^{-3} HCl(aq). From the results $\Delta_f H^0(298.15\,K) = -(1006.9 \pm 1.5)$ kJ mol^{-1} has been obtained. Almost the same value, but of significantly less reliability, has been obtained when combining the result of Spedding and Flynn [20] for the enthalpy of solution of Gd(cr) with the enthalpy of solution of $GdCl_3$(cr) by Bommer and Hohmann [18], $\Delta_f H^0(298.15\,K) = -(1005.0 \pm 1.3)$ kJ mol^{-1}. The uncertainty of the latter value has been increased due to the difference in the molarities of the solvents used in these studies. Tiflova et al. [68] determined the enthalpy of formation of $GdCl_3$(cr) by solution measurements of well-characterized samples of Gd(cr) and $GdCl_3$(cr) in 2.19 mol dm^{-3} HCl(aq), yielding $\Delta_f H^0(298.15\,K) = -(1006.1 \pm 0.5)$ kJ mol^{-1}.

Significantly different values were found by Merli et al. [23]. These authors dissolved high purity Gd(cr) and $GdCl_3$(cr) samples in 1.0 and 6.0 mol dm^{-3} HCl(aq), from which we obtain $\Delta_f H^0(298.15\,K) = -(1017.5 \pm 1.3)$ and $-(1018.9 \pm 1.3)$ kJ mol^{-1}, respectively. The reason for this discrepancy with the earlier data is to be found in the enthalpies of solution of the metal, which are much more negative in the study of Merli et al.

The selected value is the mean of two concordant results of Merli et al. [23], which are preferred in view of the better quality of the metal sample:

$$\Delta_f H^0(GdCl_3, cr, 298.15\,K) = -(1018.2 \pm 1.5)\,kJ\,mol^{-1}.$$

3.8.2. $GdBr_3$(cr)

The only experimental determination leading to the standard enthalpy of formation of $GdBr_3$(cr) was reported by Hurtgen et al. [31], who measured the enthalpies of solution of a well-analyzed sample of $GdBr_3$(cr) in 1.0, 0.1, and 0.001 mol dm^{-3} HCl(aq). When the result obtained in 1.0 mol dm^{-3} HCl(aq) are combined with the enthalpy of solution of Gd(cr) measured by Furkaliouk et al. [69] in the same solvent, the resulting enthalpy of formation is $\Delta_f H^0(298.15\,K) = -(827.0 \pm 1.6)$ kJ mol^{-1}. The value $\Delta_f H^0(298.15\,K) = -(838.2 \pm 1.8)$ kJ mol^{-1} has been calculated by combining the enthalpy of solution of $GdBr_3$ with the enthalpy of solution of Gd(cr) in the same medium as measured by Merli et al. [23]. The latter value is selected here because of better quality of the metal sample used by Merli et al.:

$$\Delta_f H^0(GdBr_3, cr, 298.15\,K) = -(838.2 \pm 2.0)\,kJ\,mol^{-1}.$$

3.8.3. GdI_3(cr)

The first value for the standard enthalpy of formation of GdI_3(cr) was reported by Hohmann and Bommer [18,33], based on the results of solution calorimetric measurements of Gd(cr) and GdI_3 in 0.1 mol dm^{-3} HCl(aq). From these results the value $\Delta_f H^0(298.15\,K) = -(618.9 \pm 3.4)$ kJ mol^{-1} is obtained. This value can be considered only as approximate in view of insufficient purity of the samples. This is especially true for the specimen of gadolinium tri-iodide, which contained a significant amount of GdOI(cr) impurity. Furkaliouk et al. [69] measured the enthalpies of solution of well-analyzed samples of Gd(cr) and GdI_3(cr) in oxygen-free 1.0 mol dm^{-3} HCl(aq). From their results we calculate $\Delta_f H^0(298.15\,K) = -(612.9 \pm 0.9)$ kJ mol^{-1}. However, when the enthalpy of solution of Gd(cr) in 1 mol dm^{-3} HCl(aq) reported by Merli et al. [23] is used, we obtain $\Delta_f H^0(298.15\,K) = -(624.1 \pm 1.1)$ kJ mol^{-1}. As discussed for $GdCl_3$, the measurements by Merli et al. for Gd(cr) are considered the most accurate the selected enthalpy of formation of GdI_3(cr) is therefore the following:

$$\Delta_f H^0(GdI_3, cr, 298.15\,K) = -(624.1 \pm 3.0)\,kJ\,mol^{-1}.$$

3.9. Terbium

3.9.1. $TbCl_3$(cr)

There are two solution calorimetry studies of the enthalpy of formation of $TbCl_3$(cr), as shown in Table 9. The value $\Delta_f H^0(298.15\,K) = -997.1$ kJ

Table 9
The enthalpy of formation of TbX_3(cr) at 298.15 K and the enthalpies of solution of Tb(cr) and TbX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$TbCl_3$					
Stuve [70]	1967	S (4.0)	−689.9	−167.9	−997.1
Fitzgibbon and Holley [72]	1968	S (1.0)	−701.7 ± 2.5		
Spedding and Bisbee in [4]	[b]	S (0.89)	−696.2	−181.5	−1008.6 −1013.9[c] −1009.2[d] −998.2[e]
Bettoville et al. [71]	1987	S (1.0)	−697.0 ± 1.2		
Furkaliouk et al. [73]	1993	S (1.0)	−686.0 ± 0.6		
Selected value					−1010.6 ± 3.0
$TbBr_3$					
Bettoville et al. [71]	1987	S (1.0)	−697.0 ± 1.2	−216.0 ± 1.5	−842.1 ± 2.0 −841.5[f] −846.8 ± 3.0[c]
Selected value					−843.5 ± 3.0
TbI_3					
Furkaliouk [96]	1993	S (1.0)	−682.7 ± 0.4	−240.7 ± 0.3	−608.1 ± 0.5
Furkaliouk et al. [73]	1993	S (1.0)	−686.0 ± 0.6	−240.7 ± 0.3	−611.4 ± 0.7 −621.8[f] −627.1 ± 1.2[c] −622.4 ± 2.5[d]
Selected value					−623.8 ± 3.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[b] Cited in [4].
[c] Using ΔH_1^0 from Fitzgibbon and Holley [72].
[d] Using ΔH_1^0 from Bettonville et al. [71].
[e] Using ΔH_1^0 from Furkaliouk et al. [73].
[f] Using ΔH_1^0 from Spedding and Bisbee in [4].

mol^{-1} is obtained from the measurements by Stuve [70], who determined the enthalpies of solution of Tb(cr) and $TbCl_3$(cr) in 4.0 mol dm^{-3} HCl(aq). This value differs significantly from the other experimental value, $\Delta_f H^0(298.15\,K) = -1008.6$ kJ mol^{-1}, obtained from similar measurements in 0.89 mol dm^{-3} HCl(aq) by Spedding and Bisbee, as reported by Morss [4] with reference to an unpublished series of measurements. The cause of discrepancy is not clear since a number of important experimental details were not given [4].

More recently Bettonville et al. [71] determined the enthalpy of solution of a high-purity sample of terbium metal in 1.0 mol dm^{-3} HCl(aq). When combining their result with the enthalpy of solution of $TbCl_3$(cr) measured by Spedding and Bisbee in [4], the value $\Delta_f H^0(298.15\,K) = -1009.2$ kJ mol^{-1} has been calculated. The latter value includes a small correction made to account for a difference in the molarities of the solvents used by these authors. The results for the enthalpy of solution of Tb(cr) in 1.0 mol dm^{-3} HCl(aq) obtained by Fitzgibbon and Holley [72], and Furkaliouk et al. [73], are also presented in Table 9. The value of Fitzgibbon and Holley [72] for the enthalpy of solution of the metal agrees reasonably with the value reported by Bettonville et al. for a the sample of significantly higher purity. The value by Furkaliouk et al. [73] deviates considerably, probably due to a significant higher amount of impurities in their sample.

The selected enthalpy of formation of $TbCl_3$(cr) is the mean of the values derived from the results by Spedding and Bisbee in [4], and the values obtained by combining the enthalpy of solution of $TbCl_3$ of Spedding and Bisbee with the results of Bettonville et al. [71] and Fitzgibbon and Holley [72]. The uncertainty has been estimated as ±3.0 kJ mol^{-1}:

$$\Delta_f H^0(\mathrm{TbCl_3, cr, 298.15\,K}) = -(1010.6 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.9.2. *$TbBr_3$(cr)*

The standard enthalpy of formation of $TbBr_3$(cr) has been derived from measurements by Bettonville et al. [71] who performed solution-calorimetry measurements of Tb(cr) and $TbBr_3$(cr) in 1.0 mol dm^{-3} HCl(aq). As discussed in the previous section, the enthalpy of solution of Tb(cr) in 1.0 mol dm^{-3} HCl(aq) has also been measured by Fitzgibbon et and Holley [72], and Furkaliouk et al. [73] and in 0.89 mol dm^{-3} HCl(aq) by Spedding and Bisbee (see [4]). Because they are concordant with the result of Bettonville et al., except the measurements of Furkaliouk et al., we select the mean of the three values thus derived (Table 9):

$$\Delta_f H^0(\mathrm{TbBr_3, cr, 298.15\,K}) = -(843.5 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.9.3. *TbI_3(cr)*

The thermodynamic data from which the standard enthalpy of formation of TbI_3(cr) can be derived, are summarized in Table 9. The only experimental value for the enthalpy of solution of TbI_3(cr) was obtained by Furkaliouk et al. [73] by calorimetric measurements in 1.0 mol dm^{-3} HCl(aq). At the same time, several values for the enthalpy of solution of Tb(cr) in that medium are available in the literature. The results obtained by different authors show a considerable scatter. Taking into the consideration the purity of the terbium metal sample and number of measurements carried out as discussed above, the results of Spedding and Bisbee in [4], Fitzgibbon and Holley [72] and Bettonville et al. [71] for the standard molar enthalpy of solution of Tb(cr) in 1.0 mol dm^{-3} HCl(aq) have been selected here as the most reliable. When these values are combined with the reported enthalpy of solution of TbI_3(cr) and other auxiliary data, the standard enthalpy of formation of TbI_3(cr) is obtained:

$$\Delta_f H^0(\mathrm{TbI_3, cr, 298.15\,K}) = -(623.8 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}.$$

The uncertainty has been estimated and reflects the discrepancy in the values for the enthalpy of solution of terbium metal.

3.10. *Dysprosium*

3.10.1. *$DyCl_3$(cr)*

The results of various measurements used for the calculation of the standard molar enthalpy of formation of $DyCl_3$(cr) are summarized in Table 10. The results of these studies show a large scatter. The value for the enthalpy of formation of $DyCl_3$(cr) derived from the results by Bommer and Hohmann [17,18], based on the solution calorimetry measurements of Dy(cr) and $DyCl_3$(cr) in 0.1 mol dm^{-3} HCl(aq), should be considered as an approximate result only, due to the significant amount of impurities in the metal sample used by these authors.

Several values for the enthalpy of solution of dysprosium metal in 4.0 mol dm^{-3} HCl(aq) are available in the literature (see Table 10). For unclear reasons, the results obtained by Montgomery and Stuve, cited in [4], Huber et al. [74], and Tiflova [75] differ more than 14 kJ mol^{-1}. The quality of the dysprosium metal sample used by Huber et al. [74] was high as is evident from the fact that the values for the enthalpy of formation of Dy_2O_3(cr) obtained by combustion calorimetry and by solution calorimetry measurements of Dy(cr) and Dy_2O_3(cr) in 4.0 mol dm^{-3} HCl(aq), are in perfect agreement (see [16]). Combining the value for the enthalpy of solution of Dy(cr) in 4.0 mol dm^{-3} HCl(aq) reported by Huber et al. with that for $DyCl_3$(cr) in the same medium obtained by Montgomery and Stuve, yields for the enthalpy of formation: $\Delta_f H^0(298.15\,\mathrm{K}) = -989.9\,\mathrm{kJ\,mol^{-1}}$. A concordant value, $\Delta_f H^0(298.15\,\mathrm{K}) = -987.1\,\mathrm{kJ\,mol^{-1}}$, was derived from unpublished measurements of the enthalpy of solution of Dy(cr) and $DyCl_3$(cr) in 4.0 mol dm^{-3} HCl(aq) by Montgomery and Stuve, as reported by Morss [4].

The values for the enthalpy of formation of $DyCl_3$(cr) derived from the enthalpies of solution of Dy(cr) and $DyCl_3$(cr) in 1.07, 2.19, and 4.0 mol dm^{-3} HCl(aq), respectively, measured in the same laboratory by Monaenkova et al. [76], and Tiflova [75] show much scatter, possibly due to undetected systematic errors. The result obtained for the solution of the lowest molarity, seems to be more reliable, since the enthalpy of solution of Dy(cr) in 1.07 mol dm^{-3} HCl(aq) and that measured in 0.88 mol dm^{-3} $HClO_4$(aq), are in reasonable agreement.

Table 10
The enthalpy of formation of DyX_3(cr) at 298.15 K and the enthalpies of solution of Dy(cr) and DyX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$DyCl_3$					
Bommer and Hohmann [17,18][b]	1941	S (0.1)	−695.5 ± 0.2	−197.9 ± 0.4	−996.4 ± 0.5
Montgomery and Stuve	1961[c]	S (4.0)	−692.4	−180.4	−987.0
					−989.9 ± 3.0[d]
Huber et al. [74]	1971	S (4.0)	−695.3 ± 2.9		
Morss and Fahey [52]	1976	S (4.0)	−691 ± 9	−180.4 ± 1.1	−985.6 ± 9.1
Monaenkova et al. [76]	1989	S (2.19)	−704.2 ± 0.6	−190.7 ± 0.2	−999.9 ± 0.7
Tiflova [75]	1990	S (1.07)	−701.0 ± 0.6	−198.8 ± 0.3	−995.0 ± 0.7
		S (4.01)	−706.5 ± 0.4	−177.2 ± 0.5	−1004.4 ± 0.7
					−993.1 ± 3.0[d]
					−992.9 ± 3.1[e]
Cordfunke et al. [46]	1996	S (4.0)	−699.4 ± 1.3	−180.1 ± 0.2	−994.4 ± 1.3
					−990.0 ± 3.0[e]
Selected value					−993.1 ± 3.0
$DyBr_3$					
Bommer and Hohmann [17][b]	1941	S (0.1)	−694.0 ± 0.2		
Hurtgen et al. [31]	1980	S (1.0)		−218.9 ± 0.2	−840.2 ± 0.7[f]
		S (0.1)		−223.2 ± 1.4	−834.4 ± 1.5[g]
		S (0.1)		−223.2 ± 1.4	−838.3 ± 1.7[h]
Cordfunke and Booij [77]	1995	S (1.0)			−835.0 ± 1.5
				−224.9 ± 0.4[i]	−834.3 ± 2.2[h]
Selected value					−834.3 ± 3.0
DyI_3					
Hohmann and Bommer [33][b]	1941	S (0.1)	−694.8 ± 0.2	−256.7 ± 1.0	−606.7 ± 1.0
Morss and Spence [78]	1992	S (1.0)	−691 ± 9	−242 ± 8	−615.1 ± 12.0
Cordfunke and Booij [77]	1997	S (1.0)			−619.3 ± 1.8
				−248.9 ± 0.4[i]	−616.7 ± 2.1[h]
Leonidov and Furkalyuk [79]	1999	S (4.0)		−229.0 ± 0.6	−621.7 ± 1.4[j]
Selected value					−616.7 ± 3.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[b] The measurements were carried out at 294 K.
[c] Cited in [4].
[d] Using ΔH_1^0 from Huber et al. [74].
[e] Cycle based on $\Delta_f H^0$(Dy_2O_3(cr)).
[f] Using ΔH_1^0 from Tiflove [75].
[g] Using ΔH_1^0 from Bommer and Hohmann [17].
[h] Cycle based on $\Delta_f H^0$($CeCl_3$(cr)).
[i] Estimated from Cordfunke and Booij [77].
[j] Using ΔH_1^0 from Cordfunke and Booij [77].

Two more enthalpy of formation values can be derived by combining the result of Tiflova [75] for the enthalpy of solution of $DyCl_3$(cr) in 4.0 mol dm^{-3} HCl(aq), with the results of Huber et al. [74] for the enthalpies of solution of Dy(cr) to yield $\Delta_f H^0(298.15\,\mathrm{K}) = -(993.1 \pm 3.0)$ kJ mol^{-1} and by combining with the enthalpy of solution of Dy_2O_3 (cr) and the enthalpy of formation of Dy_2O_3(cr) derived from combustion calorimetry [16], to yield $\Delta_f H^0(298.15\,\mathrm{K}) = -(992.9 \pm 3.1)$ kJ mol^{-1}. Both values are within the uncertainties with the aforesaid two values.

Cordfunke et al. [46] determined the enthalpies of Dy metal and $DyCl_3$ in 4.0 mol dm^{-3} HCl(aq) from which we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(994.4 \pm 1.3)$ kJ mol^{-1}. When combined with the enthalpy of solution of Dy_2O_3(cr) [74] we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(990.0 \pm 3.0)$ kJ mol^{-1}.

The selected enthalpy of formation of $DyCl_3$(cr) is the mean of the values derived from measurements by Tiflova [75] in 1.07 mol dm^{-3} HCl(aq) and Cordfunke et al. [46] in 4.0 mol dm^{-3} HCl(aq), and the values obtained by combining the enthalpies of solution of $DyCl_3$ in 4.0 mol dm^{-3} HCl(aq) from these studies with the enthalpies of solution of Dy(cr) or Dy_2O_3(cr) in the same medium [74]:

$$\Delta_f H^0(\mathrm{DyCl_3, cr, 298.15\,K}) = -(993.1 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.10.2. $DyBr_3$(cr)

The only experimental values for the enthalpy of solution of pure $DyBr_3$(cr) were reported by Hurtgen et al. [31]. Combining their result for the enthalpy of solution of $DyBr_3$(cr) in 1.0 mol dm^{-3} HCl(aq) with the value for solution of Dy(cr) in the same medium reported by Tiflova [75], the value $\Delta_f H^0(298.15\,K) = -(840.2 \pm 0.7)$ kJ mol^{-1} has been derived. Their result for 0.1 mol dm^{-3} HCl(aq) can be combined with the enthalpy of solution of Dy(cr) in 0.1 mol dm^{-3} HCl(aq) reported by Bommer and Hohmann [18], which is the only value available at this concentration, yielding $\Delta_f H^0(298.15\,K) = -(834.4 \pm 1.5)$ kJ mol^{-1}.

Cordfunke and Booij [77] determined the enthalpy of solution of a mixture of $DyBr_3$ + KCl in 0.1025 mol dm^{-3} HCl(aq) and, based on a cycle involving the enthalpies of formation of KCl(cr) and KBr(cr), the value $\Delta_f H^0(298.15\,K) = -(835.0 \pm 1.5)$ kJ mol^{-1} is derived. When we deduce the enthalpy of solution of pure $DyBr_3$ in 0.1 HCl(aq) from the measurements by Cordfunke and Booij, we obtain $\Delta_{sln} H^0(298.15\,K) = -(224.9 \pm 0.4)$ kJ mol^{-1}, which yields $\Delta_f H^0(298.15\,K) = -(834.3 \pm 2.2)$ kJ mol^{-1} when combined with the enthalpy of solution of $DyCl_3$(cr) in the same solvent, measured by Cordfunke et al. [46].

The latter approach can also be applied for the result of Hurtgen et al. [31] in 0.1 mol dm^{-3} HCl(aq), yielding $\Delta_f H^0(298.15\,K) = -(838.3 \pm 1.7)$ kJ mol^{-1}.

The selected value is based on the latter two results in which the chloride cycle was applied:

$$\Delta_f H^0(\mathrm{DyBr_3, cr, 298.15\,K}) = -(834.3 \pm 2.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.10.3. DyI_3(cr)

The available literature data on the enthalpy of formation of DyI_3(cr) are presented in Table 10. The value derived from the measurements of DyI_3 (cr) reported by Hohmann and Bommer [33], $\Delta_f H^0(298.15\,K) = -(606.7 \pm 1.0)$ kJ mol^{-1}, is based on solution calorimetric measurements of Dy(cr) in 0.1 mol dm^{-3} HCl(aq) and DyI_3(cr) in water, carried out at 293 K. More recently, Morss and Spence [78] measured the enthalpies of solution of DyI_3(cr) in 1.0 and 0.001 mol dm^{-3} HCl(aq). According to the chemical analysis, the sample of DyI_3(cr) used in that work, contained 3% of insoluble DyOI(cr). Therefore, the result of this study has not been used.

Cordfunke and Booij [77] determined the enthalpy of solution of a mixture of DyI_3 + KCl in 0.1025 mol dm^{-3} HCl(aq) and based on a cycle involving the enthalpies of formation of KCl(cr) and KI(cr), the value $\Delta_f H^0(298.15\,K) = -(619.3 \pm 1.8)$ kJ mol^{-1} is derived. When we deduce the enthalpy of solution of pure DyI_3 in 0.1 HCl(aq) from the measurements by Cordfunke and Booij, we obtain $\Delta_{sln} H^0(298.15\,K) = -(284.9 \pm 0.4)$ kJ mol^{-1}, which yields $\Delta_f H^0(298.15\,K) = -(616.7 \pm 2.1)$ kJ mol^{-1} when combined with the enthalpy of solution of $DyCl_3$(cr) $_3$(cr) in the same solvent, measured by Cordfunke et al. [46].

Leonidov and Furkaliouk [79] measured the enthalpy of solution of DyI_3 in 4.0 mol dm^{-3} HCl(aq) using a high purity sample, and obtained the value $\Delta_{sln} H^0(298.15\,K) = -(229.0 \pm 0.6)$ kJ mol^{-1}. From this value we derive $\Delta_f H^0(298.15\,K) = -(621.7 \pm 1.4)$ kJ mol^{-1} when combined with the enthalpy of solution of the metal measured by Cordfunke et al. [46].

We select the value derived from the results of Cordfunke et al. [46] using the chloride cycle:

$$\Delta_f H^0(\mathrm{DyI_3, cr, 298.15\,K}) = -(616.7 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.11. Holmium

3.11.1. $HoCl_3$(cr)

The values for the standard molar enthalpy of formation of $HoCl_3$(cr) available in the literature, are rather contradictory (Table 11). Bommer and Hohmann [17,18] reported the first value for the enthalpy of formation of $HoCl_3$(cr) based on the

Table 11
The enthalpy of formation of HoX_3(cr) at 298.15 K and the enthalpies of solution of Ho(cr) and HoX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$HoCl_3$					
Bommer and Hohmann [17][b]	1941	S (0.1)	−686.2	−209.2	−975.8
Stuve [70]	1967	S (4.0)	-710.5 ± 7.1	-180.5 ± 0.3	-1005.1 ± 7.1
Spedding and Bisbee	[c]	S (0.87)	−698.3	−202.3	−980.8 −997.4[d]
Bettonville et al. [71]	1987	S (1.0)[e]	-705.9 ± 1.9		
Lezhava [80]	1992	S (1.07)	-704.5 ± 2.2	-199.2 ± 0.8	-998.0 ± 2.4
Selected value					-997.7 ± 2.5
$HoBr_3$					
Bettonville et al. [71]	1987	S (1.0)[e]	-705.9 ± 2.4	-221.9 ± 1.2	-842.1 ± 2.7
Selected value					-842.1 ± 3.0
HoI_3					
Bommer and Hohmann [17][b]	1941	S (0.1)	−686.2	−259.4	−596.4
Lezhava [80]	1990	S		-255.1 ± 1.2	-622.9 ± 3.2
Selected value					-622.9 ± 3.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[b] The measurements were carried out at 293 K.
[c] Cited in [4].
[d] Using ΔH_1^0 from Bettonville et al. [71].
[e] Two different samples of Ho(cr) were used.

results of a single calorimetric measurement of Ho(cr) as well as $HoCl_3$(cr) in ~0.1 mol dm^{-3} HCl(aq). From their results we derive $\Delta_f H^0(298.15\,K) = -975.8$ kJ mol^{-1}. A more reliable value, $\Delta_f H^0(298.15\,K) = -(1005.1 \pm 7.1)$ kJ mol^{-1}, has been derived from the results obtained by Stuve [70] for the solution enthalpies of Ho(cr) and $HoCl_3$(cr) in 4.0 mol dm^{-3} HCl(aq). Lezheva [80] measured the enthalpies of solution of well-characterized samples of Ho(cr) and $HoCl_3$(cr) in 1.07 mol dm^{-3} HCl(aq). From these data we calculate $\Delta_f H^0(298.15\,K) = -(998.0 \pm 2.4)$ kJ mol^{-1}. It should be noted that the value for the enthalpy of solution of Ho(cr) in 1.0 mol dm^{-3} HCl(aq) reported by Lezheva is in good agreement with that measured by Bettonville et al. [71] using two high-purity holmium metal samples.

Morss [4] reported values for the enthalpy of solution of Ho(cr) and $HoCl_3$(cr) with a reference to a private communication by Spedding and Bisbee which is inaccessible to us. From these values we obtain $\Delta_f H^0(298.15\,K) = -980.8$ kJ mol^{-1}. However, when the value for the enthalpy of solution of $HoCl_3$(cr) in 0.87 mol dm^{-3} HCl(aq) is combined with that for Ho(cr) in 1.0 mol dm^{-3} HCl(aq) reported by Bettonville et al. [71], the value $\Delta_f H^0(298.15\,K) = -997.4$ kJ mol^{-1} is obtained, being in good agreement with the result of Lezhava [80].

The selected enthalpy of formation of $HoCl_3$(cr) is the mean of the value derived from the measurements by Lezhava [80] and the value obtained by combining the results of Bettonville et al. [71] and Spedding and Bisbee. The uncertainty is estimated as ±2.5 kJ mol^{-1}:

$$\Delta_f H^0(HoCl_3, cr, 298.15\,K) = -(997.7 \pm 2.5)\,kJ\,mol^{-1}.$$

3.11.2. $HoBr_3$(cr)

The only experimental value for the standard molar enthalpy of formation of $HoBr_3$(cr) was determined by Bettonville et al. [71] by solution-calorimetric measurements of high-purity samples of Ho(cr) and $HoBr_3$(cr) in 1.0 mol dm^{-3} HCl(aq). These results yield for the selected enthalpy of formation of $HoBr_3$(cr):

$$\Delta_f H^0(HoBr_3, cr, 298.15\,K) = -(842.1 \pm 3.0)\,kJ\,mol^{-1}.$$

3.11.3. $HoI_3(cr)$

The thermodynamic data from which the enthalpy of formation of $HoI_3(cr)$ can be derived, are listed in Table 11. The first experimental value was determined by Hohmann and Bommer [17,33] by solution calorimetric measurements of Ho(cr) in 0.1 mol dm^{-3} HCl(aq) (one experiment) and $HoI_3(cr)$ in water (one experiment) at 293 K. The value derived from these data is $\Delta_f H^0(298.15\,K) = -596.4\,kJ\,mol^{-1}$.

Recently, a more accurate value for the enthalpy of solution of well-characterized sample of $HoI_3(cr)$ at infinite dilution was obtained by Lezhava [80,81]. Combining this result with the assessed value for the enthalpy of formation of $Ho^{3+}(aq)$ [16], yields the enthalpy of formation of $HoI_3(cr)$, which is selected here:

$$\Delta_f H^0(HoI_3, cr, 298.15\,K) = -(622.9 \pm 3.0)\,kJ\,mol^{-1}.$$

3.12. Erbium

3.12.1. $ErCl_3(cr)$

The data for the enthalpy of formation of $ErCl_3(cr)$, summarized in Table 12, show a large scatter. The values for the enthalpies of solution of Er(cr) in HCl(aq) obtained by different authors [18,20,73,75,82] are inconsistent according to the expected dependence of the solution enthalpies of the rare earth metals on the molarity of the solvent. In particular, the results of Spedding and Flynn [20], and Fuger et al. [82] for the enthalpy of solution of Er(cr) in ~1.4 mol dm^{-3} HCl(aq) differ by about 45 kJ mol^{-1}. Among all the values for the enthalpy of solution of erbium metal, which are presented in Table 12, the result of Fuger et al. [82], seems to be the most reliable and best documented, since their sample was better characterized and of high purity. The value for the enthalpy of formation of $ErCl_3(cr)$, $\Delta_f H^0(298.15\,K) = -(994.6$

Table 12
The enthalpy of formation of $ErX_3(cr)$ at 298.15 K and the enthalpies of solution of Er(cr) and $ErX_3(cr)$ in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$ErCl_3$					
Bommer and Hohmann [17,18][b]	1941	S (0.1)	−680.1 ± 3.1	−207.3 ± 0.2	−971.6 ± 3.1
Spedding and Flynn [20]	1954	S (1.42)	−661.4 ± 0.9	−193.3 ± 0.4	−958.9 ± 1.0
Montgomery and Stuve [83]	1961	S (1.4)		−201.9 ± 0.9	−994.5 ± 1.7[c]
					−994.3 ± 2.8[d]
Gamanovich and Glybin [97][c]	1974	S (2.03)		−201.7 ± 1.2	
Fuger et al. [82]	1980	S (1.43)	−705.6 ± 1.4	−201.7 ± 0.2	−994.6 ± 1.4
Tiflova [75][e]	1990	S (2.19)	−681.9 ± 0.7	−197.3 ± 0.2	−971.1 ± 0.8
		S (2.19)	−682.9 ± 1.8	−197.3 ± 0.2	−972.1 ± 1.8
Furkaliouk et al. [73]	1993	S (1.0)	−681.8 ± 0.7		
Merli et al. [23]	1998	S (6.0)	−707.0 ± 1.2		
Selected value					−994.4 ± 2.0
$ErBr_3$					
Hurtgen et al. [31]	1980	S (1.0)	−705.0 ± 3.0[f]	−226.0 ± 0.5	−837.1 ± 3.0
Selected value					−837.1 ± 3.0
ErI_3					
Bommer and Hohmann [17][b]	1941	S (0.1)	−680.1 ± 3.1	−261.1 ± 0.6	−587.6 ± 3.2
Furkaliouk et al. [37]	1995	S (1.0)	−681.8 ± 0.7	−252.1 ± 0.2	−595.8 ± 0.7
			−705.0 ± 3.0[f]		−619.0 ± 3.0[f]
Selected value					−619.0 ± 3.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.

[b] The measurements were carried out at 293 K.

[c] Using ΔH_1^0 from Fuger and Morss [82].

[d] Based on the enthalpy of solution of $Er_2O_3(cr)$.

[e] Two sets of measurements with different samples of Er(cr).

[f] The value estimated from the results of Fuger et al. [82] and Merli et al. [23].

$\pm$ 1.4) kJ mol^{-1}, obtained from the data by Fuger et al. [82], is in perfect agreement with the result of Montgomery and Stuve [83] who measured the solution enthalpies of $ErCl_3$(cr) and Er_2O_3(cr) in 1.4 mol dm^{-3} HCl(aq), from which the values $\Delta_f H^0(298.15\,K) = -(994.5 \pm 1.7)$ and $-(994.3 \pm 2.8)$ kJ mol^{-1}, respectively, have been derived. For the standard enthalpy of formation of Er_2O_3(cr) the value obtained by combustion calorimetry, $-(1897.8 \pm 3.8)$ kJ mol^{-1}, has been used [84] to assure a truly independent reaction cycle.

The enthalpy of solution of $ErCl_3$(cr) in 2.19 mol dm^{-3} HCl(aq) reported by Tiflova [75] is in reasonable agreement with the values obtained in $\sim$1.2 mol dm^{-3} HCl(aq) [82,83], with respect to the dependence of the solution enthalpies of erbium trichloride on the concentration of the solvent. However, the inconsistent value for the enthalpy of solution of Er(cr) obtained by Tiflova [75], is responsible for the significant disagreement in the values obtained.

The selected value is the mean of the results of Montgomery and Stuve [83] and Fuger et al. [82]:

$$\Delta_f H^0(ErCl_3, cr, 298.15\,K) = -(994.4 \pm 2.0)\,kJ\,mol^{-1}.$$

3.12.2. *$ErBr_3$(cr)*

The standard enthalpy of formation of $ErBr_3$(cr) has been derived from the experimental results by Hurtgen et al. [31], who measured the solution enthalpy of a well-characterized sample of $ErBr_3$(cr) in 1.0 HCl(aq) (Table 12). Combining the result obtained with the enthalpy of solution of Er(cr) in the same medium by Furkaliouk et al. [85], is difficult since these values are not consistent with respect to the dependence of the solution enthalpies on the molarity of the solvent. It has already been emphasized above that the enthalpy of solution of Er(cr) in 1.4 mol dm^{-3} HCl(aq) reported by Fuger et al. [82], is considered in the present assessment as the most reliable. This value being extrapolated to 1.0 mol dm^{-3} HCl(aq) taking into account the result of Merli et al. [23] for 6.0 mol dm^{-3} $-(705.0 \pm 3.0)$ kJ mol^{-1}, and combined with the result of Hurtgen et al. obtained in 1.0 mol dm^{-3} HCl(aq) yields the enthalpy of formation of $ErBr_3$(cr):

$$\Delta_f H^0(ErBr_3, cr, 298.15\,K) = -(837.1 \pm 3.0)\,kJ\,mol^{-1}.$$

The uncertainty is estimated.

3.12.3. *ErI_3(cr)*

The first value for the standard enthalpy of formation of ErI_3(cr) has been obtained by Hohmann and Bommer [17,33] based on solution calorimetric measurements of Er(cr) in 0.1 mol dm^{-3} HCl(aq) and ErI_3(cr) in water (two measurements) at 293 K. The value thus obtained, $\Delta_f H^0(298.15\,K) = -(587.6 \pm 3.2)$ kJ mol^{-1}, seems to be not reliable due to the insufficient quality of the sample of the rare earth metal.

Furkaliouk et al. [85] determined the enthalpy of formation of ErI_3(cr) from the solution enthalpies of both Er(cr) and ErI_3(cr) in 1.0 mol dm^{-3} HCl(aq). From the results we obtain $\Delta_f H^0(298.15\,K) = -(595.8 \pm 0.7)$ kJ mol^{-1}. However, as discussed above, the enthalpy of solution of Er(cr) measured by Furkaliouk et al [85], is questionable. A significantly different value, $\Delta_f H^0(298.15\,K) = -(619.0 \pm 3.0)$ kJ mol^{-1}, has been calculated by combining the result of Furkaliouk et al. for the enthalpy of solution of ErI_3(cr) with the enthalpy of solution of Er(cr) reported by Fuger and Morss [82], extrapolated to 1.0 mol dm^{-3} HCl(aq). Taking into the consideration that the result of Fuger and Morss has been adopted in the present assessment as the most accurate and best documented value for the enthalpy of solution of Er(cr), the latter enthalpy of formation of ErI_3(cr) seems to be more reliable. This value is selected here, with an estimated uncertainty:

$$\Delta_f H^0(ErI_3, cr, 298.15\,K) = -(619.0 \pm 3.0)\,kJ\,mol^{-1}.$$

3.13. *Thulium*

3.13.1. *$TmCl_3$(cr)*

Table 13 lists the available literature data for the enthalpy of formation of $TmCl_3$(cr). The enthalpy of formation obtained from the results by Bommer and Hohmann [17,18] deviates more than 25 kJ mol^{-1} from later solution calorimetric studies [4,86,87], probably due to a significant amount of impurities in the samples of Tm(cr) and $TmCl_3$(cr) used by these authors.

The first thermochemical investigation of the enthalpy of formation of $TmCl_3$(cr) using a sample of thulium metal of acceptable purity was carried out by Stuve [87] by solution calorimetric measurements of both Tm(cr) and $TmCl_3$(cr) in 4.0 mol dm^{-3} HCl(aq). For unclear reasons the result obtained,

Table 13
The enthalpy of formation of TmX_3(cr) at 298.15 K and the enthalpies of solution of Tm(cr) and TmX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$TmCl_3$					
Bommer and Hohmann [17,18][b]	1941	S (0.1)	−675.7 ± 0.4	−212.9 ± 0.1	−961.6 ± 0.5
Stuve [87]	1967	S (4.0)	−698.0 ± 1.3	−186.6 ± 0.9	−986.5 ± 1.6
Spedding and Bisbee	[c]	S (0.89)	−705.7	−205.8	−993.8
Lezhava et al. [80][d]	1992	S (1.07)	−709.3 ± 0.8	−203.3 ± 0.4	−998.7 ± 0.9
Selected value					−996.3 ± 2.5
TmI_3					
Bommer and Hohmann [17,33][b]	1941	S (0.1)	−675.7 ± 0.4	−261.9	−583.4
Lezhava et al. [80]	1992	S (H_2O)		−261.8 ± 1.8	−619.7 ± 3.5
Selected value					−619.7 ± 3.5

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.
[b] The measurements were carried out at 293 K.
[c] Cited in [4].
[d] Two sets of measurements with different samples of Tm(cr).

$\Delta_f H^0(298.15\,K) = -(986.5 \pm 1.6)$ kJ mol^{-1}, differs noticeably from the value, $\Delta_f H^0(298.15\,K) = -993.8$ kJ mol^{-1}, derived from measurements by Spedding and Bisbee, as reported by Morss [4]. The accuracy of the latter value is difficult to evaluate, since no experimental details were given. In view of aforesaid discrepancy, Lezhava et al. [86] redetermined the enthalpy of formation of $TmCl_3$(cr) by measuring the enthalpies of solutions of well-characterized sample of $TmCl_3$(cr) and two specimens of Tm(cr) in 1.07 mol dm^{-3} HCl(aq). From their results we obtain $\Delta_f H^0(298.15\,K) = -(998.7 \pm 0.9)$ kJ mol^{-1}.

Taking into consideration the general quality of the work by Spedding and Bisbee, as well as the reliability of the results of Lezhava et al., the selected enthalpy of formation of $TmCl_3$(cr) is the mean of the values obtained by these authors, the uncertainty of the mean being estimated as ±2.5 kJ mol^{-1}:

$$\Delta_f H^0(TmCl_3, cr, 298.15\,K) = -(996.3 \pm 2.5)\,kJ\,mol^{-1}.$$

3.13.2. $TmBr_3$(cr)

Experimental values for the standard molar enthalpy of formation are not available. The estimated value, based on the dependence of $\{\Delta_r H^0(LnBr_3, cr) - \Delta_r H^0(Ln^{3+}, aq)\}$ on the atomic radii of the trivalent lanthanides (see Section 4), is

$$\Delta_f H^0(TmBr_3, cr, 298.15\,K) = -(832 \pm 10)\,kJ\,mol^{-1}.$$

3.13.3. TmI_3(cr)

Literature values for the standard enthalpy of formation of TmI_3(cr) are presented in Table 13. The first value was reported by Hohmann and Bommer [17,33] based on the results of solution calorimetric measurements of Tm(cr) in ~0.1 mol dm^{-3} HCl(aq) (two experiments), and a single measurement of TmI_3(cr) in water, carried out at 293 K. The value thus obtained, $\Delta_f H^0(298.15\,K) = -583.4$ kJ mol^{-1}, is not reliable, since the samples, especially thulium metal, contained a significant amount of impurities.

Lezhava [80,81] measured the enthalpy of solution of a well-analyzed sample of TmI_3(cr) in water at the average concentration of 0.0006 mol kg^{-1}, $\Delta_{sln} H^0(298.15\,K) = -(261.8 \pm 1.8)$ kJ mol^{-1}. This value leads to the following enthalpy of formation of TmI_3(cr), using the enthalpy of formation of the Tm^{3+} ion [16], being selected here:

$$\Delta_f H^0(TmI_3, cr, 298.15\,K) = -(619.7 \pm 3.5)\,kJ\,mol^{-1}.$$

3.14. Ytterbium

3.14.1. $YbCl_3$(cr)

The enthalpy of formation of $YbCl_3$(cr) is based on the concordant results of solution-calorimetric measurements by Stuve [87], and Machlan et al. [60], as shown in Table 14. The former value is based on the enthalpies of solution of the Yb(cr) and $YbCl_3$(cr) in 4.0 mol dm^{-3} HCl(aq). The latter is derived by

Table 14
The enthalpy of formation of YbX_3(cr) at 298.15 K and the enthalpies of solution of Yb(cr) and YbX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$YbCl_3$					
Bommer and Hohmann [17][b]	1941	S (0.05)		−213.2 ± 0.2	
Machlan et al. [60]	1955	S (6.0)		−165.7 ± 1.3	−959.4 ± 1.7[c]
Stuve [87]	1967	S (4.0)	−671.7 ± 2.8	−187.2 ± 0.8	−959.5 ± 2.9
Bettonville et al. [71]	1987	S (6.0)	−664.9 ± 1.1		
Selected value					−959.5 ± 3.0
$YbBr_3$					
Burgess and Kijowski [88]	1981	S (H_2O)		−253.3 ± 3.2	−787.2 ± 4.4
Bettonville et al. [71]	1987	S (6.0)	−664.9 ± 1.1	−199.9 ± 1.4	−792.6 ± 1.8
		S (1.0)	−663.0 ± 3.0[d]	−229.8 ± 1.5	−791.9 ± 3.4
Selected value					−791.9 ± 5.0

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.

[b] The measurements were carried out at 293 K.

[c] Using ΔH_1^0 from Bettonville et al. [71].

[d] Estimated by present authors.

combining the enthalpy of solution of $YbCl_3$(cr) in 6.0 mol dm^{-3} HCl(aq) reported by Machlan et al., with the result of Bettonville et al. [71] for the solution of high-purity Yb(cr) sample in the same medium. The selected value is mean of the two values:

$$\Delta_f H^0(\mathrm{YbCl_3, cr, 298.15\,K}) = -(959.5 \pm 3.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.14.2. $YbBr_3$(cr)

Literature values for the enthalpy of formation of $YbBr_3$(cr) are summarized in Table 14. Bettonville et al. [71] measured the enthalpies of solution of high-purity samples of Yb(cr) and $YbBr_3$(cr) in 6.0 mol dm^{-3} HCl(aq) as well as $YbBr_3$(cr) in 1.0 and 0.001 mol dm^{-3} HCl(aq). However, due to the intermediate formation of Yb^{2+} in the solution, the dissolution reaction proceeds slowly, and therefore a catalyst was added. The enthalpy of formation of $YbBr_3$(cr) based on the results in 6.0 mol dm^{-3} HCl(aq) is $\Delta_f H^0(298.15\,\mathrm{K}) = -(792.6 \pm 1.8)$ kJ mol^{-1}. The derivation of the enthalpy of formation from the results of solution experiments in 1.0 mol dm^{-3} HCl(aq) is only possible using an estimated value for the enthalpy of solution of Yb(cr) in that medium, since an experimental determination has not been reported. From the general trend in the enthalpies of solution of the lanthanide metals we estimate $\Delta_f H^0(298.15\,\mathrm{K}) = -(663.0 \pm 3.0)$ kJ mol^{-1}, which then yields $-(791.3 \pm 3.4)$ kJ mol^{-1}.

The value, $\Delta_f H^0(298.15\,\mathrm{K}) = -(787.2 \pm 4.4)$ kJ mol^{-1}, has been derived from the enthalpy of solution of $YbBr_3$(cr) in water measured by Burgess and Kijowski [88,89] and the assessed value for the enthalpy of the Yb^{3+} ion [16]. This value is less reliable since the analysis of the bromide sample was not given. However, it agrees quite well with the value derived from the work of Bettonville et al. [71].

The selected value is the mean of the two values derived from the work of Bettonville et al. [71]:

$$\Delta_f H^0(\mathrm{YbBr_3, cr, 298.15\,K}) = -(791.9 \pm 2.0)\,\mathrm{kJ\,mol^{-1}}.$$

3.14.3. YbI_3(cr)

Experimental values for the standard molar enthalpy of formation are not available. The estimated value is based the dependence of $\{\Delta_r H^0(\mathrm{LnI_3, cr}) - \Delta_r H^0(\mathrm{Ln^{3+}, aq})\}$ on the atomic radii of the trivalent lanthanides (see Section 4):

$$\Delta_f H^0(\mathrm{YbI_3, cr, 298.15\,K}) = -(578 \pm 10)\,\mathrm{kJ\,mol^{-1}}.$$

3.15. Lutetium

3.15.1. $LuCl_3$(cr)

The calorimetric studies of the enthalpy of formation of $LuCl_3$(cr) are shown in Table 15. The value derived from the results by Bommer and Hohmann

Table 15
The enthalpy of formation of LuX_3(cr) at 298.15 K and the enthalpies of solution of Lu(cr) and LuX_3(cr) in HCl(aq) are given by ΔH_1^0 and ΔH_2^0, respectively

Reference	Year	Method[a]	ΔH_1^0 (kJ mol^{-1})	ΔH_2^0 (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$LuCl_3$					
Bommer and Hohmann [17][b]	1941	S (0.1)	−670.7	−214.6	−954.9
Spedding and Bisbee	[c]	S (0.89)	−700.0	−208.1	−985.6
					−973.3[d]
					−987.9[e]
Tiflova [75]	1990	S (2.19)	−694.9 ± 1.0	−199.5 ± 0.3	−981.9 ± 1.1
			−702.7 ± 2.5[f]		−989.7 ± 2.6
Furkaliouk et al. [73]	1993	S (1.0)	−687.7 ± 0.5		
Merli et al. [23]	1998	S (1.0)	−702.3 ± 2.2	−210.5 ± 0.74	−984.9 ± 2.3
		S (3.0)	−703.1 ± 1.3		
		S (6.0)	−703.9 ± 2.2	−175.9 ± 0.94	−988.2 ± 3.0
Selected value					−987.1 ± 2.5
LuI_3					
Hohmann and Bommer [33][b]	1941	S (0.1)	−670.7	−279.8	−559.5
Furkaliouk et al. [37]	1995	S (1.0)	−685.0 ± 0.5	−263.3 ± 0.4	−587.8 ± 0.7
					−605.1 ± 2.2[e]
Selected value					−605.1 ± 2.2

[a] E: emf measurements; S: solution calorimetry; values in parentheses give the concentration of the solvent in mol dm^{-3}.

[b] The measurements were carried out at 293 K.

[c] Cited in.

[d] Using ΔH_1^0 from Furkaliouk et al. [37].

[e] Using ΔH_1^0 from Merli et al. [23].

[f] Estimated value.

[17,18], based on the results of a single enthalpy of solution measurement of Lu(cr), as well as $LuCl_3$(cr), in ~0.1 mol dm^{-3} HCl(aq) at 293 K, deviates about 30 kJ mol^{-1} from more recent results [4,75].

Studies by Spedding and Bisbee, cited in [4], and Tiflova [75] yield the enthalpy of formation of $LuCl_3$(cr) from dissolution cycles in 0.89 and 2.19 mol dm^{-3} HCl(aq), respectively. The results derived from these studies agree almost within the range of the uncertainties, despite a noticeable disagreement on the values for the enthalpies of solution of Lu(cr) in 0.89 and 2.19 mol dm^{-3} HCl(aq) with respect to dependence of the solution enthalpies of rare earth metal on the molarity of the solvent. However, when the result of Tiflova is combined with the enthalpy of solution of Lu(cr) in 2.19 mol dm^{-3} HCl(aq) estimated from the results by Merli et al., we obtain $-(989.7 \pm 2.6)$ kJ mol^{-1}. Similarly, when the results of Spedding and Bisbee for the enthalpy of solution of $LuCl_3$ in 0.89 mol dm^{-3} HCl(aq) are combined with the enthalpy of solution of Lu(cr) in 1.0 mol dm^{-3} HCl(aq) obtained by Furkaliouk et al. [85], we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -973.3$ kJ mol^{-1}, which is significantly different from the previous values.

Merli et al. [23] dissolved both Lu(cr) and $LuCl_3$(cr) in 1.0 and 6.0 mol dm^{-3} HCl(aq), from which we obtain $\Delta_f H^0(298.15\,\mathrm{K}) = -(984.9 \pm 2.3)$ and $-(988.4 \pm 3.0)$ kJ mol^{-1}, respectively, which are in good agreement with the results derived from Tiflova [75], and Spedding and Bisbee in [4]. The selected enthalpy of formation is the mean of the two values derived from the work of Merli et al. and the value obtained by combining the results of Tiflova [75] for $LuCl_3$(cr) with those for Lu(cr) by Merli et al.:

$$\Delta_f H^0(\mathrm{LuCl_3, cr, 298.15\,K}) = -(987.1 \pm 2.5)\,\mathrm{kJ\,mol^{-1}}.$$

The uncertainty reflects the discrepancy in the enthalpies of solution of Lu(cr).

3.15.2. $LuBr_3$(cr)

Experimental values for the standard molar enthalpy of formation are not available. The estimated value based on the general trend in the lanthanide bromide series (see Section 4), is

$$\Delta_f H^0(\mathrm{LuBr_3, cr, 298.15\,K}) = -(814 \pm 10)\,\mathrm{kJ\,mol^{-1}}.$$

3.15.3. $LuI_3(cr)$

The first value for the standard enthalpy of formation of LuI_3(cr) has been published by Hohmann and Bommer [17,33] who carried out one single solution calorimetric measurement of Lu(cr) in ~0.1 mol dm^{-3} HCl(aq), and LuI_3(cr) in water at 293 K. The value derived from these measurements, $\Delta_f H^0(298.15\,K) = -559.5$ kJ mol^{-1}, seems to be in error due to a poor quality of the lutetium metal sample used by these authors.

A more recent result was obtained by Furkaliouk et al. [85] based on the solution calorimetric measurements of Lu(cr) and LuI_3(cr) in 1.0 mol dm^{-3} HCl(aq). The value obtained, $\Delta_f H^0(298.15\,K) = -(587.8 \pm 0.7)$ kJ mol^{-1}, differs appreciably from the value, $\Delta_f H^0(298.15\,K) = -(605.1 \pm 2.2)$ kJ mol^{-1}, obtained when the results of Furkaliouk are combined with the enthalpy of solution of the metal in 1.0 mol dm^{-3} HCl(aq) reported by Merli et al. [23]. As the quality of the results of Merli et al. for Lu metal is considered to be better, we select

$$\Delta_f H^0(\mathrm{LuI_3, cr, 298.15\,K}) = -(605.1 \pm 2.2)\,\mathrm{kJ\,mol^{-1}}.$$

4. Discussion and conclusions

The values for the standard molar enthalpies of formation of the trivalent rare earth metal compounds assessed in the present review, are collected in Table 16. The major source of uncertainty in the assessed values is the relative poor knowledge of the enthalpies of solution of the metals in aqueous solvents. In general, there is significant scatter in the data among the different sources, and in many cases the data for a particular metal do not show any dependence upon concentration, except when systematic studies have been made as is the case for the work of Merli et al. [23]. As an example the enthalpies of solution of Gd metal, for which a relatively large number of determinations is available, are shown in Fig. 1. The general trend seems to indicate that the enthalpy of solution becomes slightly more negative with increasing molarity of the solvent but the values at 1 mol dm^{-3} are highly discordant, being about 10 kJ mol^{-1} apart. The lack of data on the enthalpy of solution of the metals is problematic in many cases. For example, all thermodynamic data for the cerium trihalides are essentially based on the value of the enthalpy of solution of cerium metal in 0.25 mol dm^{-3} HCl(aq) measured by Spedding and Miller [19] in 1952. This value could be in error due to the insufficient analytical characterization of the cerium metal, which is highly difficult to obtain in pure form.

Table 16
Summary of the selected enthalpies of formation (kJ mol^{-1})

	Cl	Br	I
La	−1071.6 ± 1.5	−904.4 ± 1.5	−673.9 ± 2.0
Ce	−1059.7 ± 1.5	−891.2 ± 1.5	−666.8 ± 3.0
Pr	−1058.6 ± 1.5	−890.5 ± 4.0	−664.7 ± 5.0
Nd	−1040.9 ± 1.0	−864.0 ± 3.0	−639.2 ± 4.0
Pm	−1030 ± 10	−858 ± 10	−634 ± 10
Sm	−1025.3 ± 2.0	−853.4 ± 3.0	−621.5 ± 4.0
Eu	−935.4 ± 3.0	−759 ± 10	−538 ± 10
Gd	−1018.2 ± 1.5	−838.2 ± 2.0	−624.1 ± 3.0
Tb	−1010.6 ± 3.0	−843.5 ± 3.0	−623.8 ± 3.0
Dy	−993.1 ± 3.0	−834.3 ± 2.5	−616.7 ± 3.0
Ho	−997.7 ± 2.5	−842.1 ± 3.0	−622.9 ± 3.0
Er	−994.4 ± 2.0	−837.1 ± 3.0	−619.0 ± 3.0
Tm	−996.3 ± 2.5	−832 ± 10	−619.7 ± 3.5
Yb	−959.5 ± 3.0	−791.9 ± 2.0	−578 ± 10
Lu	−987.1 ± 2.5	−814 ± 10	−605.1 ± 2.2

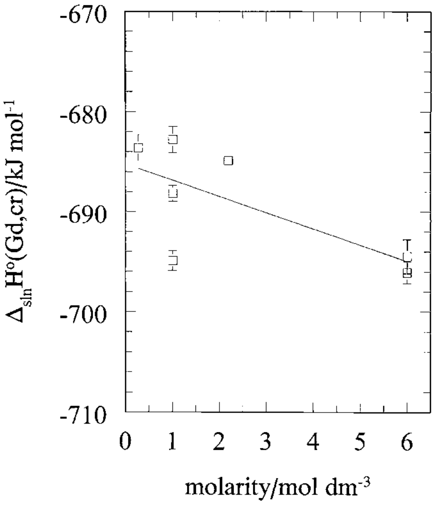

Fig. 1. The variation of the enthalpy of solution of Gd in HCl(aq) as a function of concentration.

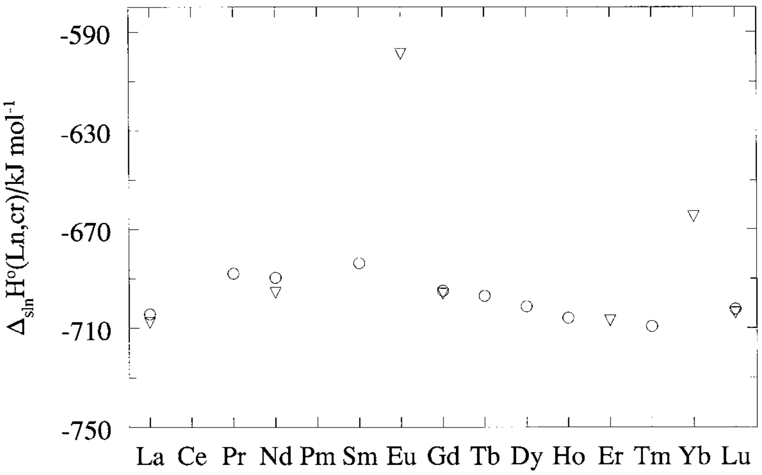

Fig. 2. The variation of the enthalpy of solution of the lanthanide metals in (○) 1.0 mol dm^{-3} HCl(aq) and (▽) 6.0 mol dm^{-3} HCl(aq).

In Fig. 2 the systematics of the enthalpy of solution of the lanthanide metals at a specific molarity of the solvent are shown. It can be seen that a smooth variation in the lanthanide series exist, with the exception of Eu and Yb. This systematic is typical for many properties of the lanthanide series such as molar volume or enthalpy of vaporization and can be related to the electronic configuration [90]. Fig. 3 shows the relation between the molar volume and the enthalpy of solution at 6 mol dm^{-3} HCl(aq) for the lanthanide metals. It is clear that the data fall into two groups and within each group an approximately linear relation exists. La (electronic configuration 5d6s^2), Eu (4f^{7}6s^2) and Yb (4f^{14}6s^2) form the first group in which the enthalpy of solution varies quite strongly. The second group is formed by the other lanthanide elements, and shows a much less pronounced dependence upon the molar volume. This difference can be understood partially from the Ln^{3+}(aq)–Ln(cr)–Ln(g)–Ln^{3+}(g) relationship as pointed out by Nugent et al. [91] and Morss [5], which will be discussed in Part II of this series.

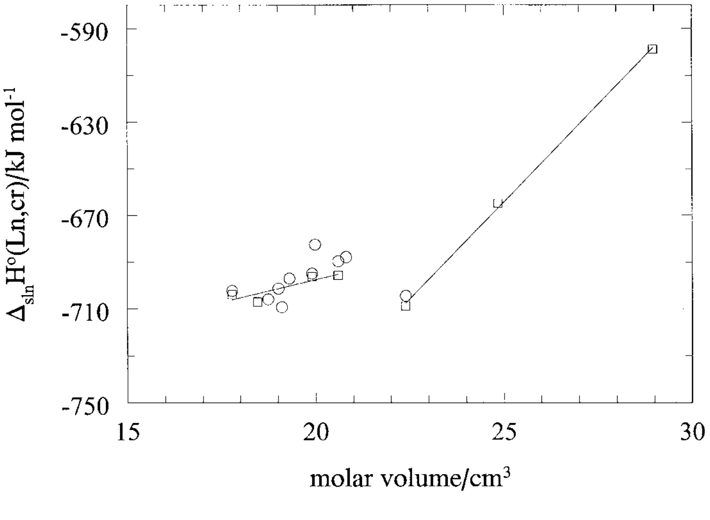

Fig. 3. The variation of the enthalpy of solution of Ln(cr) as a function of the molar volume of the metal in (□) 6.0 mol dm^{-3} HCl(aq) and (○) 1.0 HCl(aq). The lines are least-squares fits of the data for 6.0 mol dm^{-3} HCl(aq).

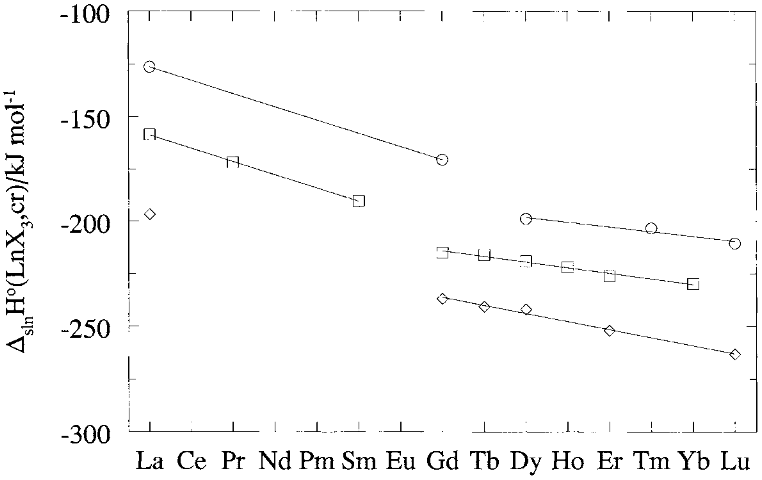

Fig. 4. The variation of the enthalpy of solution of the lanthanide trihalides in 1.0 mol dm^{-3} HCl(aq): (○) $LnCl_3$; (□) $LnBr_3$; (◇) LnI_3.

The enthalpy of solution of the lanthanide halides at a specific molarity of the solvent shows a very clear variation in the lanthanide series which can be related to the crystal structure of the LnX_3 compounds. From Fig. 4 it is clear that the enthalpy of solution varies linearly for each structure type (see Table 17 for the domains of existence of lanthanide trihalides in various crystalline forms).

Such correlations help us to verify the consistency of the assessed values for the molar enthalpies of formation, and allow us to estimate missing values of the enthalpies of solution of the lanthanide metals and halides, as has been done in this work to complete the thermochemical cycles used to derive the enthalpies of formation.

Missing values for the enthalpies of formation of the LnX_3 compounds have been derived from the trends in the assessed values obtained in this work. Fig. 5 shows the variation in the $\Delta_f H^0(\text{LnX}_3)$ in the lanthanide halide series, where EuX_3 and YbX_3 are clearly exceptions to the general trend, as also observed for the enthalpy of solution of the metals. It has been

Table 17
Structural properties of the anhydrous lanthanide trihalides at room temperature and standard pressure [98–100]

	Hexagonal *P6* $_3$/*m* (UCl_3)	Orthorhombic *Cmcm* ($PuBr_3$)	Monoclinic *C2*/*m* ($AlCl_3$)	Rhombohedral $R\overline{3}$ (BiI_3)
La	Cl	I		
Ce	Cl, Br	I		
Pr	Cl, Br	I		
Nd	Cl	Br, I		
Pm	Cl	Br, I		
Sm	Cl	Br		I
Eu	Cl	Br		
Gd	Cl			Br, I
Tb			Cl	Br, I
Dy			Cl	Br, I
Ho			Cl	Br, I
Er			Cl	Br, I
Tm			Cl	Br, I
Yb			Cl	Br, I
Lu			Cl	Br, I

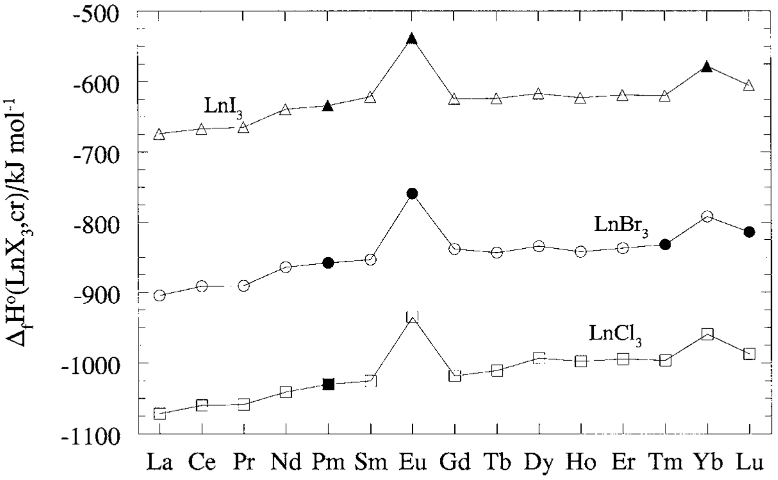

Fig. 5. The variation of the enthalpy of formation of LnX_3 in the lanthanide series; estimated values are indicated by closed symbols.

demonstrated [5,71], however, that the relation between $\Delta_fH^0(LnX_n,cr) - \Delta_fH^0(Ln^{3+},aq)$ and the Ln^{3+} ionic radius is a more practical one as it gives a linear dependence for the isostructural compounds. Apparently, the use of this relation is equivalent to the use of the standard molar enthalpy of solution of lanthanide compounds: $\Delta_fH^0(LnX_n,cr) - \Delta_fH^0(Ln^{3+},aq) = \Delta_{sln}H^0(LnX_n,cr) - n\Delta_fH^0(X^-,aq)$. In Figs. 6–8 this relation is shown for the lanthanide chlorides, bromides and iodides based on the assessed values for the molar enthalpies of formation of lanthanide trihalides and those for the lanthanide aqueous ions [16]. For the ionic radii of the trivalent lanthanides (co-ordination number CN = 6) the values given by Shannon were used [92]. The general slope of the graphs illustrates the common trend that the enthalpies of solution change linearly from LaX_3 to LuX_3. It indicates that the hydration enthalpies, which for the

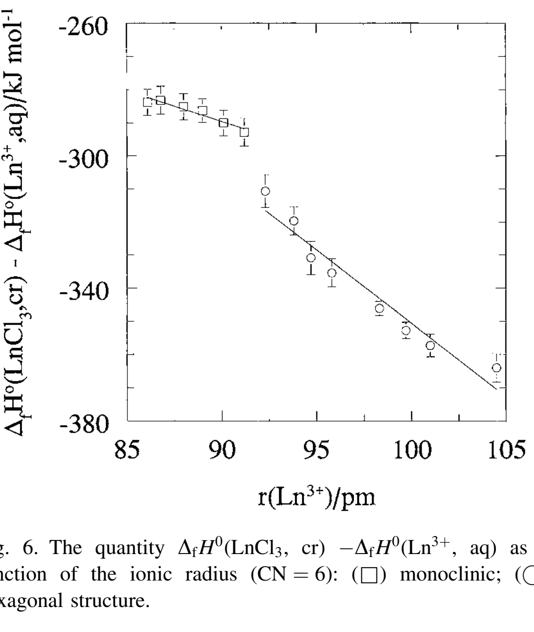

Fig. 6. The quantity $\Delta_fH^0(LnCl_3, cr) - \Delta_fH^0(Ln^{3+}, aq)$ as a function of the ionic radius (CN = 6): (□) monoclinic; (○) hexagonal structure.

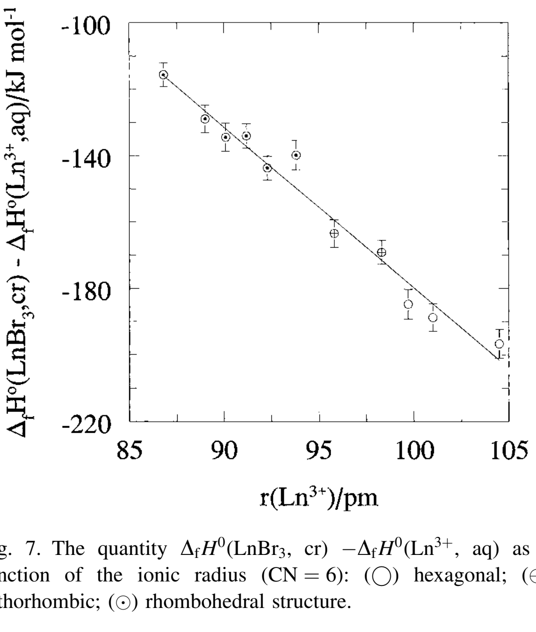

Fig. 7. The quantity $\Delta_fH^0(LnBr_3, cr) - \Delta_fH^0(Ln^{3+}, aq)$ as a function of the ionic radius (CN = 6): (○) hexagonal; (⊕) orthorhombic; (⊙) rhombohedral structure.

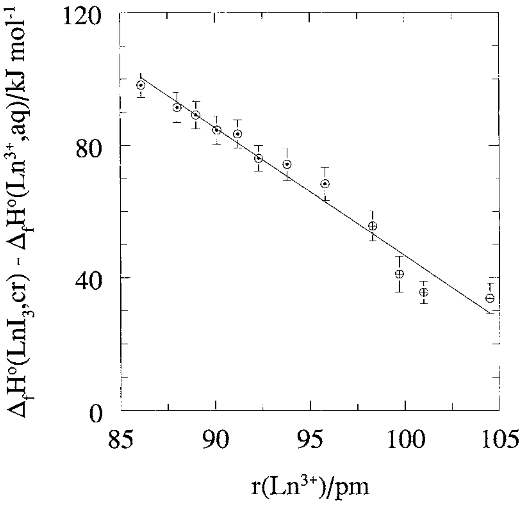

Fig. 8. The quantity $\Delta_f H^0(LnI_3, cr) - \Delta_f H^0(Ln^{3+}, aq)$ as a function of the ionic radius (CN = 6): (⊕) orthorhombic; (⊙) rhombohedral structure.

tripositive cations are increasing in the direction as the ionic radii are decreasing, dominate increasingly over the lattice enthalpies. The $\Delta_f H^0(298.15\,K)$ values for the lanthanide trichlorides perfectly fit the two linear dependencies for the different crystal structures (hexagonal and monoclinic). For the bromides and iodides, the difference between the hexagonal, orthorhombic and rhombohedral compounds is not evident (Fig. 7 and 8) and noticeably higher average deviations from the linear dependencies are observed. Especially the poor agreement of the values for the orthorhombic lanthanide tri-iodide series is evident. The values for PrI_3 and, to a lesser extent, CeI_3, are, however, subjected to significant uncertainties due to the lack of reliable experimental data.

Despite the discrepancies mentioned above, the trends found for the lanthanum trihalide series, allow us to estimate the unknown values for the standard molar enthalpy of formation of LnX_3 compounds, such as $PmCl_3$, $PmBr_3$, PmI_3, $TmBr_3$(cr), $LuBr_3$ (cr), EuI_3(cr) and YbI_3(cr), as presented in Table 16. The average uncertainty of the estimation procedure has been adopted as $\pm 10\,kJ\,mol^{-1}$.

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References

[1] F.H. Spedding, A.H. Daane, J. Phys. Chem. 74 (1952) 2783.
[2] K.A. Gschneider Jr., J. Capellen, J. Less-Common Met. 126 (1986) xvii.
[3] J.M. Haschke, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of the Rare Earths, Vol. 4, North-Holland, Amsterdam, 1979, Chapter 32, pp. 89–151.
[4] L.R. Morss, Chem. Rev. 76 (1976) 827–840.
[5] L.R. Morss, in: K.A. Gschneidner Jr., L. Eyring, G.R. Choppin, G.H. Lander (Eds.), Handbook on the Physics and Chemistry of the Rare Earths, Vol. 18, North-Holland, Amsterdam, 1994, Chapter 122, pp. 239–291.
[6] S. Bratsch, H.B. Silber, Polyhedron 1 (1982) 219.
[7] M.W.M. Hisham, S.W. Benson, J. Phys. Chem. 91 (1987) 3631.
[8] L.G. Lishenko, T.S. Nazarova, Yu.I. Polyakov, A.A. Rozen, Russ. J. Inorg. Chem. 18 (1973) 484.
[9] C.W. Struck, J.A. Baglio, High Temp. Sci. 31 (1992) 209.
[10] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.
[11] V.B. Parker, D.D. Wagman, D. Garvin, Technical Report NBSIR 75, National Bureau Standards, Washington, October 1976.
[12] O. Söhnel, P. Novotný, Densities of Aqueous Solutions of Inorganic Substances, Elsevier, Amsterdam, 1985.
[13] C. Matignon, Ann. Chim. Phys. 10 (1906) 101.
[14] A. Sieverts, A. Gotta, Z. Anorg. Allgem. Chem. 172 (1928) 1.
[15] W. Biltz, H. Pieper, Z. Anorg. Allgem. Chem. 134 (1924) 13.
[16] E.H.P. Cordfunke, R.J.M. Konings, Thermochim. Acta, 375 (2001) 53.
[17] H. Bommer, E. Hohmann, Z. Anorg. Allgem. Chem. 248 (1941) 373–382.
[18] H. Bommer, E. Hohmann, Z. Anorg. Allgem. Chem. 248 (1941) 357–372.
[19] F.H. Spedding, C.F. Miller, J. Am. Chem. Soc. 74 (1952) 4195–4198.
[20] F.H. Spedding, J.P. Flynn, J. Am. Chem. Soc. 76 (1954) 1474–1477.
[21] G.C. Fitzgibbon, C.E. Holley Jr., I. Wadsö, J. Phys. Chem. 69 (1965) 2464–2466.
[22] E.H.P. Cordfunke, A.S. Booij, J. Chem. Thermodyn. 27 (1995) 897–900.
[23] L. Merli, F. Rorif, J. Fuger, Radiochim. Acta 82 (1998) 3–9.
[24] L.R. Morss, Technical Report UCRL-18951, Lawrence Radiation Laboratory, University of California, Berkeley, 1969.

[25] R.L. Montgomery, Technical Report USBM-RI-5445, US Bureau of Mines, 1959.

[26] H. Oppermann, A. Morgenstern, S. Ehrlich, Z. Naturforsch. B 52 (1997) 1062–1066.

[27] E.J. Huber Jr., C.E. Holley Jr., J. Am. Chem. Soc. 75 (1953) 5645.

[28] D.M. Laptev, T.V. Kiseleva, V.V. Vasil'ev, Zh. Fiz. Khim. 64 (1990) 1472–1476.

[29] V.P. Glushko, L.V. Gurvich, G.A. Bergman, I.V. Veyts, V.A. Medvedev, G.A. Khachkuruzov, V.S. Yungman, Termodinamicheskie Svoistva Individual'nykh Veshchestv, Tom IV, Nauka, Moscow, 1982.

[30] L.B. Pankratz, Thermodynamic properties of halides, Bulletin 674, US Bureau of Mines, Washington, DC, 1984.

[31] C. Hurtgen, D. Brown, J. Fuger, J. Chem. Soc., Dalton Trans. (1980) 70–75.

[32] H. von Wartenberg, Z. Anorg. Allgem. Chem. 299 (1959) 227.

[33] E. Hohmann, H. Bommer, Z. Anorg. Allgem. Chem. 248 (1941) 383–396.

[34] M.Yu. Furkaliouk, A.S. Booij, E.H.P. Cordfunke, J. Chem. Thermodyn. 27 (1995) 293–297.

[35] D.M. Laptev, T.V. Kiseleva, V.V. Vasil'ev, Zh. Fiz. Khim. 64 (1990) 1489–1493.

[36] R.L. Montgomery, Technical Report USBM-RI-6146, US Bureau of Mines, 1962.

[37] M.Yu. Furkaliouk, E.H.P. Cordfunke, J. Chem. Thermodyn. 28 (1996) 255–259.

[38] G.C. Fitzgibbon, E.J. Huber Jr., C.E. Holley Jr., Rev. Chim. Miner. 10 (1973) 29.

[39] H.R. Lohr, B.B. Cunningham, J. Am. Chem. Soc. 73 (1951) 2025–2028.

[40] C.T. Stubblefield, Rev. Sci. Instr. 40 (1969) 456.

[41] O.G. Polyachenok, G.I. Novikov, Russ. J. Inorg. Chem. 8 (1963) 816–820.

[42] J.M. Stuve, Technical Report USBM-RI-6697, US Bureau of Mines, 1965.

[43] G.C. Fitzgibbon, D. Pavone, C.E. Holley Jr., J. Chem. Eng. Data 13 (1968) 547.

[44] E.J. Huber Jr., C.E. Holley Jr., J. Am. Chem. Soc. 74 (1952) 5530.

[45] L.A. Tiflova, L.V. Medvedeva, A.S. Monaenkova, V.F. Goryushkin, in: Proceedings of the Abstracts of the 12th All-Union Conference on Chemical Thermodynamics and Calorimetry, Part I, 13–15 September, Gorky, Russia, p. 32.

[46] E.H.P. Cordfunke, A.S. Booij, M.Yu. Furkaliouk, J. Chem. Thermodyn. 28 (1996) 1387–1393.

[47] C. Hennig, H. Oppermann, Z. Naturforsch. B 53 (1998) 175–183.

[48] C. Hennig, H. Oppermann, Z. Naturforsch. B 54 (1999) 1283–1294.

[49] C. Hennig, H. Oppermann, Z. Naturforsch. B 55 (2000) 65–73.

[50] R.L. Montgomery, T.D. Hubert, Technical Report USBM-RI-5525, US Bureau of Mines, 1959.

[51] F.B. Baker, G.C. Fitzgibbon, D. Pavone, C.E. Holley Jr., L.D. Hansen, E.A. Lewis, J. Chem. Thermodyn. 4 (1972) 621.

[52] L.R. Morss, J.A. Fahey, in: Proceedings of the 12th Rare Earth Research Conference, Vol. 1, Vail, CO, 1976, pp. 443–450.

[53] E.I. Khanaev, T.P. Storozhenko, L.D. Il'ina, Russ. J. Phys. Chem. 61 (1987) 926–929.

[54] C. Hennig, H. Oppermann, Z. Naturforsch. B 52 (1997) 1517–1525.

[55] G.G. Gvelesiani, T.S. Yashvili, Z. Neorg. Khim. 12 (1967) 3233.

[56] J.M. Stuve, Technical Report USBM-RI-6640, US Bureau of Mines, 1965.

[57] G.C. Fitzgibbon, E.J. Huber Jr., C.E. Holley Jr., J. Chem. Thermodyn. 4 (1972) 349.

[58] J.L. Burnett, B.B. Cunningham, Technical Report UCRL-11126, US Atomic Energy Commission, 1964.

[59] J.L. Burnett, Technical Report UCRL-11850, 1964.

[60] G.R. Machlan, C.T. Stubblefield, L. Eyring, J. Am. Chem. Soc. 77 (1955) 2975.

[61] C.T. Stubblefield, J.L. Rutledge, R. Phillips, J. Phys. Chem. 69 (1965) 991.

[62] C. Hennig, H. Oppermann, A. Blonska, Z. Naturforsch. B 53 (1998) 1169–1179.

[63] J.M. Haschke, J. Chem. Thermodyn. 5 (1973) 283–290.

[64] J.A. Rard, Chem. Rev. 85 (1985) 555.

[65] J.M. Haschke, H.A. Eick, J. Phys. Chem. 74 (1970) 1808.

[66] J.M. Haschke, High Temp. Sci. 9 (1977) 77.

[67] D.M. Laptev, T.V. Kiseleva, V.V. Vasil'ev, D.I. Oshchepkov, Russ. J. Phys. Chem. 67 (1993) 2172–2174.

[68] L.A. Tiflova, A.S. Monaenkova, V.F. Goryushkin, Russ. J. Phys. Chem. 63 (1989) 1082–1084.

[69] M.Yu. Furkaliouk, M.E. Efimov, V.F. Goryushkin, Z. Fiz. Khim. 66 (1992) 1108.

[70] J.M. Stuve, Technical Report USBM-RI-7046, US Bureau of Mines, 1967.

[71] S. Bettonville, J. Goudiakas, J. Fuger, J. Chem. Thermodyn. 19 (1987) 595–604.

[72] G.C. Fitzgibbon, C.E. Holley Jr., J. Chem. Eng. Data 13 (1968) 63.

[73] M.Yu. Furkaliouk, V.Ya. Leonidov, V.F. Goryushkin, Z. Fiz. Khim. 67 (1993) 1947–1949.

[74] E.J. Huber Jr., G.C. Fitzgibbon, C.E. Holley Jr., J. Chem. Thermodyn. 3 (1971) 643.

[75] L.A. Tiflova, PhD Thesis, Chemistry Department, Moscow State University, Moscow, 1990.

[76] A.S. Monaenkova, L.A. Tiflova, V.F. Goryushkin, Russ. J. Phys. Chem. 63 (1989) 595.

[77] E.H.P. Cordfunke, A.S. Booij, J. Chem. Thermodyn. 29 (1997) 715.

[78] L.R. Morss, T.G. Spence, Z. Anorg. Allgem. Chem. 616 (1992) 162.

[79] V.Ya. Leonidov, M.Yu. Furkalyuk, Russ. J. Phys. Chem. 73 (1999) 937–939.

[80] S.A. Lezhava, PhD Thesis, Chemistry Department, Moscow State University, Moscow, 1992.

[81] S.A. Lezhava, L.A. Tiflova, A.S. Monaenkova, V.F. Goryushkin, in: Proceedings of the Abstracts of the 13th All-Union Conference on Chemical Thermodynamics and Calorimetry, Krasnoyarsk, Russia, September 1991, p. 131.

[82] J. Fuger, L.R. Morss, D. Brown, J. Chem. Soc., Dalton Trans. (1980) 1076–1078.
[83] R.L. Montgomery, J.M. Stuve, Technical Report USBM-RI-5892, US Bureau of Mines, 1961.
[84] E.J. Huber Jr., E.L. Head, C.E. Holley Jr., J. Phys. Chem. 60 (1956) 1582.
[85] M.Yu. Furkaliouk, V.Ya. Leonidov, V.F. Goryushkin, Russ. J. Phys. Chem. 67 (1993) 1222–1224.
[86] S.A. Lezhava, L.A. Tiflova, A.S. Monaenkova, V.F. Goryushkin, Z. Fiz. Khim. 67 (1993) 633.
[87] J.M. Stuve, Technical Report USBM-RI-6902, US Bureau of Mines, 1967.
[88] J. Burgess, J. Kijowski, J. Inorg. Nucl. Chem. 43 (1981) 2389.
[89] J. Burgess, J. Kijowski, Adv. Inorg. Chem. Radiochem. 24 (1981) 57.
[90] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 3rd Edition, Wiley/Interscience, New York, 1972.
[91] L.J. Nugent, J.L. Burnett, L.R. Morss, J. Chem. Thermodyn. 5 (1973) 665–678.
[92] R.D. Shannon, Acta Cryst. A32 (1976) 751.
[93] A.A. Popova, A.S. Monaenkova, Z. Fiz. Khim. 63 (1989) 2340.
[94] M. Daire, C. R. Acad. Sci., Paris, Ser. C 266 (1968) 1111.
[95] T.S. Yashvili, G.G. Gvelesiani, Russ. J. Phys. Chem. 45 (1971) 551.
[96] M.Yu. Furkaliouk, PhD Thesis, Chemistry Department, Moscow State University, Moscow, 1993.
[97] N.M. Gamanovich, V.P. Glybin, Z. Fiz. Khim. 48 (1974) 2883.
[98] JCPDF Powder Diffraction File, International Centre for Diffraction Data, PA, USA.
[99] H.P. Beck, E. Gladrow, Z. Anorg. Allgem. Chem. 453 (1979) 79–92.
[100] A.L. Harris, C.R. Veale, J. Inorg. Nucl. Chem. 27 (1965) 1437–1439.