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Thermochimica Acta 375 (2001) 51–64

thermochimica acta

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The enthalpies of formation of lanthanide compounds
II. Ln^{3+}(aq)

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Received 28 July 2000; received in revised form 14 March 2001; accepted 16 March 2001

Abstract

The enthalpies of formation of the lanthanide aqueous ions have been evaluated from the experimental data available in literature. All experimental results have been recalculated using a consistent set of the auxiliary data for the lanthanide trihalides, which have been analysed in parallel.

Keywords: Lanthanide(III) aqueous ions; Enthalpy of formation; Critical evaluation

1. Introduction

The standard molar enthalpies of formation of the anhydrous lanthanide trihalides have been reviewed in Part I of this series [1]. As a result, for most of the compounds, a consistent set of recommended values is available now. This permits us to assess the standard enthalpies of formation of the trivalent aqueous lanthanide ions from the enthalpies of solution of the lanthanide trihalides in water. Since the standard enthalpies of formation of the halide ions are key values in thermochemistry [2], we obtain from the reaction

$$\mathrm{LnX_3(cr) = Ln^{3+}(aq) + 3X^-(aq)}$$

the standard enthalpy of formation of the trivalent lanthanide ions

$$\Delta_f H^0(\mathrm{Ln^{3+}, aq}) = \Delta_r H^0(298.15\,\mathrm{K}) + \Delta_f H^0(\mathrm{LnX_3, s}) - 3 \times \Delta_f H^0(\mathrm{X^-, aq})$$

Since we are dealing with a series of ions with identical charge, we will also discuss the trends in the enthalpies of formation, enabling us to derive estimates when no measurements are available.

The thermodynamic properties of the trivalent lanthanide ions have been reviewed previously by Morss [3,4] in 1976 and 1985, and by David [5] in 1986. The present study covers the literature up to 2000. All data have been processed together with those for the halides, assuring the highest degree of consistency.

2. Methods

The standard state of an aqueous ion is its hypothetical 'one molal' solution which, in case of the enthalpy, corresponds to the infinitely dilute state. Since the tripositive lanthanide ions are only slightly hydrolysed in neutral solutions, the standard enthalpies of formation of the ions have been calculated from the enthalpies of solution of lanthanide trihalides in pure water, being recalculated to the standard state of infinite dilution, and the assessed values of the

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PII: S0040-6031(01)00508-1

enthalpies of formation of LnX_3(cr). The experimental enthalpies of solution of LnX_3(cr) in water, measured at a specified molarity of the salt, were extrapolated into the range of infinite dilution using the extended Debye–Huckel equation [6,7]. The possibility of using this method for aqueous solutions of rare earth trihalides was confirmed by Spedding and coworkers [8,9], who used the experimental results of the enthalpies of dilution of rare earth trichlorides to show satisfactory agreement between the experimental and the theoretical limiting slope.

All data have been stored in a spreadsheet and have been processed simultaneously with those for the lanthanide trihalides $LnCl_3$, $LnBr_3$ and LnI_3 [1]. The CODATA values for the standard enthalpies of formation of the aqueous halide ions [2] have been used throughout this paper. 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.

3. Results

3.1. La^{3+}(aq)

The standard enthalpy of formation of the aqueous La^{3+} ion at infinite dilution has been derived from the enthalpies of solution of $LaCl_3$(cr), $LaBr_3$(cr), and LaI_3(cr) in water and appropriate auxiliary data; the values calculated from the results of different studies are summarised in Table 1.

The enthalpy of solution of $LaCl_3$(cr) has been the subject of various investigations since 1907. The experimental values for the enthalpy of solution of $LaCl_3$(cr) at a specified molarity have been recalculated to the infinite dilution using the molar enthalpies of dilution given by Spedding et al. [8] for $LaCl_3$(cr). The Debye–Huckel limiting law gave essentially the same values within 0.1 kJ mol^{-1}. The value of the enthalpy of solution obtained by Novikov and Baev [10] was not corrected to the state of infinite dilution, since the final molarities of the investigated solutions were not indicated.

The first values for the enthalpies of solution of $LaCl_3$(cr) reported by Matignon [11] and Bommer and Hohmann [12] were obtained at 290 and 293 K, respectively. Much later, a study of the temperature dependence of solution enthalpies [13] of rare earth trichlorides suggests that the values at 298.15 K would

Table 1
The enthalpy of formation of La^{3+}(aq) at 298.15 K[a]

References	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Matignon [11]	1906	−131.4 ± 1.0[b,e]	−701.8 ± 1.8
Bommer and Hohmann [33]	1941	−134.1 ± 0.2[b,e]	−704.5 ± 1.5
Spedding and Flynn [26]	1954	−137.8 ± 0.2[b]	−708.2 ± 1.5
Montgomery [17]	1959	−137.1 ± 0.5[b]	−707.5 ± 1.6
Novikov and Baev [10]	1961	−133.7 ± 0.8[b]	−704.1 ± 1.7
Clark and Bear [24]	1969	−136.5 ± 2.1[b]	−706.9 ± 2.6
Krestov et al. [13]	1972	−134.9 ± 0.4[b]	−705.3 ± 1.6
Hurtgen et al. [14]	1980	−167.5 ± 0.7[c]	−707.7 ± 2.1
Burgess and Kijowski [15]	1981	−136.9 ± 3.6[b]	−707.3 ± 3.9
		−174.0 ± 3.1[c]	−714.2 ± 3.7
		−207.8 ± 3.2[d]	−711.4 ± 3.8
Selected value			−707.6 ± 2.5

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of LaX_3(cr) in aqueous solution (aq) corrected to infinite dilution.

[b] The enthalpy of solution of $LaCl_3$(cr) at infinite dilution.

[c] The enthalpy of solution of $LaBr_3$(cr) at infinite dilution.

[d] The enthalpy of solution of LaI_3(cr) at infinite dilution.

[e] Value corrected to 298.15 K.

be 2–3 kJ mol^{-1} more negative. Such an adjustment brings these values closer to the more recent values obtained at 298.15 K. Overall, there is a considerable agreement between the enthalpies of solution of $\mathrm{LaCl_3(cr)}$ at infinite dilution derived from different studies.

The values calculated from the enthalpy of solution of $\mathrm{LaBr_3(cr)}$ at infinite dilution obtained by Hurtgen et al. [14] and Burgess and Kijowski [15] differ considerably. The reason for this is not clear. The results calculated from the results of Burgess and Kijowski [15] for the solution enthalpy of $\mathrm{LnI_3(cr)}$ at infinite dilution agree quite well with the results derived from the chlorides, but are considered of significantly less accuracy.

The selected value is the mean of the results of Spedding and Flynn [16], Montgomery [17] and Krestov et al. [18] for the dissolution of $\mathrm{LaCl_3(cr)}$:

$$\Delta_f H^0(\mathrm{La}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -707.6 \pm 2.5\,\mathrm{kJ\,mol^{-1}}$$

3.2. $Ce^{3+}(aq)$

The standard enthalpy of formation of the aqueous Ce^{3+} ion at infinite dilution can be calculated from the enthalpies of solution of $\mathrm{CeCl_3(cr)}$ as well as $\mathrm{CeI_3(cr)}$ in water and the assessed values for the enthalpies of formation of the cerium trihalides [1]. The validity of that method was confirmed by solution calorimetric measurements [10] of $\mathrm{CeCl_3(cr)}$ in water and $\mathrm{H_2O_2(aq)}$. Comparison of the results obtained in two sets of measurements showed that the possible side reaction of oxidation of $\mathrm{Ce}^{3+}\mathrm{(aq)}$ to $\mathrm{Ce}^{4+}\mathrm{(aq)}$ by dissolved oxygen was negligible and completely within the range of experimental error.

The available literature data on the enthalpy of solution of $\mathrm{CeX_3(cr)}$ in water are presented in Table 2. The experimental values for the enthalpy of solution at specified molarity have been recalculated to the state of infinite dilution using the molar enthalpies of dilution given by Spedding and Miller [9] for $\mathrm{CeCl_3(aq)}$. The values of the enthalpies of solution obtained by Novikov and Baev [10] were not corrected to the state of infinite dilution, since the final molarities of the investigated solutions were not indicated.

The enthalpies of solution of $\mathrm{CeCl_3(cr)}$ and $\mathrm{CeI_3(cr)}$ reported by Bommer and Hohmann [12,13] were measured at 293 K. More recent studies [6,13] of the temperature dependence of solution enthalpies of rare earth chlorides suggest that the value at 298 K would be ~2 kJ mol^{-1} more negative. Such an adjustment does bring the value [12] closer to the more recent values obtained at 298.15 K.

The studies by Spedding and Miller [9] and Monaenkova et al. [20] are the most accurate and best documented, and the results are in excellent agreement with each other. The value derived from the results by Blachnik and Selle [21] is in reasonable agreement but essential details of measurements were not given.

The selected value is the mean of the results of Spedding and Miller [9] and Monaenkova et al. [20]:

$$\Delta_f H^0(\mathrm{Ce}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -702.4 \pm 2.0\,\mathrm{kJ\,mol^{-1}}$$

Table 2
The enthalpy of formation of $\mathrm{Ce}^{3+}\mathrm{(aq)}$ at 298.15 K[a]

Reference	Year	$\Delta_{\mathrm{sln}}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Bommer and Hohmann [12]	1941	$-139.0 \pm 0.8^{\mathrm{b,d}}$	-697.4 ± 1.7
Hohmann and Bommer [19]	1941	-206.8^{c}	-703.3
Spedding and Miller [9]	1954	$-144.0 \pm 0.2^{\mathrm{b}}$	-702.4 ± 1.5
Novikov and Baev [10]	1961	$-137.2 \pm 0.6^{\mathrm{b}}$	-695.6 ± 1.6
Blachnik and Selle [21]	1979	-140.7^{b}	-699.1
Monaenkova et al. [20]	1982	$-143.9 \pm 0.4^{\mathrm{e}}$	-702.3 ± 1.6
Selected value			-702.4 ± 2.0

[a] $\Delta_{\mathrm{sln}}H^0$ is the enthalpy of solution of $\mathrm{CeX_3(cr)}$ in aqueous solution (aq) corrected to infinite dilution.

[b] The enthalpy of solution of $\mathrm{CeCl_3(cr)}$ at infinite dilution.

[c] The enthalpy of solution of $\mathrm{CeI_3(cr)}$ at infinite dilution.

[d] Value corrected to 298.15 K.

[e] Three different samples of $\mathrm{CeCl_3}$ were used.

Table 3
The enthalpy of formation of Pr^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Matignon [11]	1906	$-140.2 \pm 1.0^{b,e}$	-697.5 ± 1.8
Bommer and Hohmann [12]	1941	$-144.2 \pm 0.2^{b,e}$	-701.5 ± 1.5
Hohmann and Bommer [19]		$-212.7 \pm 1.5^{c,e}$	-707.1 ± 5.2
Spedding and Flynn [26]	1954	-149.3 ± 0.10^{b}	-706.6 ± 1.5
Novikov and Baev [10]	1961	-144.3^{b}	-701.6
Krestov et al. [13]	1972	-148.5 ± 0.5^{b}	-705.8 ± 1.6
Blachnik and Selle [21]	1979	-147.7^{b}	-705.0
Hurtgen et al. [14]	1980	-178.9 ± 1.6^{d}	-705.2 ± 4.3
Vorob'ev et al. [22]	1987	-147.5 ± 0.3^{b}	-704.8 ± 1.6
Selected value			-705.7 ± 2.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of PrX_3(cr) in aqueous solution (aq) corrected to infinite dilution.
[b] The enthalpy of solution of $PrCl_3$(cr) at infinite dilution.
[c] The estimated enthalpy of solution of PrI_3(cr) at infinite dilution.
[d] The enthalpy of solution of $PrBr_3$(cr) at infinite dilution.
[e] Value corrected to 298.15 K.

3.3. Pr^{3+}(aq)

The standard enthalpy of formation of the aqueous Pr^{3+} ion at infinite dilution can be derived from the enthalpies of solution of $PrCl_3$(cr), $PrBr_3$(cr) and PrI_3(cr) in water and appropriate auxiliary data, as shown in Table 3.

The experimental values on the enthalpy of solution of PrX_3(cr) have been corrected to the standard state of infinite dilution using the molar enthalpies of dilution given by Spedding et al. [8] for $PrCl_3$(aq), being in perfect agreement with the values calculated according to the Debye–Huckel limiting law. The values of the enthalpies of solution obtained by Novikov and Baev [10] were not corrected to infinite dilution, since the final molarities of the investigated solutions were not indicated.

The results of the earlier works by Matignon [11] and Bommer and Hohmann [12] were obtained at 290 and 293 K, respectively. A more recent study [13] on the temperature dependence of the solution enthalpies of the rare earth chlorides suggests that the value at 298.15 K would be 2–3 kJ mol^{-1} more negative. Such an adjustment does bring the values [11,12] closer to the more recent values obtained at 298.15 K.

The results of the best-documented studies on the enthalpy of solution of $PrCl_3$(cr) by Spedding and Flynn [16], Krestov et al. [13] and Vorob'ev et al. [22] are in excellent agreement (see Table 3). Almost the same value was reported by Blachnik and Selle [21], although the accuracy could not be evaluated due to the lack of experimental data presented. The enthalpy of formation derived from the results of Hurtgen et al. [14] for the solution of $PrBr_3$(cr) is somewhat lower. Finally, a value has been obtained from the enthalpy of solution of PrI_3(cr) at infinite dilution, estimated from the enthalpy of solution in dilute HCl(aq) at 293 K obtained by Hohmann and Bommer [19]. Taking into account the poor quality of the sample used by the authors, as well as the insufficient accuracy of the corrections to the infinite dilution, the latter result should be considered as a tentative value only.

The selected value is the mean of the results of Spedding and Flynn [16], Krestov et al. [13] and Vorob'ev et al. [22]:

$$\Delta_f H^0(\mathrm{Pr}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -705.7 \pm 2.0\,\mathrm{kJ\,mol}^{-1}$$

3.4. Nd^{3+}(aq)

The standard enthalpy of formation of the aqueous neodymium 3+ ion at infinite dilution has been evaluated using the enthalpy of solution of $NdCl_3$(cr) in water as well as the assessed value for the standard enthalpy of formation of neodymium trichloride [1].

Table 4 lists the experimental enthalpies of solution of $NdCl_3$(cr) corrected to the standard state of infinite dilution using the molar enthalpies of dilution given

Table 4
The enthalpy of formation of Nd^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Matignon [11]	1906	-151.4 ± 1.0[b]	-691.1 ± 1.4
Bommer and Hohmann [12]	1941	-152.3[b]	-692.0
Spedding and Miller [9]	1952	-156.9 ± 0.2	-696.6 ± 1.1
Novikov and Baev [10]	1961	-147.7	-687.4
Clark and Bear [24]	1969	-151.1 ± 2.9	-690.8 ± 3.1
Krestov et al. [13]	1972	-155.3 ± 0.5	-695.0 ± 1.2
Blachnik and Selle [21]	1979	-153.3	-693.0
Monaenkova et al. [20]	1982	-154.4 ± 0.4[c]	-694.1 ± 1.1
		-154.1 ± 0.4	-693.8 ± 1.1
Tiflova [23]	1990	-154.8 ± 0.3	-694.5 ± 1.1
Selected value			-694.8 ± 2.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of $NdCl_3$(cr) in aqueous solution (aq) corrected to infinite dilution.
[b] Value corrected to 298.15 K.
[c] Two sets of measurements with five different samples of $NdCl_3$(cr).

by Spedding et al. [8] for $NdCl_3$(aq). These values are in perfect agreement with those calculated according to the Debye–Huckel limiting law. The solution enthalpy reported by Novikov and Baev [10] was not corrected to infinite dilution, since the final molarities of the investigated solutions were not indicated.

The results of the earlier works by Matignon [11] and Bommer and Hohmann [12] were obtained at 290 and 293 K, respectively. According to the results of a later study [13] on the temperature dependence of the solution enthalpies of rare earth chlorides, the value at 298.15 K would be 2–3 kJ mol^{-1} more negative. Such an adjustment does bring the values [11,12] closer to the more recent values obtained at 298.15 K.

There is a good agreement between the values for the standard enthalpy of formation of Nd^{3+}(aq) derived from different studies, and the selected value is based on the results by Spedding and Miller [9], Krestov et al. [13], Monaenkova et al. [20] and Tiflova [23]:

$$\Delta_f H^0(\mathrm{Nd}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -694.8 \pm 2.0\,\mathrm{kJ\,mol}^{-1}$$

3.5. Pm^{3+}(aq)

Experimental values for the standard enthalpy of formation of the aqueous Pm^{3+} ion at infinite dilution are not available.

The common trend of the $\Delta_f H^0(\mathrm{Ln}^{3+}, \mathrm{aq})$ values observed for the light lanthanides (see Section 4) allows us to estimate the standard enthalpy of formation of Pm^{3+}(aq), which is selected here:

$$\Delta_f H^0(\mathrm{Pm}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -693 \pm 10\,\mathrm{kJ\,mol}^{-1}$$

3.6. Sm^{3+}(aq)

The standard enthalpy of formation of the aqueous Sm^{3+} ion at infinite dilution has been calculated from the enthalpy of solution of $SmCl_3$(cr) and $SmBr_3$(cr) at infinite dilution as well as from the enthalpy of solution of samarium metal in dilute solutions of perchloric acid and appropriate auxiliary data [1].

The available literature values for the enthalpy of solution of $SmCl_3$(cr) in water are presented in Table 5. The experimental enthalpies of solution of $SmCl_3$(cr) at definite molarity have been recalculated to infinite dilution, using the molar enthalpies of dilution given by Spedding et al. [8] for $SmCl_3$(aq). The Debye–Huckel limiting law gave essentially the same values within 0.1 kJ mol^{-1}. The first enthalpies of solution reported by Matignon [11] and Bommer and Hohmann [12] were obtained at 290 and 293 K, respectively. The results of the later study on the temperature dependence of solution enthalpies [13] suggests that the values at 298 K would be 2–3 kJ mol^{-1} more negative.

Table 5
The enthalpy of formation of Sm^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Matignon [11]	1906	$-159.8 \pm 1.0^{b,e}$	-684.0 ± 3.2
Bommer and Hohmann [12]	1941	$-165.7^{b,e}$	-689.9
Spedding and Flynn [26]	1954	-167.1 ± 0.1^{b}	-691.3 ± 3.0
Clark and Bear [24]	1969	-161.2 ± 0.8^{b}	-685.4 ± 3.1
Krestov et al. [13]	1972	-166.9 ± 0.5^{b}	-691.1 ± 3.1
Morss and Fahey [3]	1976	-166.1^{b}	-690.3
Blachnik and Selle [21]	1979	-165.9^{b}	-690.1
Hurtgen et al. [14]	1980	$-197.8 \pm 1.7^{c,d}$	-687.0 ± 3.5
Khanaev et al. [25]	1987		-690.2 ± 0.8
Selected value			-690.0 ± 2.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of SmX_3(cr) in aqueous solution (aq) corrected to infinite dilution.
[b] The enthalpy of solution of $SmCl_3$(cr) at infinite dilution.
[c] The enthalpy of solution of $SmBr_3$(cr) at infinite dilution. The measurements were carried out in 0.05–0.008 mol dm^{-3} $HClO_4$(aq).
[e] Value corrected to 298.15 K.

There is considerable agreement between the enthalpies of solution of $SmCl_3$(cr) at infinite dilution derived from different studies, with the exception of the study by Clark and Bear [24]. The reason for this deviation is not clear due to the lack of experimental data reported. The values obtained by Spedding and Flynn, [16] and Krestov et al. [13] seem to be more accurate and better documented.

The value, $\Delta_f H^0(298.15\,\mathrm{K}) = -687.0 \pm 3.5$ kJ mol^{-1}, was derived from the enthalpy of solution of $SmBr_3$(cr) at infinite dilution reported by Hurtgen et al. [14] (see Table 5) and the assessed value for the standard enthalpy of formation of $SmBr_3$(cr).

Recently, the enthalpy of formation of the aqueous Sm^{3+} ion was determined by measuring the enthalpy of solution of Sm(cr) in 0.05–0.008 mol dm^{-3} $HClO_4$(aq) by Khanaev et al. [25]. The experimental values of the enthalpies of solution of Sm(cr) have been recalculated to infinite dilution using the molar enthalpies of dilution given by Spedding et al. [8] for the rare earth perchlorates. The value, $\Delta_f H^0(298.15\,\mathrm{K}) = -690.2 \pm 0.8$ kJ mol^{-1}, was obtained from the results being in excellent agreement with the aforesaid values [13,26].

The selected value is the mean of the results of Spedding and Flynn [26], Krestov et al. [13], Morss [3], Hurtgen et al. [14] and Khanaev et al. [25]:

$$\Delta_f H^0(\mathrm{Sm}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -690.0 \pm 2.0\,\mathrm{kJ\,mol^{-1}}$$

3.7. Eu^{3+}(aq)

The enthalpy of solution of $EuCl_3$(cr) in dilute acid (0.015 mol dm^{-3} HCl(aq)) measured by Machlan et al. [27] has been extrapolated to the infinite dilution to give $\Delta_{sln}H^0(298.15\,\mathrm{K}) = -168.2 \pm 1.3\,\mathrm{kJ\,mol^{-1}}$. Morss and Haug [28] estimated the final molality of $EuCl_3$(aq) in the calorimeter as 0.008 mol kg^{-1}, and corrected the results of Machlan et al. to the standard state of infinite dilution, $\Delta_{sln}H^0(298.15\,\mathrm{K}) = -170.3 \pm 2.1\,\mathrm{kJ\,mol^{-1}}$. This value corresponds to the following value for the enthalpy of formation of Eu^{3+}(aq) being selected here:

$$\Delta_f H^0(\mathrm{Eu}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -605.4 \pm 4.0\,\mathrm{kJ\,mol^{-1}}$$

3.8. Gd^{3+}(aq)

The standard enthalpy of formation of the aqueous Gd^{3+} ion can be derived from the enthalpies of solution of $GdCl_3$(cr), $GdBr_3$(cr) and GdI_3(cr) at infinite dilution and appropriate auxiliary data. The results of numerous determinations are summarised in Table 6. The experimental results for the enthalpy of solution have been recalculated to the standard state of infinite dilution using the molar enthalpies of dilution of $GdCl_3$(aq) reported by Spedding et al. [8]. There is a reasonable agreement in the values for the enthalpy of formation of Gd^{3+} derived from the results of

Table 6
The enthalpy of formation of Gd^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Bommer and Hohmann [12]	1941	$-179.6^{b,e}$	-696.5
Hohmann and Bommer [19]		$-256.0 \pm 2.5^{d,e}$	-709.8 ± 3.9
Spedding and Flynn [26]	1954	-179.8 ± 0.2^{b}	-696.7 ± 1.5
Jekel et al. [6]	1964	-182.0 ± 0.2^{b}	-698.9 ± 1.5
Clark and Bear [24]	1969	-168.3 ± 4.2^{b}	-685.2 ± 4.5
Krestov and Abrosimov [29]	1972	-181.8^{b}	-698.7
Blachnik and Selle [21]	1979	-180.8^{b}	-697.7
Hurtgen et al. [14]	1980	-220.9^{c}	-694.9
Burgess and Kijowski [15]	1981	-183.0 ± 1.6^{b}	-699.9 ± 3.4
		-250.3 ± 2.3^{d}	-704.1 ± 3.8
Monaenkova et al. [30]	1982	-181.9 ± 0.4^{b}	-698.8 ± 1.6
Tiflova et al. [31]	1989	-182.8 ± 0.2^{b}	-699.7 ± 1.5
Merli et al. [32]	1998	-180.7 ± 1.3^{b}	-697.6 ± 2.0
Selected value			-698.4 ± 2.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of GdX_3(cr) in aqueous solution (aq) corrected to infinite dilution.
[b] The enthalpy of solution of $GdCl_3$(cr) at infinite dilution.
[c] The enthalpy of solution of $GdBr_3$(cr) at infinite dilution.
[d] The enthalpy of solution of GdI_3(cr) at infinite dilution.
[e] Value corrected to 298.15 K.

different authors, with exception of the value reported by Clark and Bear [24]. The constant deviation of the enthalpies of solution of rare earth chlorides measured by these authors from the more accurate data indicates the presence of an undetected systematic error in their results.

Taking into consideration the purity of the samples applied in the various studies, as well as the accuracy of the calorimetric measurements carried out, the concordant results obtained by Spedding and Flynn [26], Jekel et al. [6], Krestov and Abrosimov [29], Hurtgen et al. [14], Monaenkova et al. [30], Tiflova et al. [31] and Merli et al. [32] seem to be the most reliable and best documented. The mean of these results is selected here:

$$\Delta_f H^0(\mathrm{Gd}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -698.4 \pm 2.0\,\mathrm{kJ\,mol}^{-1}$$

3.9. Tb^{3+}(aq)

The standard enthalpy of formation of the aqueous Tb^{3+} ion at infinite dilution can be derived from the enthalpy of solution of $TbCl_3$(cr) and the appropriate auxiliary data, as listed in Table 7. The experimental enthalpies of solution of $TbCl_3$(cr) have been corrected to the state of infinite dilution using the molar enthalpies of dilution given by Spedding et al. [8] for $TbCl_3$(aq). There is a reasonable agreement for the

Table 7
The enthalpy of formation of Tb^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Bommer and Hohmann [12]	1941	-194.2	-703.5
Krestov et al. [8]	1973	-187.0 ± 0.7	-696.3 ± 4.1
Spedding and Bisbee[b]		-192.4	-701.7
Monaenkova et al. [30]	1982	-192.1 ± 0.3	-701.4 ± 4.0
Selected value			-699.8 ± 4.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of $TbCl_3$(cr) in aqueous solution (aq), corrected to infinite dilution; values corrected to 298.15 K.
[b] Quoted in [3].

values of the enthalpy of formation of Tb^{3+}(aq) obtained by different authors. Taking into account the poor quality of the sample used for one solution measurement by Bommer and Hohmann [33], as well as insufficient experimental details reported by Morss [3] concerning the unpublished work of Spedding and Bisbee, the value based on the result of Krestov et al. [18] and Monaenkova et al. [30] has been selected here as the most reliable and best documented:

$$\Delta_f H^0(\mathrm{Tb}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -699.8 \pm 4.0\,\mathrm{kJ\,mol^{-1}}$$

3.10. Dy^{3+}(aq)

The standard enthalpy of formation of the aqueous Dy^{3+} ion at infinite dilution can be derived from the enthalpies of solution of $DyCl_3$(cr), $DyBr_3$(cr) and DyI_3(cr) in water and the assessed values for the enthalpies of formation of DyX_3(cr) [1], as summarised in Table 8. The experimental enthalpies of solution of $DyCl_3$(cr) have been recalculated to the infinite dilution using the molar enthalpies of dilution given by Spedding et al. [8] for $DyCl_3$(aq).

The first enthalpy of solution of $DyCl_3$(cr) reported by Bommer and Hohmann [12] was obtained at 293 K. The later studies [6,13] of the temperature dependence of solution enthalpies of rare earth chlorides suggest that the values at 298 K would be about 2 kJ mol^{-1} more negative. In general, there is a good agreement among the values for the enthalpy of solution of $DyCl_3$(cr) at infinite dilution derived from different studies, with the exception of the results of Blachnik and Selle [21].

The accuracy of the result of Montgomery and Stuve, as reported by Morss [3] is difficult to evaluate, since the work is inaccessible to us. The values for the enthalpies of solution of $DyCl_3$(cr) at infinite dilution obtained by Monaenkova et al. [30,34] in two different sets of measurements are accurate and well documented. Table 8 also presents the values for the enthalpy of formation of Dy^{3+}(aq) derived from the results of Bommer and Hohmann [12] and Morss and Spence [35] for the enthalpy of solution of DyI_3(cr) and appropriate auxiliary data. These values are in agreement with the other values, but are significantly less accurate.

The selected value for the enthalpy of formation of Dy^{3+}(aq) is the mean of the results derived from the two studies by Monaenkova et al. [30,34]:

$$\Delta_f H^0(\mathrm{Dy}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -700.2 \pm 3.0\,\mathrm{kJ\,mol^{-1}}$$

3.11. Ho^{3+}(aq)

The standard enthalpy of formation of the aqueous Ho^{3+} ion at infinite dilution can be derived from the enthalpies of solution of $HoCl_3$(cr) and HoI_3(cr) in water, in combination with the appropriate auxiliary

Table 8
The enthalpy of formation of Dy^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Bommer and Hohmann [12]	1941	-199.9 ± 0.6[b,e]	-691.7 ± 3.1
Hohmann and Bommer [19]	1941	-256.7 ± 1.0[d,e]	-703.1 ± 2.1
Montgomery and Stuve[f]	1961	-207.4[b]	-699.2
Clark and Bear [24]	1969	-206.8 ± 4.2[b]	-698.6 ± 5.2
Blachnik and Selle [21]	1979	-198.1[b]	-689.9
Hurtgen et al. [14]	1980	-227.8[c]	-697.8
Monaenkova et al. [30]	1982	-209.0 ± 0.5[b]	-700.8 ± 3.1
Monaenkova et al. [34]	1989	-207.8 ± 0.3[b]	-699.6 ± 3.0
Morss and Spence [35]	1992	-253 ± 7[d]	-699.4 ± 7.2
Selected value			-700.2 ± 3.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of DyX_3(cr) in aqueous solution (aq) corrected to infinite dilution.
[b] The enthalpy of solution of $DyCl_3$(cr) at infinite dilution.
[c] The enthalpy of solution of $DyBr_3$(cr) at infinite dilution.
[d] The enthalpy of solution of DyI_3(cr) at infinite dilution.
[e] Value corrected to 298.15 K.
[f] Quoted in [3].

Table 9
The enthalpy of formation of Ho^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Bommer and Hohmann [33]	1941	$-211.2^{b,e}$	−707.7
		$-259.4^{c,d}$	−713.1
Clark and Bear [24]	1969	-199.7 ± 4.6^{b}	−696.2 ± 5.2
Spedding and Bisbee[e]		-213.4^{b}	−709.9
Blachnik and Selle [21]	1979	-210.3^{b}	−706.8
Lezhava [36]	1992	-211.2 ± 1.0^{b}	−707.7 ± 2.7
Selected value			−707.7 ± 3.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of HoX_3(cr) in aqueous solution (aq) corrected to infinite dilution.
[b] The enthalpy of solution of $HoCl_3$(cr) at infinite dilution.
[c] The enthalpy of solution of HoI_3(cr) at infinite dilution.
[d] Value corrected to 298.15 K.
[e] Quoted in [3].

data. The enthalpies of solution of HoX_3(cr) have been corrected to the standard state of infinite dilution using the molar enthalpies of dilution given by Spedding et al. [8] for $HoCl_3$(aq) (see Table 9).

There is reasonable agreement between the values for the solution of $HoCl_3$(cr) at infinite dilution obtained by different authors, except for the result of Clark and Bear [24]. The reason for this deviation is not quite clear, although a systematic discrepancy of the enthalpies of solution obtained by Clark and Bear for a number of rare earth chlorides (see [1]) from the most reliable data suggests an undetected systematic error in their results. The values based on the results of solution measurements of $HoCl_3$(cr) and HoI_3(cr) by Bommer and Hohmann [12,19] have to be considered as approximate results only, due to a doubtful quality of the HoX_3(cr) samples and insufficient number of calorimetric measurements.

The enthalpy of formation of Ho^{3+}(aq) derived from the result of Lezhava [36] is the best documented. Additional values for the enthalpy of formation of Ho^{3+}(aq) calculated from the results of Blachnik and Selle [21], and the values reported by Morss [3] with a reference to a private communication by Spedding and Bisbee are in reasonable agreement with the aforesaid result.

The selected value is based on the results of Lezhava [36] only, the uncertainty being estimated as ±3.0 kJ mol^{-1}:

$$\Delta_f H^0(Ho^{3+}, aq, 298.15\,K) = -707.7 \pm 3.0\,kJ\,mol^{-1}$$

3.12. Er^{3+}(aq)

The standard enthalpy of formation of the aqueous Er^{3+} ion has been calculated from the enthalpies of solution of $ErCl_3$(cr), $ErBr_3$(cr) and ErI_3(cr) at infinite dilution and the appropriate auxiliary data. The results of the various measurements of the enthalpy are summarised in Table 10. The experimental enthalpies of solution have been corrected to the standard state of infinite dilution according to the molar enthalpies of dilution given by Spedding et al. [8] for $ErCl_3$(aq). Although, the values for the enthalpy of formation of Er^{3+}(aq) derived from the results of different authors, show a substantial scatter, the concordant results by Montgomery and Stuve [37], Fuger et al. [38] and Tiflova [23] seem to be far more precise and reliable, because their samples and methods are better characterised.

Two more values for the enthalpy of formation of Er^{3+} can be derived from enthalpy-of-solution measurements of the bromide and iodide. The first is calculated from the enthalpy of solution of $ErBr_3$(cr) at infinite dilution, estimated from the solution enthalpies of erbium tribromide in 0.1 mol dm^{-3} HCl(aq) reported by Hurtgen et al. [14] (see Table 10). The second is been calculated from the results of Hohmann and Bommer [19], who carried out two solution measurements of ErI_3(cr) in water at 293 K. The latter value, being almost within a combined error limits of the aforesaid enthalpies, seems to be less accurate due to a doubtful quality of the sample of rare earth halide

Table 10
The enthalpy of formation of Er^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Bommer and Hohmann [12]	1941	$-209.3 \pm 0.3^{b,c}$	-702.5 ± 2.0
Hohmann and Bommer [19]	1941	$-261.0 \pm 0.6^{d,e}$	-709.7 ± 3.1
Spedding and Flynn [16]	1954	-208.3 ± 0.2^{b}	-701.5 ± 2.0
Montgomery and Stuve [37]	1961	-215.1 ± 0.5^{b}	-708.3 ± 2.1
Clark and Bear [24]	1969	-197.2 ± 2.5^{b}	-690.4 ± 3.2
Krestov et al. [18]	1973	-210.0 ± 0.6^{b}	-703.2 ± 2.1
Blachnik and Selle [21]	1979	-215.0^{b}	-708.2
Hurtgen et al. [14]	1980	-233.3 ± 2.2^{c}	-706.2 ± 3.7
Fuger et al. [38]	1980	-214.8 ± 0.3^{b}	-708.0 ± 2.0
Tiflova [23]	1990	-215.0 ± 0.2^{b}	-708.2 ± 2.0
Selected value			-708.2 ± 3.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of ErX_3(cr) in aqueous solution (aq) corrected to infinite dilution.
[b] The enthalpy of solution of $ErCl_3$(cr) at infinite dilution.
[c] Estimated value for the enthalpy of solution of $ErBr_3$(cr) at infinite dilution.
[d] The enthalpy of solution of ErI_3(cr) at infinite dilution.
[e] Value corrected to 298.15 K.

available at that time and insufficient number of measurements carried out in that study.

The selected value for the standard enthalpy of formation of Er^{3+}(aq) is the mean of the results of Montgomery and Stuve [37], Fuger et al. [38] and Tiflova [23]:

$$\Delta_f H^0(Er^{3+}, aq, 298.15\,K) = -708.2 \pm 3.0\,kJ\,mol^{-1}$$

3.13. Tm^{3+}(aq)

The standard enthalpy of formation of the aqueous Tm^{3+} ion has been derived from the values for the enthalpies of solution of $TmCl_3$(cr) at infinite dilution and the appropriate auxiliary data [1], as summarised in Table 11. The corrections of the experimental enthalpy-of-solution values to the state of infinite dilution have been made according to the molar enthalpies of dilution given by Spedding et al. [8] for $TmCl_3$(aq).

The first enthalpies of formation reported by Bommer and Hohmann [33] could not be considered as reliable mainly due to a poor quality of their $TmCl_3$(cr) sample. A much more precise value was obtained by Lezhava [36] by measuring the enthalpy of solution of a well-analysed sample of $TmCl_3$(cr) in water. Almost the same value has been derived from the results reported by Morss [3] with reference to a

Table 11
The enthalpy of formation of Tm^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Bommer and Hohmann [12]	1941	-215.1 ± 0.2^{b}	-710.1 ± 2.5
Hohmann and Bommer [19]	1941	$-255.6^{c,d}$	-704.9
Spedding and Bisbee[e]		-215.8	-710.8
Lezhava [36]	1992	-216.1 ± 0.7	-711.1 ± 3.0
Selected value			-711.1 ± 3.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of TmX_3(cr) in aqueous solution (aq) corrected to infinite dilution.
[b] The enthalpy of solution of $TmCl_3$(cr) at infinite dilution.
[c] The enthalpy of solution of TmI_3(cr) at infinite dilution.
[d] Value corrected to 298.15 K.
[e] Quoted in [3].

private communication of Spedding and Bisbee, which is not accessible to us. The accuracy of the latter value could not be evaluated, since experimental details are not presented.

The selected value is based on the result of Lezhava [36] for the enthalpy of solution of $TmCl_3(cr)$:

$$\Delta_f H^0(\mathrm{Tm}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -711.1 \pm 3.0\,\mathrm{kJ\,mol^{-1}}$$

3.14. $Yb^{3+}(aq)$

The standard enthalpy of formation of the aqueous Yb^{3+} ion at infinite dilution has been derived from the enthalpies of solution of $YbCl_3(cr)$ at infinite dilution and appropriate auxiliary data.

The literature values on the enthalpy of solution of $YbX_3(cr)$ in water listed in Table 12 show considerable scatter. The experimental enthalpies of solution have been corrected to the state of infinite dilution according to the molar enthalpies of dilution given by Spedding et al. [8] for $YbCl_3(aq)$. The enthalpy of solution obtained by Bommer and Hohmann [12] at 293 K seems not to be reliable enough in view of the poor quality of $YbCl_3(cr)$ sample and limited number of measurements carried out. The value derived from the results by Spedding and Flynn [16] is considered as much more accurate and better documented. Different values have been derived from the enthalpies of solution of $YbBr_3(cr)$ at infinite dilution reported by Bettonville et al. [39] and Burgess and Kijowski [15], respectively. As discussed before, the deviation of the values obtained by Clark and Bear [24] from the more accurate calorimetric data is probably caused by an undetected systematic error. For that reason, the value derived from their results was rejected from the selection.

The selected enthalpy of formation of $Yb^{3+}(aq)$ is the mean of the values derived from the enthalpy of solution of $YbCl_3(cr)$ measured by Spedding and Flynn [26] and Burgess and Kijowski [15]:

$$\Delta_f H^0(\mathrm{Yb}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -676.3 \pm 3.0\,\mathrm{kJ\,mol^{-1}}$$

3.15. $Lu^{3+}(aq)$

The standard enthalpy of formation of the aqueous Lu^{3+} ion at infinite dilution has been derived from the enthalpy of solution of $LuCl_3(cr)$ in water (see Table 13) and appropriate auxiliary data [1]. The experimental values for the enthalpy of solution of $LuCl_3(cr)$ available in the literature have been recalculated to the state of infinite dilution using the molar enthalpies of dilution given by Spedding et al. [8] for $LuCl_3(aq)$.

The enthalpies of formation of $Lu^{3+}(aq)$ derived from the solution calorimetric measurements of $LuCl_3(cr)$ and $LuI_3(cr)$ by Hohmann and Bommer [19] should be considered approximate values due to a poor quality of the samples and insufficient number of measurements. A more reliable value for the enthalpy of formation of $Lu^{3+}(aq)$ was obtained by Tiflova [23] by measuring the enthalpy of solution of a well-analysed sample of $LuCl_3(cr)$ in 0.006 M HCl(aq). Another value, being almost within the error

Table 12
The enthalpy of formation of $Yb^{3+}(aq)$ at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Bommer and Hohmann [12]	1941	-215.5 ± 0.2[b,d]	-673.8 ± 3.0
Spedding and Flynn [16]	1954	-216.1 ± 0.2[b]	-674.4 ± 3.0
Clark and Bear [24]	1969	-205.5 ± 3.8[b]	-663.8 ± 4.9
Blachnik and Selle [21]	1979	-215.4[c]	-673.7
Burgess and Kijowski [15]	1981	-219.9 ± 1.9[b]	-678.2 ± 3.6
		-240.4 ± 1.4[c]	-668.1 ± 2.5
Bettonville et al. [39]	1987	-241.0 ± 0.9[c]	-668.7 ± 2.2
Selected value			-676.3 ± 3.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of $YbX_3(cr)$ in aqueous solution (aq) corrected to infinite dilution.

[b] The enthalpy of solution of $YbCl_3(cr)$ at infinite dilution.

[c] The enthalpy of solution of $YbBr_3(cr)$ at infinite dilution.

[d] Value corrected to 298.15 K.

Table 13
The enthalpy of formation of Lu^{3+}(aq) at 298.15 K[a]

Reference	Year	$\Delta_{sln}H^0$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
Bommer and Hohmann [12]	1941	−216.8[b,d]	−702.7
Hohmann and Bommer [19]	1941	−263.7[c]	−698.5
Spedding and Bisbee[e]		−218.5[b]	−704.4
Tiflova [23]	1990	−215.5 ± 0.4[d]	−701.4 ± 2.5
Merli et al. [32]	1998	−219.4 ± 0.9	−705.3 ± 2.7
Selected value			−703.3 ± 3.0

[a] $\Delta_{sln}H^0$ is the enthalpy of solution of LuX_3(cr) in aqueous solution (aq) corrected to infinite dilution.

[b] The enthalpy of solution of $LuCl_3$(cr) at infinite dilution.

[c] The enthalpy of solution of LuI_3(cr) at infinite dilution.

[d] Value corrected to 298.15 K.

[e] Quoted in [3].

limit of the value by Tiflova [23], was derived from data reported by Morss [3] with reference to a private communication by Spedding and Bisbee, which is inaccessible to us. The accuracy of the latter value could not be evaluated, since no experimental details were given [3]. Also Merli et al. [32] measured the enthalpy of solution of $LuCl_3$ in diluted (10^{-3} mol dm^{-3}) HCl(aq) from which we derive a highly concordant value.

The selected value is the mean of the results of Tiflova [23] and Merli et al. [32], the error limit of the mean being estimated as ±3.0 kJ mol^{-1}:

$$\Delta_f H^0(\mathrm{Lu}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -703.3 \pm 3.0\,\mathrm{kJ\,mol}^{-1}$$

4. Discussion

Table 14 lists the assessed values for the enthalpies of formation of the trivalent lanthanide ions; Fig. 1 shows the results as a function of the atomic number. It is obvious that (Ln^{3+}, aq) changes smoothly in the series of the light lanthanide elements La to Sm as well as for the heavy lanthanide elements Gd to Lu, as is the case for many properties of the lanthanide series [40]. Europium and ytterbium form exceptions to this smooth change. This can be explained by the relatively high stability of the electron configurations of Eu and Yb, which is $4f^7 6s^2$ and ($4f^{14}6s^2$), respectively, as has been discussed extensively by Nugent et al. [41] and Morss [42]. These authors showed that for the ions of the lanthanide metals that are trivalent in the condensed phase, a continuous variation in the enthalpy of formation of the ions with the atomic number exists. Eu and Yb, however, are divalent metals and an extra step with an associated energy effect is needed for the divalent → trivalent transition. Nevertheless, the overall trend permits us to estimate the value for the Pm^{3+} ion by linear interpolation.

Table 14
Summary of the selected enthalpies of formation of the lanthanide aqueous trivalent ions

	$\Delta_f H^0$(298.15 K) (kJ mol^{-1})		$\Delta_f H^0$(298.15 K) (kJ mol^{-1})
La^{3+}	−707.6 ± 2.5	Tb^{3+}	−699.8 ± 4.0
Ce^{3+}	−702.4 ± 2.0	Dy^{3+}	−700.2 ± 3.0
Pr^{3+}	−705.7 ± 2.0	Ho^{3+}	−707.7 ± 3.0
Nd^{3+}	−694.8 ± 2.0	Er^{3+}	−708.2 ± 3.0
Pm^{3+}	−693 ± 10	Tm^{3+}	−711.1 ± 3.0
Sm^{3+}	−690.0 ± 2.0	Yb^{3+}	−676.3 ± 3.0
Eu^{3+}	−605.4 ± 4.0	Lu^{3+}	−703.3 ± 3.0
Gd^{3+}	−698.4 ± 2.0		

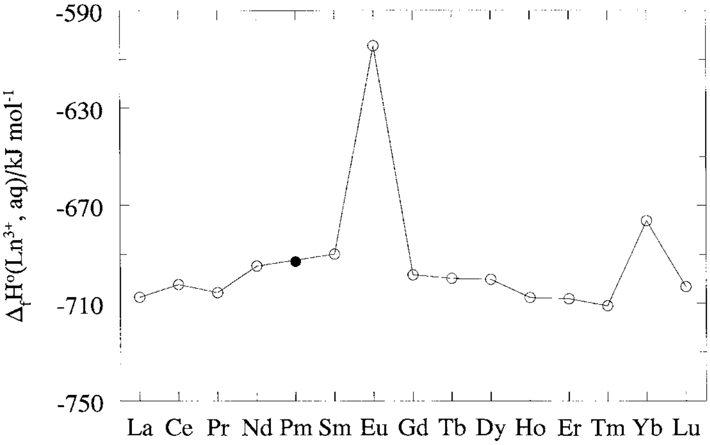

Fig. 1. The variation of the enthalpy of formation of Ln^{3+} ions in the lanthanide series; the closed circle indicates the estimated value for Pm^{3+}.

Acknowledgements

The assistance of Dr. M. Furkaliouk (Institute for High Temperatures IVTAN, Moscow) to this project is gratefully acknowledged. Prof. J. Fuger (University of Liège) is thanked for his constructive and careful review of the work.

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