



Thermochemistry of lanthanum, neodymium, samarium and americium trihydroxides and their relation to the corresponding hydroxycarbonates

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Abstract

The enthalpies of solutions of La(OH)₃ (cr), Nd(OH)₃ (cr), Sm(OH)₃ (cr) and Am(OH)₃ (cr) and of La (cr), Nd (cr) and Sm (cr) in 6.00 mol dm⁻³ HCl have been measured at 298.15 K. From these measurements, the following standard molar enthalpies of formation $\Delta_f H_m^\circ$ (kJ mol⁻¹) are calculated as La(OH)₃ (cr): $-(1416.7 \pm 1.3)$; Nd(OH)₃ (cr): $-(1415.6 \pm 2.3)$; Sm(OH)₃ (cr): $-(1406.6 \pm 2.2)$; Am(OH)₃ (cr): $-(1343.6 \pm 1.8)$. From these values combined with measured and estimated entropy values, the solubility products of the hydroxides are obtained. These results are compared with existing literature data and thermodynamic relationships between the hydroxides and the corresponding hydroxycarbonates are established. © 1997 Elsevier Science B.V.

1. Introduction

Hydrolysis and, in CO₂ containing water, interactions with carbonate ions will play an essential long term role in the solubilization/recrystallization processes which may occur, should, in a long term, natural waters come in contact with high level radioactive waste under the conditions of deep underground storage. In view of the long half life of several actinide isotopes the knowledge of the thermodynamic parameters associated with the formation of relevant actinide compounds is important. The study of the behavior of the light lanthanides is also of relevance because they are often used in studies as stand-ins for trivalent actinides.

In this spirit we have recently reported results on the thermochemistry of a few neptunium and neodymium oxides and hydroxides [1] and of lanthanide and americium

hydroxycarbonates [2]. This paper is concerned with new thermochemical results on crystalline hydroxides of lanthanum, neodymium, samarium and americium.

2. Experimental

As described previously [1], Nd(OH)₃ (ca. 200 mg samples) was obtained according to the technique described by Morss and Williams [3] for Am(OH)₃, i.e., by contacting Nd₂O₃ (99.9% purity – Janssen Chimica, Geel, Belgium), freshly calcined at 1173 K with water vapor at 500–510 K in a pyrex vessel. Using oxides of the same origin and similarly calcined, the other hydroxides have been obtained by reaction with decarbonated water (0.25 cm³) in a gold crucible in a small (6.8 cm³) stainless steel autoclave at 573–583 K and saturating H₂O pressures of 8.6–10 MPa for a maximum duration of 5 days. The higher temperature and pressure as compared to the conditions described in Ref. [3] were selected to overcome difficulties in obtaining hydroxides heavier than neodymium in a pure form. For Am(OH)₃ the starting material was aged ²⁴¹AmO₂ (from Oak Ridge National Laboratory, TN, USA) purified from its daughter ²³⁷Np as

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described previously [4] and from the other remaining impurities using a 'clean up' column procedure [5]. The dioxide was then reduced in a gold crucible to Am_2O_3 (hex) by a H_2 flow at 1090 K for 16 h. The americium hydroxide was obtained using the same procedure as for lanthanum and samarium hydroxide but, as additional precaution, the reaction was carried out in a sealed pyrex tube. Dissolved gases (especially O_2) were removed from the water used by freeze–evacuate–thaw cycles. Water was also added directly in the autoclave to equilibrate pressures on the sealed tube walls. The reaction was carried out for 10 days at 403 ± 5 K corresponding to a water saturation pressure of 275 kPa. All samples were dried in vacuum overnight. The lanthanide hydroxides, prepared in duplicate or triplicate, were analyzed by gravimetry of the sesquioxide or complexometry with EDTA using potentiometric detection [6]. $\text{Am}(\text{OH})_3$ was analyzed by gravimetry (6 mg samples) as AmO_2 . The analytical results are given in Table 1.

Equipment and procedures for FTIR spectroscopy and X-ray diffraction have been described [2]. Between 400 and 4000 cm^{-1} the only observed bands were due to ν_{OH} and δ_{OH} . ν_{OH} is found at $3608 \pm 1\text{ cm}^{-1}$ for the three lanthanide compounds and 3596 ± 5 for $\text{Am}(\text{OH})_3$. δ_{OH} is at 643, 673, 692 and 682 cm^{-1} , respectively for the lanthanum, neodymium, samarium and americium compounds, respectively. A microscope attachment to the FTIR spectrometer was used for $\text{Am}(\text{OH})_3$, allowing a considerable reduction of the required amount of sample. No bands were found in the region $1425\text{--}1500\text{ cm}^{-1}$ thus ascertaining the absence of carbonate species. For the lanthanide compounds all observed diffraction lines of the various compounds were indexed in the hexagonal system and intensities were consistent with the space group $\text{P6}_3/\text{m}$. In the case of $\text{Am}(\text{OH})_3$ one weak extraneous line was present at $d = 0.289\text{ nm}$; it could be attributed to the (101) most intense line of Am_2O_3 (hex.). Lattice parameters were identical for the various preparations, of the same compound, within uncertainty limits (2σ): $a_0 = 0.6532$ (8), $c_0 = 0.3854$ (6) for $\text{La}(\text{OH})_3$ (B); $a_0 = 0.6418$ (4),

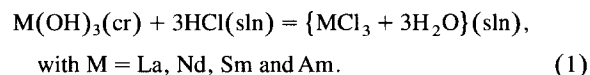
$c_0 = 0.3739$ (2) for $\text{Nd}(\text{OH})_3$ (A); $a_0 = 0.6373$ (6), $c_0 = 0.3678$ (2) for $\text{Sm}(\text{OH})_3$ (C); $a_0 = 0.6413$ (4), $c_0 = 0.3737$ (2) for $\text{Am}(\text{OH})_3$, all in nm. They agreed well with literature values [7,8].

Lanthanum (batch 100191), neodymium (batch TWE.001.AM) and samarium (batch 62188) metals were obtained from the USDOE Ames Laboratory at Iowa State University (Ames, IA 50011) in the highest available purity. Combined amounts of H, C, N and O (all in at. ppm) detected by vacuum fusion and combustion were ca. 1300 for La, 700 for Nd and 140 for Sm. Fluorine (by absorptionmetry) was ca. 200 for La, 140 for Nd and 180 at. ppm for Sm. The sum of all other impurities detected by mass spectrometry was in all cases smaller than 200 at. ppm.

Procedures for the preparation of the solutions, the weighing of the samples and the calorimetry have been described [1]. All samples were handled in glove boxes filled with N_2 or Ar atmospheres (< 10 ppm O_2 , H_2O). The metals were handled in a Ar filled glove box (Jacomex, Livry Gargan, France) with gas purification insuring less than 1 ppm H_2O and O_2 . All calorimetric results are based on the Student t 95% confidence level and reported for 298.15 ± 0.05 K and $p_0 = 101.325$ kPa. Unless otherwise specified auxiliary thermodynamic data are those recommended by CODATA [9].

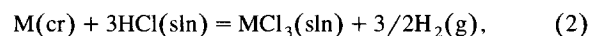
3. Results and discussion

Table 2 shows the results of the dissolution, in 6 mol dm^{-3} HCl (sln) of the hydroxides according to



In all cases the heat evolution was complete in less than three minutes.

Lanthanum, neodymium and samarium metals were also dissolved in the same medium, according to



yielding the values $\Delta_r H_m$ (Eq. (2)) = $-(707.4 \pm 1.1)$, $-(695.7 \pm 1.8)$ and $-(695.2 \pm 1.4)$, all in kJ mol^{-1} , for La, Nd and Sm, respectively.

In the case of samarium it was shown that, within uncertainty limits the same value was obtained whether the medium was deoxygenated or not or when H_2PtCl_6 was added at a $10^{-6}\text{ mol dm}^{-3}$ concentration. This reagent is known to have a marked catalytic effect on the oxidation by protons of U^{3+} to U^{4+} [10] and Yb^{2+} to Yb^{3+} [11]. Also for samarium, a very rapid reaction which could have led to projections (and therefore losses from the bulk of the solution) was avoided by wrapping the metal pieces in quartz wool. Details of these and other lanthanide metal dissolutions in various HCl media will be reported separately [12].

Table 1
Analytical results of the hydroxides

| Sample | Element | Mass percentage | | Method |
|--------------------------|---------|-----------------|----------------|---------------|
| | | calc. | obs. | |
| $\text{La}(\text{OH})_3$ | A La | 73.14 | 72.9 ± 0.1 | gravimetry |
| | B La | | 72.9 ± 0.1 | gravimetry |
| | C La | | 72.9 ± 0.1 | gravimetry |
| $\text{Nd}(\text{OH})_3$ | A Nd | 73.81 | 74.3 ± 0.5 | complexometry |
| | B Nd | | 74.2 ± 0.5 | complexometry |
| $\text{Sm}(\text{OH})_3$ | A Sm | 74.66 | 74.7 ± 0.1 | gravimetry |
| | B Sm | | 75.2 ± 0.5 | complexometry |
| | C Sm | | 75.1 ± 0.5 | complexometry |
| $\text{Am}(\text{OH})_3$ | Am | 82.53 | 81.6 ± 0.8 | gravimetry |

Table 2

Molar enthalpies of solution of the hydroxides at 298.15 ± 0.05 K and $p^{\circ} = 101.325$ kPa in 6.00 mol dm^{-3} HCl (sln)

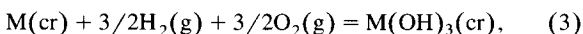
| Sample | Sample mass (mg) | ΔH° (J) | $-\Delta_{\text{sln}}H_m$ (kJ mol^{-1}) |
|-----------------------------------|------------------|------------------------|--|
| La(OH) ₃ in 25 ml sln | | | |
| A | 17.88 | 14.310 | 152.0 |
| A | 31.23 | 24.475 | 148.8 |
| A | 25.82 | 20.633 | 151.8 |
| A | 20.03 | 15.845 | 150.2 |
| A | 25.11 | 20.047 | 151.6 |
| B | 18.51 | 14.512 | 148.9 |
| B | 20.48 | 16.275 | 150.9 |
| B | 28.66 | 22.789 | 151.0 |
| B | 29.82 | 23.681 | 150.8 |
| B | 29.74 | 23.754 | 151.7 |
| C | 25.13 | 20.103 | 151.9 |
| C | 31.13 | 24.525 | 149.6 |
| C | 22.63 | 17.900 | 150.2 |
| C | 19.53 | 15.323 | 149.0 |
| | | | mean: $(150.6 \pm 0.7)^b$ |
| Nd(OH) ₃ in 25 ml sln | | | |
| Sm(OH) ₃ in 25 ml sln | | | |
| A | 11.41 | 8.563 | 151.1 |
| A | 18.68 | 13.669 | 147.4 |
| A | 10.51 | 7.650 | 146.6 |
| A | 13.02 | 9.658 | 149.4 |
| B | 18.03 | 13.464 | 150.4 |
| B | 13.04 | 9.803 | 151.4 |
| B | 19.22 | 14.185 | 148.6 |
| B | 23.97 | 17.282 | 145.2 |
| C | 18.43 | 13.839 | 151.2 |
| C | 20.63 | 15.162 | 148.0 |
| C | 26.90 | 19.204 | 143.8 |
| | | | mean: $(148.5 \pm 1.7)^{b,c}$ |
| Am(OH) ₃ in 8.5 ml sln | | | |
| | 2.608 | 1.146 | 128.3 |
| | 2.734 | 1.204 | 128.6 |
| | 4.854 | 2.163 | 130.1 |
| | 4.018 | 1.791 | 130.2 |
| | 3.858 | 1.716 | 129.9 |
| | | | mean: $(129.4 \pm 1.1)^b$ |

^a Corrected for ampoule breaking and evaporation of solvent into gas in ampoule.

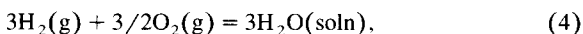
^b 95% confidence.

^c Detailed values already published [1]; the correction of $0.4\text{--}0.7$ kJ mol^{-1} due to ampoule breaking and solvent evaporation was not included in ref. [1].

The molar enthalpies of formation of the hydroxides, according to



are obtained through the use of the partial molar enthalpy of formation of water in the medium, according to



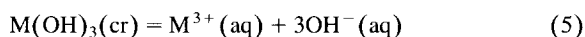
namely $\Delta H_4 = -3(286.63 \pm 0.04) \text{ kJ mol}^{-1}$ [9,13]. Thus $\Delta H_3 = \Delta_f H_m^{\circ} \{\text{M}(\text{OH})_3, \text{cr}\} = \Delta H_2 + \Delta H_4 - \Delta H_1$.

We obtain $\Delta_f H_m^{\circ} \{\text{La}(\text{OH})_3, \text{cr}\} = -(1416.7 \pm 1.3) \text{ kJ mol}^{-1}$. This value is in excellent agreement with that reported by Cordfunke et al. [14], $-(1415.5 \pm 1.4) \text{ kJ mol}^{-1}$. In the case of neodymium, the above results yield $\Delta_f H_m^{\circ} \{\text{Nd}(\text{OH})_3, \text{cr}\} = -(1415.6 \pm 2.3) \text{ kJ mol}^{-1}$. This value is significantly different from the one, $-(1404.2 \pm 3.3) \text{ kJ mol}^{-1}$, we reported earlier [1], using the same dissolution values for the hydroxide but based on $\Delta_f H_m^{\circ} \{\text{Nd}_2\text{O}_3, \text{cr}\} = -(1807.9 \pm 0.9) \text{ kJ mol}^{-1}$ [15], and the enthalpy of solution of Nd_2O_3 in 6.00 mol dm^{-3} HCl, $-(419.6 \pm 6.0) \text{ kJ mol}^{-1}$ from Morss et al. [16]. As our enthalpy of solution of Nd (cr) in 6.00 , 3.00 and 1.00 mol dm^{-3} HCl, $-(695.7 \pm 1.8)$, $-(693.9 \pm 1.3)$ and $-(689.6 \pm 2.0) \text{ kJ mol}^{-1}$ [12] are in line with the result of Tiflova [17] for 2.3 mol dm^{-3} , $-(690.8 \pm 1.6) \text{ kJ mol}^{-1}$, and Stuve [18] for 4.00 mol dm^{-3} HCl, $-(693.6 \pm 0.9) \text{ kJ mol}^{-1}$, we believe that the present value for $\Delta_f H_m^{\circ} \{\text{Nd}(\text{OH})_3, \text{cr}\} = -(1415.6 \pm 2.3) \text{ kJ mol}^{-1}$, based on the dissolution of the metal, should be preferred to that obtained from a cycle involving the enthalpy of formation and of solution of Nd_2O_3 (cr).

We obtain $\Delta_f H_m^{\circ} \{\text{Sm}(\text{OH})_3, \text{cr}\} = -(1406.6 \pm 2.2) \text{ kJ mol}^{-1}$, while Morss and Hall, in a conference abstract [19] give $-(1425.1 \pm 5.2) \text{ kJ mol}^{-1}$ and $\Delta_f H_m^{\circ} \{\text{Pr}(\text{OH})_3, \text{cr}\} = -(1409.7 \pm 4.9) \text{ kJ mol}^{-1}$, from dissolution in 2.00 mol dm^{-3} HCl. The preparation technique for the samples of Morss and Hall was similar to that used by Morss and Williams [3] for $\text{Am}(\text{OH})_3$.

We obtain $\Delta_f H_m^{\circ} \{\text{Am}(\text{OH})_3, \text{cr}\} = -(1343.6 \pm 1.8) \text{ kJ mol}^{-1}$ using for the dissolution of the metal in 6.00 mol dm^{-3} the value of $-(613.1 \pm 1.4) \text{ kJ mol}^{-1}$ very recently selected by Silva et al. [20]. Morss and Williams [3] recently reported $\Delta_f H_m^{\circ} \{\text{Am}(\text{OH})_3, \text{cr}\} = -(1371.2 \pm 7.9) \text{ kJ mol}^{-1}$, which becomes $-(1366.8 \pm 7.7) \text{ kJ mol}^{-1}$ when using the value above for the dissolution of Am (cr) in 6 mol dm^{-3} . Obviously the discrepancy lies in a difference of $(23 \pm 8) \text{ kJ mol}^{-1}$ in the dissolution of $\text{Am}(\text{OH})_3$.

The molar Gibbs energies corresponding to Eq. (5) and hence the solubility product (K_{sp}°) for the hydroxides



can now be estimated using the entropy values of the hydroxides either experimentally measured $S_m^{\circ} \{\text{La}(\text{OH})_3, \text{cr}\} = (117.8 \pm 0.2) \text{ J K}^{-1} \text{ mol}^{-1}$ [21], $S_m^{\circ} \{\text{Nd}(\text{OH})_3, \text{cr}\} = (129.9 \pm 0.2) \text{ J K}^{-1} \text{ mol}^{-1}$ [22] or estimated $S_m^{\circ} \{\text{Sm}(\text{OH})_3, \text{cr}\} = (126 \pm 5) \text{ J K}^{-1} \text{ mol}^{-1}$ and $S_m^{\circ} \{\text{Am}(\text{OH})_3, \text{cr}\} = (126 \pm 8) \text{ J K}^{-1} \text{ mol}^{-1}$ [2], the entropies of the ions $S_m^{\circ} \{\text{La}^{3+}, \text{aq}\} = -(209 \pm 5) \text{ J K}^{-1} \text{ mol}^{-1}$, $S_m^{\circ} \{\text{Nd}^{3+}, \text{aq}\} = -(206 \pm 5) \text{ J K}^{-1} \text{ mol}^{-1}$, $S_m^{\circ} \{\text{Sm}^{3+}, \text{aq}\} = -(207 \pm 5) \text{ J K}^{-1} \text{ mol}^{-1}$ (as compiled by Morss [23]), $S_m^{\circ} \{\text{Am}^{3+}, \text{aq}\} = -(201 \pm 15) \text{ J K}^{-1} \text{ mol}^{-1}$ (as selected by Silva et al. [20]), as well as auxiliary entropy value, $S_m^{\circ} \{\text{OH}^{-}, \text{aq}\} = -(10.90 \pm 0.20) \text{ J K}^{-1} \text{ mol}^{-1}$. Also needed

are the molar enthalpies of formation of the various aqueous ions at infinite dilution. To obtain $\Delta_f H_m^\circ$ (La^{3+} , aq) we make use of $\Delta_f H_m^\circ$ (LaCl_3 , cr) = $-(1072.2 \pm 1.4)$ kJ mol⁻¹ recently reported by Cordfunke and Booiij [24] in full agreement with the value selected earlier by Morss [25], $-(1073.2 \pm 1.5)$ kJ mol⁻¹, of $\Delta_f H_m^\circ$ (Cl^- , aq) = $-(167.080 \pm 0.100)$ kJ mol⁻¹ [9] and of the enthalpy of dissolution of LaCl_3 (cr) in an infinitely dilute medium, -137.7 kJ mol⁻¹ [26]. This leads to $\Delta_f H_m^\circ$ (La^{3+} , aq) = $-(708.7 \pm 1.4)$ kJ mol⁻¹, which combined with $\Delta_f H_m^\circ$ (OH^- , aq) = $-(230.015 \pm 0.040)$ kJ mol⁻¹ [9], $\Delta_f H_m^\circ$ { $\text{La}(\text{OH})_3$, cr} = $-(1416.7 \pm 1.3)$ kJ mol⁻¹ determined in this paper and the related entropy values given above leads to $\Delta_r G_m^\circ$ (react. 5, La) = (125.1 ± 2.0) kJ mol⁻¹ and $\log K_{sp}^\circ$ { $\text{La}(\text{OH})_3$, cr} = $-(21.9 \pm 0.4)$. The latter value is identical with that deduced by Cordfunke et al. [14] from calorimetric measurements and in agreement with the earlier selection of Baes and Mesmer [27], -21.7 , from solubility data.

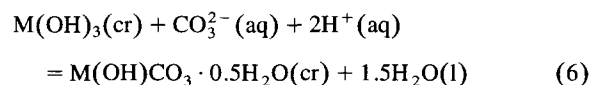
In the case of neodymium, the procedure is the same and is based on $\Delta_f H_m^\circ$ (NdCl_3 , cr) = $-(1040.1 \pm 0.8)$ kJ mol⁻¹ by Cordfunke et al. [28] in agreement with the earlier selection of Morss [25] of $-(1041.8 \pm 1.5)$ kJ mol⁻¹ and the enthalpy of solution of NdCl_3 (cr) in an infinitely dilute medium of -156.9 kJ mol⁻¹ [26]. This gives $\Delta_f H_m^\circ$ (Nd^{3+} , aq) = $-(695.8 \pm 0.8)$ kJ mol⁻¹, which in combination with our $\Delta_f H_m^\circ$ { $\text{Nd}(\text{OH})_3$, cr} = $-(1415.6 \pm 2.3)$ kJ mol⁻¹ and other data as above, yields $\Delta_r G_m^\circ$ (react. 5, Nd) = (139.7 ± 2.9) kJ mol⁻¹ and $\log K_{sp}^\circ$ { $\text{Nd}(\text{OH})_3$ } = $-(24.5 \pm 0.5)$. Based also on calorimetric data, the value $\log K_{sp}^\circ$ { $\text{Nd}(\text{OH})_3$ } = $-(22.3 \pm 0.7)$ is given by Morss et al. [16]. This value becomes $-(24.4 \pm 0.4)$ when, in the calculation, the enthalpy of solution of $\text{Nd}(\text{OH})_3$ (cr) obtained by Morss et al. [16] is used in conjunction with our thermodynamic cycle above involving $\text{Nd}(\text{cr})$ instead of Nd_2O_3 (cr). The various literature values for $\log K_{sp}^\circ$ { $\text{Nd}(\text{OH})_3$ } based on solubility measurements vary widely: -23.1 assessed by Baes and Mesmer [27] taking in account results prior to 1976, -26.0 [29] and very recently, -27.04 [30].

For $\Delta_f H_m^\circ$ (Sm^{3+} , aq), we use the value selected by Morss $-(691.1 \pm 1.7)$ kJ mol⁻¹, in agreement with a value reported by Khanaev et al. [31], $-(690.20 \pm 0.81)$ kJ mol⁻¹ from measurements in dilute perchloric acid. With our $\Delta_f H_m^\circ$ { $\text{Sm}(\text{OH})_3$, cr} = $-(1406.6 \pm 2.2)$ kJ mol⁻¹ and the other data given above we then obtain $\Delta_r G_m^\circ$ (Eq. (5), Sm) = $+(134.5 \pm 3.5)$ kJ mol⁻¹ and $\log K_{sp}^\circ$ { $\text{Sm}(\text{OH})_3$ } = $-(23.6 \pm 0.6)$. The value reported by Morss and co-workers [3,19] for $\log K_{sp}^\circ$ { $\text{Sm}(\text{OH})_3$ } is -26.9 in disagreement with our result. The essential part of the discrepancy likely lies in differences in the enthalpy of solution of the hydroxide samples. The earlier assessment by Baes and Mesmer [27] gave -25.2 . Morss and Hall [19] also determined $\log K_{sp}^\circ$ { $\text{Pr}(\text{OH})_3$, cr} = -22.1 .

For the calculation of the solubility product of $\text{Am}(\text{OH})_3$ we have taken $\Delta_f H_m^\circ$ (Am^{3+} , aq) = $-(616.7 \pm 1.5)$ kJ

mol⁻¹ recently selected by Silva et al. [20]. With our $\Delta_f H_m^\circ$ { $\text{Am}(\text{OH})_3$, cr} = $-(1343.6 \pm 1.8)$ kJ mol⁻¹ and the other enthalpy of formation and entropy values listed above we obtain $\Delta_r G_m^\circ$ (Eq. (5), Am) = (144.1 ± 5.6) kJ mol⁻¹ and $\log K_{sp}^\circ$ { $\text{Am}(\text{OH})_3$ } = $-(25.2 \pm 1.0)$. The latter value is in disagreement with that, $-(29.5 \pm 1.6)$ reported by Morss and Williams [3]. For that matter, the other literature values, all based on solubility data are scattered over several orders of magnitude. From a critical examination of all the literature data Silva et al. [20] selected $-(25.0 \pm 0.6)$ and $-(26.8 \pm 0.6)$ for the $\log K_{sp}^\circ$ of amorphous and crystalline $\text{Am}(\text{OH})_3$, respectively, realizing that the degree of crystallinity of the samples in the various experiments was difficult to ascertain. Our results are in reasonable agreement with this selection and indicate, in any case, the close similarity of the solubility of $\text{Am}(\text{OH})_3$ (cr) with that of lanthanides of similar ionic radii such as neodymium and samarium [32].

Finally, using the above enthalpy of formation and entropy values for the hydroxides, together with our recent results [2] on the hydroxycarbonates $\Delta_f H_m^\circ$ { $\text{M}(\text{OH})\text{CO}_3 \cdot 0.5\text{H}_2\text{O}$, cr} = $-(1744.9 \pm 2.1)$ kJ mol⁻¹, $-(1744.1 \pm 2.4)$ kJ mol⁻¹ and $-(1682.7 \pm 2.6)$ kJ mol⁻¹ for M = Nd, Sm and Am and using the estimates [2] S_m° { $\text{M}(\text{OH})\text{CO}_3 \cdot 0.5\text{H}_2\text{O}$, cr} = (158 ± 5) , (154 ± 7) and (154 ± 10) J K⁻¹ mol⁻¹ also for M = Nd, Sm and Am, respectively, we can evaluate the Gibbs energy change corresponding to



in standard conditions. To be internally consistent, we have recalculated the neodymium hydroxycarbonate value with $\Delta_f H_m^\circ$ (Nd^{3+} , 1.00 mol dm⁻³ HCl) = $-(689.6 \pm 2.0)$ kJ mol⁻¹. Also the value $\Delta_f H_m^\circ$ (Am^{3+} , 1.00 mol dm⁻³ HCl) = $-(616.1 \pm 0.8)$ kJ mol⁻¹ [20] instead of $-(616.3 \pm 0.8)$ kJ mol⁻¹ has been used. This calculation also makes use of $\Delta_f H_m^\circ$ (CO_3^{2-} , aq) = $-(675.23 \pm 0.25)$ kJ mol⁻¹, S_m° (CO_3^{2-} , aq) = $-(50.0 \pm 1.0)$ J K⁻¹ mol⁻¹, $\Delta_f H_m^\circ$ (H_2O , l) = $-(285.830 \pm 0.040)$ kJ mol⁻¹ and S_m° (H_2O , l) = $+(69.95 \pm 0.03)$ J K⁻¹ mol⁻¹ [9].

We obtain $\Delta_r G_m^\circ$ (Eq. (6)) = $-(137.4 \pm 3.4)$, $-(145.6 \pm 4.2)$ and $-(147.1 \pm 5.0)$ kJ mol⁻¹ for neodymium, samarium and americium, respectively. This shows once more, as is particularly well demonstrated in the case of the americium system [20] from solubility data, how the formation of the hydroxycarbonates is favoured to that of the hydroxides, even in the presence of small amounts of dissolved carbonate, and the relationship between hydroxides and hydroxycarbonates is similar, within uncertainty limits, for neodymium, samarium and americium.

Quantitative comparison of our results for reaction (6) with those obtained from solubility data would deserve further discussions but is not immediate in view of possible differences in the water content of the solid phases, especially the hydroxycarbonates.

Acknowledgements

The financial support of the Inter-University Institute for Nuclear Sciences (Brussels) to the Laboratory of Analytical Chemistry and Radiochemistry of University of Liège is acknowledged.

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