Journal of Alloys and Compounds, 194 (1993) 93–99
JALCOM 575

Solid–liquid equilibria of Nd^{3+} in carbonate solutions

G. Meinrath and H. Takeishi
Japan Atomic Energy Research Institute, Department of Chemistry, Tokai-mura, Ibaraki 319 (Japan)

(Received September 25, 1992)

Abstract

A redetermination of the solubility products of $NdOHCO_3(s)$ and $Nd_2(CO_3)_3 \cdot (4.5–6)H_2O(s)$ in 0.1 M $NaClO_4$ is presented, extending existing data to a wider variety of CO_2 partial pressures and a wider concentration range. $NdOHCO_3(s)$ is found in equilibrium with 0.03% and 0.3% CO_2 partial pressures; $Nd_2(CO_3)_3 \cdot (4.5–6)H_2O(s)$ is found in equilibrium with 1.0%, 8.0% and 100% CO_2 partial pressures. The solubility products $\log K_{sp}(NdOHCO_3) = -20.12 \pm 0.09$ and $\log K_{sp}(Nd_2(CO_3)_3 \cdot (4.5–6)H_2O) = -31.54 \pm 0.11$ have been determined. Evidence is presented that $Nd_2(CO_3)_3 \cdot (4.5–6)H_2O(s)$ is probably only metastable in equilibrium with 1.0% CO_2 partial pressure. Gibbs free energies of formation have been calculated as $\Delta G_f^\circ(Nd_2(CO_3)_3(s)) = -3115.9 \pm 4.0$ kJ mol^{-1} and $\Delta G_f^\circ(NdOHCO_3(s)) = -1476.0 \pm 2.9$ kJ mol^{-1}.

1. Introduction

Interest in the physicochemical properties of trivalent lanthanoid carbonates in recent years has been caused by the complex chemistry of the solids $Nd_2(CO_3)_3 \cdot xH_2O$, $NdOHCO_3$, $NaNd(CO_3)_2 \cdot xH_2O$ and $KNd(CO_3)_2 \cdot xH_2O$ with x in the range 0–8 [1, 2]. Neodymium carbonates have been investigated with respect to their use as starting materials for the production of ceramics [3]. In geology, the distribution patterns of rare earth elements in a mineral provide information on its geohistory [4] and this distribution may be affected by the formation of solid carbonates or carbonato complexes [5]. Despite this, thermodynamic data on the rare earth–H_2O–CO_2 system are scarce.

Recently, the lanthanoids Nd and Eu have found interest as naturally occurring analogues of the actinoid americium due to their homology (Eu) [6] and similarity of ionic radii (Nd) [7]. Americium is expected to form a major contribution to the risk potential of a disposal site for highly radioactive nuclear waste [8]. Such nuclear waste repositories are under consideration in different geological host formations in several countries all over the world [9].

The analogy between Am(III), Nd(III) and Eu(III) has recently been studied [10, 11] in a wide range of partial pressures between 0.03% and 100% CO_2. Since the solid–liquid equilibria of rare earth(III) and Am(III) carbonates depend on the CO_2 partial pressure [11, 12] and natural aquatic systems are known to have CO_2 partial pressures in the range 0.03%–10% [13, 14], such investigations are of fundamental importance.

This study of the Nd(III)–CO_2–H_2O system was motivated by several reasons: (a) to reinvestigate and address an apparent inconsistency in the current data available on the solid–liquid equilibria of Nd(III) carbonates; (b) to extend the validity range of a previous study [10, 11] to a wider variety of CO_2 partial pressures and lower Nd^{3+} concentrations; and (c) to test the reproducibility of previous results using different equipment and procedures.

2. Experimental details

Nd(III) solids were precipitated from 2×10^{-2} M Nd^{3+} solutions in closed 250 ml glass vessels by the addition of 0.05 M Na_2CO_3. A constant ionic strength of 0.1 M was maintained using $NaClO_4$ as supporting electrolyte. The data were interpreted on the concentration scale. The CO_2 partial pressures of 0.03% (air), 0.30% with N_2, 1.0% with N_2, 8.0% with N_2 and 100% were maintained by a continuous stream of the moistened gas through the respective solution. The aging of the precipitates was monitored continuously, measuring the spontaneous change in pH and Nd^{3+} concentration as a function of time. After the attainment of a steady state, the pH was changed by the addition of either 0.05 N Na_2CO_3 or 0.1 N $HClO_4$. The temperature was 24 ± 2 °C.

The pH was measured by two glass combination electrodes (model 81-15 (ROSS type) and model 91-03, Orion Res. Co.). Before each pH measurement, the electrodes were calibrated against five buffer so-

0925-8388/93/$6.00

lutions of known pH. A reproducibility of ±0.03 pH units and an accuracy of ±0.02 pH units were found.

Hydroxide concentrations were calculated using

$$H_2O \overset{K_W}{\longleftrightarrow} H^+ + OH^- \qquad (1)$$

with $\log K_{W'} = -13.78 \pm 0.01$ [15].

Carbonate concentrations were calculated using

$$CO_2(g) \overset{K_H}{\longleftrightarrow} CO_2(aq) \overset{K^*}{\longleftrightarrow} H_2CO_3(aq) \overset{K'}{\longleftrightarrow}$$

$$HCO_3^- + H^+ \overset{K_2}{\longleftrightarrow} CO_3^{2-} + 2H^+ \qquad (2)$$

with $\Sigma \log K = \log(K_H K^* K' K_2) = -17.62 \pm 0.07$ [11]. This value was redetermined with good agreement as $\Sigma \log K = -17.65 \pm 0.09$ [10].

Nd^{3+} concentrations of 10^{-4} mol l^{-1} or greater were measured by absorption spectroscopy in the ranges 830–770 nm, 770–720 nm, 600–550 nm and 540–490 nm. The molar absorptivities were determined for the given experimental conditions using Nd^{3+} standard solutions. Concentrations below 10^{-4} mol Nd^{3+} l^{-1} were measured by ICP-OES.

The solid phases were characterized by solid phase photoacoustic spectroscopy (PAS), solid phase Fourier transform IR photoacoustic spectroscopy (FTIR-PAS), simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) and X-ray powder diffraction.

TABLE 1. Comparison of experimentally determined and calculated X-ray reflections of $NdOHCO_3(s)$ and $Nd_2(CO_3)_3(s)$

$NdOHCO_3(s)$[a]			$Nd_2(CO_3)_3(s)$[b]		
h k l	*d* (pm)	*d*(calc) (pm)	*h k l*	*d* (pm)	*d*(calc) (pm)
0 1 1	552.4	552.5	2 0 0	852.4	848.0
0 2 0	430.2	430.1	0 2 0	474.8	474.1
1 1 0	424.9	424.9	0 0 2	446.6	446.5
0 2 1	369.9	369.4	4 0 0	424.7	424.0
1 1 1	366.3	366.0	0 2 2	414.0	413.7
0 1 2	333.3	332.4	2 0 2	394.9	395.0
1 0 2	292.8	290.1	0 1 4	387.1	387.0
0 3 1	263.8	266.4	1 0 4	382.8	382.9
1 3 0	248.8	247.3	1 1 4	355.9	355.1
1 2 2	241.0	240.5	2 2 0	324.6	324.9
2 0 1	232.6	231.4	0 3 0	315.8	315.9
0 4 0	214.5	214.9	2 0 4	307.2	307.4
0 4 1	205.7	206.1	2 2 2	303.2	303.4
1 3 2	203.5	203.9	1 1 5	300.6	300.7
2 1 2	198.2	197.8	1 3 0	297.8	297.8
1 2 3	193.3	192.7	2 1 4	292.4	292.4
1 4 1	188.4	189.3	2 2 3	282.4	281.7
0 3 3	183.6	184.1	0 1 6	270.8	270.8
			3 1 2	269.2	269.2
			1 2 5	263.4	263.5
			2 2 4	257.5	257.9
			3 2 2	242.6	242.7
			2 0 6	238.3	238.8
			1 2 6	233.8	234.2

[a] $a = 488.7 \pm 0.4$ pm; $b = 721.2 \pm 0.4$ pm; $c = 860.3 \pm 0.3$ pm; $\alpha = \beta = \gamma = 90°$.

[b] $a = 1696.1 \pm 0.4$ pm; $b = 947.8 \pm 0.3$ pm; $c = 893.1 \pm 0.4$ pm; $\alpha = \beta = \gamma = 90°$.

3. Results and discussion

3.1. Investigation of the physicochemical state of the solids

The solids were analysed as normal carbonate $Nd_2(CO_3)_3 \cdot (4.5\text{–}6)H_2O$ in equilibrium with 1.0%, 8.0% and 100% CO_2 partial pressures and as hydroxocarbonate $NdOHCO_3$ in equilibrium with 0.3% and 0.03% CO_2 partial pressures. The crystal water content of the normal carbonate was found to vary within the limits given in the above formula without variation in the lattice parameters. In the following we omit the crystal water content and refer to this phase as $Nd_2(CO_3)_3$.

The analysis of the solid phases gave results in close agreement with available literature data [10, 11]. Microcrystalline $Nd_2(CO_3)_3$ was found to be orthorhombic with $a = 1696.1 \pm 0.4$ pm, $b = 947.8 \pm 0.3$ pm and $c = 893.1 \pm 0.4$ pm. Microcrystalline $NdOHCO_3$ was found to be orthorhombic with $a = 488.7 \pm 0.4$ pm, $b = 721.2 \pm 0.4$ pm and $c = 860.3 \pm 0.3$ pm. As can be seen from Table 1, all reflections can be satisfactorily indexed on the basis of the given crystal parameters.

3.2. Aging behaviour

The solids were precipitated under each CO_2 partial pressure by the addition of 0.05 N Na_2CO_3 equilibrated with the CO_2 partial pressure of air. In agreement with previously reported results [10], X-ray patterns of the freshly precipitated phases initially showed characteristics of the normal carbonate even under 0.03% and 0.3% CO_2 partial pressures; hydroxocarbonate was found later as an equilibrium solid phase. The solid phases under 0.03% and 0.30% CO_2 partial pressures transformed to microcrystalline hydroxocarbonate within 7 days and 30 days respectively. The aging of the solid under 0.03% CO_2 partial pressure is shown in Fig. 1 in terms of the apparent solubility product $\log[Nd^{3+}] + \log[CO_3^{2-}] + \log[OH^-]$ as a function of time. After about 40 days, a steady state was observed. The equilibrium of the solid under 0.3% CO_2 partial pressure was observed in a much shorter time of 5–7 days, although the same solid was involved. The apparent slow aging of $NdOHCO_3$ in equilibrium with 0.03% CO_2 partial pressure seems to be partly due to the slow equilibration of the aqueous solution with the low partial pressure of 0.03% CO_2.

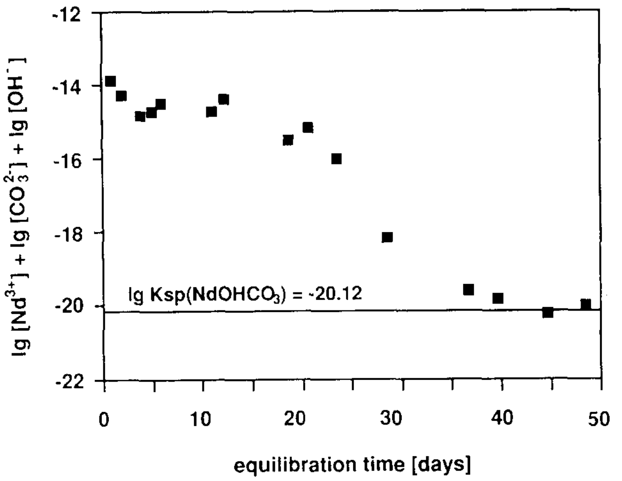

Fig. 1. Spontaneous change of the apparent solubility product of $NdOHCO_3(s)$ as a function of time after precipitation. The mean value in equilibrium with $NdOHCO_3(s)$ as determined in this study is indicated by the straight line.

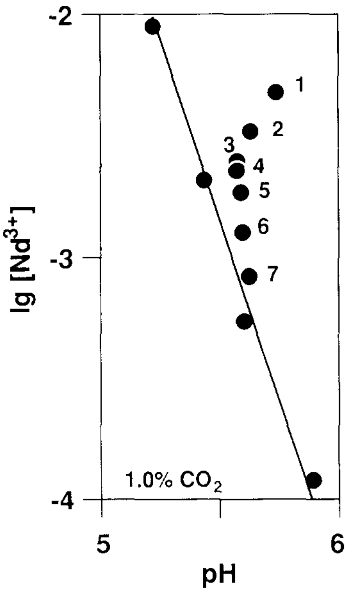

Fig. 2. Initial deviation of the Nd^{3+} concentrations determined in equilibrium with 1.0% CO_2. Each point seemed to represent a steady state, since neither pH nor $\log[Nd^{3+}]$ changed spontaneously within 7–31 days. The straight line represents the equilibrium correlation of $Nd_2(CO_3)_3(s)$ with slope -3.

Under 1.0% CO_2 partial pressure, a different aging phenomenon was observed. The measured Nd^{3+} concentrations initially deviated from the straight line of slope -3, that was identified later as the equilibrium correlation of the normal carbonate under these conditions. This is shown in Fig. 2. However, each point seemed to correspond to a steady state, since neither pH nor $[Nd^{3+}]$ changed spontaneously within 7–25 days. Each of the points 1–7 was attained in this sequence from supersaturation by the addition of 0.05 M Na_2CO_3 from one point to the next and reached a steady state within 3–4 days.

3.3. Solubility study

As outlined previously [10, 11], the following relationships (3)–(6) describe the solid–liquid equilibria as a function of pH, $\log[CO_3^{2-}]$ and CO_2 partial pressure ($\log p_{CO_2}$) (in atmospheres) for $Nd_2(CO_3)_3(s)$

$$\log[Nd^{3+}] = 0.5(\log K_{sp}(Nd_2(CO_3)_3) - 3\Sigma \log K) - 1.5 \log p_{CO_2} - 3\ \mathrm{pH} \quad (3)$$

$$\log[Nd^{3+}] = 0.5 \log K_{sp}(Nd_2(CO_3)_3) - 1.5 \log[CO_3^{2-}] \quad (4)$$

and $NdOHCO_3(s)$

$$\log[Nd^{3+}] = \log K_{sp}(NdOHCO_3) - \Sigma \log K - \log K_W - \log p_{CO_2} - 3\ \mathrm{pH} \quad (5)$$

$$\log[Nd^{3+}] = \log K_{sp}(NdOHCO_3) + 0.5\Sigma \log K - \log K_W + 0.5 \log p_{CO_2} - 1.5 \log[CO_3^{2-}] \quad (6)$$

Figure 3 gives the experimentally determined solubilities of $Nd_2(CO_3)_3(s)$ and $NdOHCO_3(s)$ as a function of $\log[CO_3^{2-}]$. The data are interpreted by linear correlations of slope -1.5. The solubilities measured under 100%, 8.0% and 1.0% CO_2 partial pressures are scattered around the same correlation, whereas the data determined under 0.03% and 0.3% CO_2 partial pressures correlate with different lines of slope -1.5 for each partial pressure. This is in agreement with eqns. (4) and (6), since the solubilities of $Nd_2(CO_3)_3(s)$ are independent of the CO_2 partial pressure, whereas

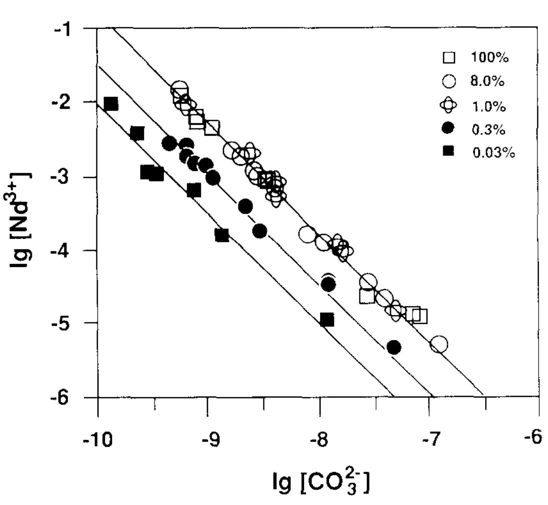

Fig. 3. Nd^{3+} concentrations in equilibrium with 100%, 8.0%, 1.0%, 0.3% and 0.03% CO_2 partial pressure as a function of $\log[CO_3^{2-}]$.

the solubilities in equilibrium with $NdOHCO_3(s)$ further depend on p_{CO_2}. As a function of pH, eqns. (3) and (5) suggest that $\log[Nd^{3+}]$ in equilibrium with both phases should further depend on p_{CO_2} and therefore correlate with separate lines of slope −3. Figure 4 shows the experimental data as a function of pH. The solubilities of $Nd_2(CO_3)_3(s)$ under 1% and $NdOHCO_3(s)$ under 0.3% CO_2 partial pressure coincide. This coincidence is accidental, since the difference in the solubility products is just balanced by the other parameters in eqns. (3) and (5).

The solubility products determined from the data given in Figs. 3 and 4 are as follows: 100% CO_2, $\log K_{sp}(Nd_2(CO_3)_3) = -31.64 \pm 0.23$; 8.0% CO_2, $\log K_{sp}(Nd_2(CO_3)_3) = -31.53 \pm 0.17$; 1% CO_2, $\log K_{sp}(Nd_2(CO_3)_3) = -31.44 \pm 0.20$; 0.3% CO_2, $\log K_{sp}(NdOHCO_3) = -20.09 \pm 0.12$; 0.03% CO_2, $\log K_{sp}(NdOHCO_3) = -20.15 \pm 0.19$. These data are compared in Table 2 with the data available in the literature.

Table 2 shows that there is good agreement between the literature data and the results obtained in this study with the exception of ref. 17. Since $\log K_{sp}(Nd_2(CO_3)_3) = 2 \log[Nd^{3+}] + 3 \log \Sigma \log K + 3 \log p_{CO_2} + 6$ pH depends on the pH with a factor of 6, a high reproducibility of the pH measurement can be assumed.

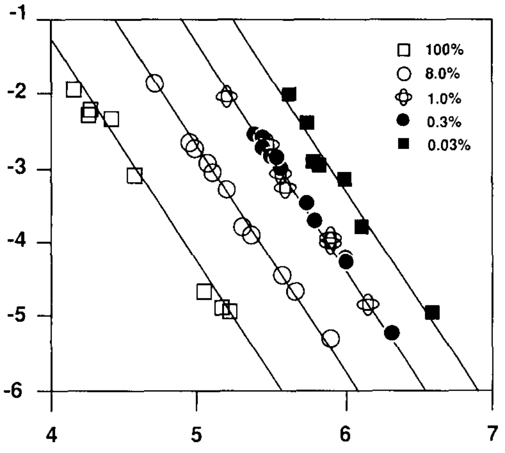

Fig. 4. Nd^{3+} concentrations in equilibrium with 100%, 8.0%, 1.0%, 0.3% and 0.03% CO_2 partial pressure as a function of pH.

Jordanov and Havezov [16] determined the solubilities of $Nd_2(CO_3)_3(s)$ after an equilibration time of 24 h in a carbonate solution flushed by N_2. Firsching and Mohammadzadel [17] determined solubilities in the pH range 5.00–6.18 by dissolution of normal carbonate in pure water, after an equilibration time of 3 months. The low solubility product has been explained by a change in the composition of the solid phase during the long equilibration time [10]. These workers did not control the CO_2 partial pressure or report the structural analysis of the solid phases.

Combining the results of the previous [11] and present work, the following data are obtained: $\log K_{sp}(Nd_2(CO_3)_3) = -31.44 \pm 0.09$ and $\log K_{sp}(NdOHCO_3) = -20.09 \pm 0.09$.

In Fig. 5, $\log[Nd^{3+}]$ in equilibrium with $Nd(OH)_3(s)$, $NdOHCO_3(s)$ and $Nd_2(CO_3)_3(s)$ is calculated as a function of p_{CO_2} for an arbitrarily chosen pH 7 in the partial pressure range $-8 \leqslant \log p_{CO_2} \leqslant 0$. To describe the solid phase chemistry of Nd(III) in carbonate-containing solutions of low ionic strength as a function of the CO_2 partial pressure, the formation of $Nd(OH)_3(s)$ at low CO_2 partial pressures has to be taken into account. A recent review of the available data on $\log K_{sp}(Nd(OH)_3)$ is given in ref. 18 and the recommended value of -23.5 ± 0.5 is used in Fig. 5. Current data suggest that $Nd(OH)_3(s)$ is very sensitive to the presence of traces of CO_2.

In equilibrium with $Nd(OH)_3(s)$, $\log[Nd^{3+}]$ is independent of the CO_2 partial pressure, whereas $\log[Nd^{3+}]$ decreases in equilibrium with $NdOHCO_3(s)$ (*cf.* eqn. (5)) as a function of p_{CO_2}. Hence, at $\log p_{CO_2} = -6.5 \pm 0.6$, $NdOHCO_3(s)$ becomes the solubility-limiting phase.

TABLE 2. Comparison of solubility products of $NdOHCO_3(s)$ and $Nd_2(CO_3)_3(s)$

Solid Ref.	$\log K_{sp}$	Conditions
$Nd_2(CO_3)_3(s)$		
16	-31.68^a (−33.0)	25±0.1 °C, 0.1 M $NaClO_4$
17	-32.48 ± 0.48^a (−34.10)	25±1 °C, self-medium
10, 11	-31.35 ± 0.13	22±1 °C, 0.1 M $NaClO_4$
this work	-31.54 ± 0.11	24±2 °C, 0.1 M $NaClO_4$
$NdOHCO_3(s)$		
10	-19.94 ± 0.27	22±1 °C, 0.1 M $NaClO_4$
this work	-20.12 ± 0.09	24±2 °C, 0.1 M $NaClO_4$

[a] Data is recalculated from the original data for $\Sigma \log K = -17.62$. Original data is shown in brackets.

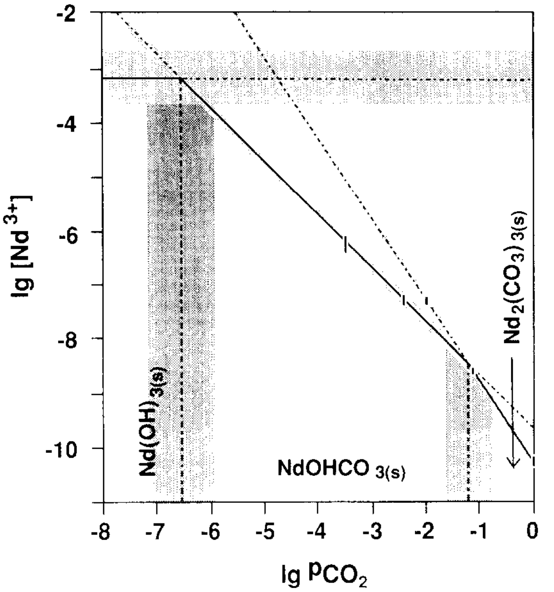

Fig. 5. Mutual stabilities of $Nd(OH)_3$(s), $NdOHCO_3$(s) and $Nd_2(CO_3)_3$(s) as a function of log p_{CO_2} at an arbitrarily chosen pH 7. The shaded areas account for uncertainties of the solubility products and the resulting uncertainties in the stability limits. The filled squares (■) represent the experimentally determined data at 100%, 8.0%, 1.0%, 0.3% and 0.03% CO_2 partial pressures as calculated from the solubility products at pH 7.

According to eqn. (5), log[Nd^{3+}] depends on log p_{CO_2} with a factor of -1 in equilibrium with $NdOHCO_3$(s); eqn. (3) indicates that log[Nd^{3+}] depends on log p_{CO_2} with a factor of -1.5 in equilibrium with $Nd_2(CO_3)_3$(s). Consequently, on raising the partial pressure above log $p_{CO_2} = -1.20 \pm 0.27$, $Nd_2(CO_3)_3$(s) becomes the solubility-limiting solid phase (shaded areas in Fig. 5 account for uncertainty).

The mutual stability limits of the solid phases as a function of the CO_2 partial pressure are given by eqn. (7) for $Nd(OH)_3(s) \leftrightarrow NdOHCO_3(s)$

$$\log p_{CO_2} = \log K_{sp}(NdOHCO_3) - \log K_{sp}(Nd(OH)_3) - \Sigma \log K + 2 \log K_W \quad (7)$$

and by eqn. (8) for $NdOHCO_3(s) \leftrightarrow Nd_2(CO_3)_3(s)$

$$\log p_{CO_2} = \log K_{sp}(Nd_2(CO_3)_3) - 2 \log K_{sp}(NdOHCO_3) - \Sigma \log K + 2 \log K_W \quad (8)$$

The partial pressures, where a transformation occurs, are independent of pH.

However, an obvious discrepancy between experiment and calculation is observed. At a partial pressure of 1% CO_2, the normal carbonate $Nd_2(CO_3)_3$(s) was found to be the solubility-limiting solid phase, whereas the calculation shows that the hydroxocarbonate $NdOHCO_3$(s) should be solubility limiting. The solid–liquid equilibria of normal carbonate and hydroxocarbonate have been investigated repeatedly [10–12, 19] with good agreement. Each time, the normal carbonate was found to be the solubility-limiting solid phase in equilibrium with 1.0% CO_2 partial pressure. The same observation has been made for Eu(III) carbonates [10].

The initial formation of poorly crystalline $Nd_2(CO_3)_3$(s) on addition of Na_2CO_3 solution to Nd^{3+}(aq) and Eu^{3+}(aq) has been described previously in solutions even in equilibrium with 0.03% CO_2 partial pressure [10]. The same observations have been made in the present study in equilibrium with 0.03% and 0.30% CO_2 partial pressures. Nitsche [20] has reported the formation of a metastable solid state of ^{241}Am-spiked Nd(III) in equilibrium with 1.57% CO_2 partial pressure at pH 7 and 25 °C. The solid aged to lower solubility after an apparent steady state of 30 days. No structural analysis of the solids involved was given and the actual process, which was observed by following the concentration change with time, is not clear. However, the present results offer a reasonable interpretation for the phenomenon observed in ref. 20.

The precipitation of metal ions from an aqueous solution, *e.g.* by the addition of Na_2CO_3 or NaOH solution, is a non-equilibrium process which usually leads to activated states [21, 22]. According to Ostwald's empirical "law of successive transformations" [23], the final thermodynamically stable state will be obtained by passing through all intermediate states between the initial and the final state. Solid phases in a metastable state are well known, with aragonite as a prominent example [21, 24].

It seems that the formation of $Nd_2(CO_3)_3$(s) in equilibrium with $\log p_{CO_2} \leq 1.20 \pm 0.27$ is kinetically favoured over the formation of $NdOHCO_3$(s) in the investigated precipitation processes. This metastable state ages readily to the thermodynamically stable state of $NdOHCO_3$(s) in equilibrium with 0.3% CO_2 and only reluctantly in equilibrium with 0.03% CO_2 partial pressure. The difference between the solubilities of $Nd_2(CO_3)_3$(s) and $NdOHCO_3$(s) under 1.0% CO_2 partial pressure seems to be too small to provide the driving force towards transformation in equilibrium and the transformation has not been observed within the time scale of this investigation. In equilibrium with 1.57% CO_2 partial pressure [20], radiation damage induced by the α-activity of the ^{241}Am spike may result in an additional driving force towards transformation. For $^{241}AmOHCO_3$(s) and $^{241}Am_2(CO_3)_3$(s), the twofold greater solubility compared with their Nd analogues may be explained by the effect of the α-activity [10, 11]. Further work is necessary to clarify this point.

3.4. *Thermodynamic calculations*

From the experimentally obtained equilibrium constants, the Gibbs free energy ΔG°_R of the dissolution reaction

$$Nd_2(CO_3)_3(s) \longleftrightarrow 2Nd^{3+}(aq)+3CO_3^{2-}(aq) \tag{9}$$

and

$$NdOHCO_3(s) \longleftrightarrow Nd^{3+}(aq)+OH^-(aq)+CO_3^{2-}(aq) \tag{10}$$

can be calculated using $\Delta G° = -RT \ln K_{sp}$ where $RT = 2.479$ kJ mol^{-1} and the solubility products $\log K_{sp}(Nd_2(CO_3)_3) = -31.44 \pm 0.09$ and $\log K_{sp}(NdOHCO_3) = -20.09 \pm 0.09$. From these data, $\Delta G_R°(Nd_2(CO_3)_3) = +179.23 \pm 0.23$ kJ mol^{-1} for eqn. (9) and $\Delta G_R°(NdOHCO_3) = +114.67 \pm 0.21$ kJ mol^{-1} for eqn. (10) are obtained.

$\Delta G_f°(CO_3^{2-}(aq))$ is obtained from $\Delta G_f°(CO_2(g)) = -394.373 \pm 0.140$ kJ mol^{-1} [25] and eqn. (2) as $\Delta G_f°(CO_3^{2-}(aq)) = -530.94 \pm 0.58$ kJ mol^{-1}. Similarly, $\Delta G_f°(OH^-(aq))$ is calculated from $\Delta G_f°(H_2O(l)) = -237.140 \pm 0.040$ kJ mol^{-1} [25] and eqn. (1) as $\Delta G_f°(OH^-(aq)) = -158.49 \pm 0.10$ kJ mol^{-1}.

Using $\Delta G_f°(Nd^{3+}(aq)) = -672.0 \pm 2.0$ kJ mol^{-1} [26] (the standard deviation was estimated on the basis of data given in ref. 26), Gibbs free energies of formation of $Nd_2(CO_3)_3(s)$ and $NdOHCO_3(s)$ have been calculated as follows: $\Delta G_f°(Nd_2(CO_3)_3) = -3115.9 \pm 4.0$ kJ mol^{-1} and $\Delta G_f°(NdOHCO_3) = -1476.0 \pm 2.9$ kJ mol^{-1}. Since a certain variation of the crystal water content of $Nd_2(CO_3)_3(s)$ has been observed without an influence on the crystal parameters of the solid, the contribution of the crystal water is not considered in the calculation of $\Delta G_f°(Nd_2(CO_3)_3)$. The data refer to the solid with the crystal parameters given in Table 1.

4. Conclusions

The concentrations of Nd(III) in an aqueous solution at a given pH depend strongly on the CO_2 partial pressure (*cf.* Fig. 4). The phases $Nd(OH)_3(s)$, $NdOHCO_3(s)$ and $Nd_2(CO_3)_3(s)$ may form in solutions of low ionic strength, depending on the CO_2 partial pressure. $NdOHCO_3(s)$ has been experimentally found as the solubility-limiting solid phase at CO_2 partial pressures of 0.03% and 0.3%, whereas $Nd_2(CO_3)_3(s)$ is formed at 1.0%, 8.0% and 100% CO_2 partial pressures. The solubility products of these phases have been determined as $\log K_{sp}(Nd_2(CO_3)_3) = -31.54 \pm 0.11$ and $\log K_{sp}(NdOHCO_3) = -20.12 \pm 0.09$. Calculating the stability areas of the solid phases $Nd(OH)_3(s)$, $NdOHCO_3(s)$ and $Nd_2(CO_3)_3(s)$ as a function of $\log p_{CO_2}$, the following stability limits have been obtained: $Nd(OH)_3(s)$ at $\log p_{CO_2} \leqslant -6.5 \pm 0.6$, $NdOHCO_3(s)$ at $-6.5 \pm 0.6 \leqslant \log p_{CO_2} \leqslant -1.20 \pm 0.27$ and $Nd_2(CO_3)_3(s)$ at $\log p_{CO_2} \geqslant -1.20 \pm 0.27$. The calculations are in disagreement with the experimental facts in so far as $Nd_2(CO_3)_3(s)$ is found as the solubility-limiting solid phase in equilibrium with $\log p_{CO_2} = -2$. This inconsistency is interpreted by the assumption of a metastable state of $Nd_2(CO_3)_3(s)$ in equilibrium with 1.0% CO_2 partial pressure.

On the basis of the experimentally determined solubility products, free energies of formation $\Delta G_f°(Nd_2(CO_3)_3(s)) = -3115.9 \pm 4.0$ kJ mol^{-1} and $\Delta G_f°(NdOHCO_3(s)) = -1476.0 \pm 2.9$ kJ mol^{-1} have been calculated.

The present data quantitatively support the assumption [12] that $NdOHCO_3(s)$ and $Nd_2(CO_3)_3(s)$ play an important role with respect to the geochemistry of neodymium. Natural aquatic systems are known to have CO_2 partial pressures in the range 0.03%–10% [13, 14]. Therefore both solid phases $NdOHCO_3(s)$ and $Nd_2(CO_3)_3(s)$ may form in natural aquatic systems.

References

1 *JCPDS Power Diffraction File,* International Centre for Diffraction Data, Swarthmore, USA, 1991.
2 G. Meinrath and T. Kimura, to be published.
3 M. A. Aknic, D. J. Sordelet and M. Munson, *Adv. Ceram. Mater., 3* (1988) 211.
4 R. Bowen, *Isotopes in the Earth Science,* Elsevier Applied Science, Barking, 1988, p. 270.
5 H. J. W. DeBaar, M. P. Bacon and P. G. Brewer, *Nature, 301* (1983) 324.
6 R. R. Rao and A. Chatt, *Radiochim. Acta, 54* (1991) 181.
7 G. Meinrath and J. I. Kim, *Radiochim. Acta, 52/53* (1991) 29.
8 J. Levi, C. Izabel and Y. Kaluzny, in *Safety Assessment of Radioactive Nuclear Waste Repositories,* OECD, Paris, 1990, p. 81.
9 Geological Disposal of Radioactive Waste, *REPORT EUR-9130 EN,* OECD/NEA, Paris, 1984.
10 W. Runde, G. Meinrath and J. I. Kim, *Radiochim. Acta,* in press.
11 G. Meinrath and J. I. Kim, *Eur. J. Inorg. Solid State Chem., Suppl., 29* (1991) 383.
12 P. Caro and M. Lemaitre-Blaise, *C.R. Acad. Sci. Paris, C269* (1969) 687.
13 D. E. White, J. D. Hem and G. A. Waring, *Geol. Survey Proc.,* US Geological Survey, Washington, 1963.
14 J. I. Kim, Chemical behaviour of actinides in natural aquatic systems, in Freeman and Keller (eds.), *Handbook of the Physics and Chemistry of the Actinides,* Vol. 7, Elsevier Science, Amsterdam, 1986.
15 R. Fischer and J. Byé, *Bull. Chim. Soc. Fr.,* (1964) 220.
16 N. Jordanov and I. Havezov, *Z. Anorg. Allg. Chem., 347* (1966) 101.
17 F. H. Firsching and J. Mohammadzadel, *J. Chem. Eng. Data, 31* (1986) 40.
18 L. R. Morss, Ch. M. Haar and S. Mroczkowsky, *J. Chem. Thermodyn., 21* (1989) 1079.
19 P. Caro, M. Lemaitre-Blaise and F. Trombe, *C.R. Acad. Sci. Paris, C267* (1968) 1594.

20 H. Nitsche, *Radiochim. Acta, 51/52* (1991) 3; the partial pressure given is a personal communication to G.M., 1992.
21 W. Stumm and J. J. Morgan, *Aquatic Chemistry,* Wiley, Chichester, 1981, p. 286.
22 S. Lewin, *The Solubility Product Principle,* Interscience, New York, 1960.
23 W. Ostwald, *Z. Phys. Chem., 22* (1897) 306.
24 L. N. Plummer and E. Busenberg, *Geochim. Cosmochim. Acta, 46* (1982) 1011.
25 Garvin, Parker and White, Jr. (eds.), *CODATA Thermodynamic Tables,* Springer Verlag, Heidelberg, 1987.
26 L. R. Morss, *Chem. Rev., 76* (1976) 829.