Solid-Solute Phase Equilibria in Aqueous Solutions IX. Thermodynamic Analysis of Solubility Measurements: $La(OH)_m(CO_3)_q \cdot rH_2O$

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

The aqueous solubilities of $La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\,H_2O$, basic lanthanum carbonate of ancylite type, have been investigated as a function of ionic strength at 25.0 °C. The stoichiometric solubility constants defined by $\log^* K^I_{ps0} = \log[La^{3+}] + 1.1 \log p_{CO_2} - 3 \log[H^+]$ have the values 11.10, 11.32, 11.42, 11.63, and 11.70 for $I = 0.1$, 0.25, 1.0, 2.0, and 4.0 mol kg^{-1} (Na)ClO_4 respectively. The extrapolation to infinite dilution using the Pitzer equations resulted in a "thermodynamic" solubility constant, $\log^* K^0_{pz0} = 10.48 \pm 0.08$. This in turn led to the Gibbs energy of ancylite formation: $\Delta_f G^\ominus_{298}\{La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\,H_2O\} = -1.531.5$ kJ mol^{-1}.

Key words: Solubility; Carbonates; Lanthanum; Thermodynamics; Pitzer model.

Introduction

Recently the Gibbs energy of formation of lanthanite, $La_2(CO_3)_3 \cdot 8H_2O$, has been determined by combining solubility and standard potential data [1]. Solubility constants for unspecified lanthanum carbonates given in the literature are approximately 10 [2] and 500 times [3] higher than the mean value found in our previous study. Such discrepancies indicate that different solid substances have been investigated. In fact an ancylite type basic lanthanum carbonate, $La(OH)_m(CO_3)_q \cdot rH_2O$, can be prepated by precipitation from solution similar to lanthanite. For this compound the molar ratios of $La:OH:CO_3$ vary from 1:0.6:1.2 to 1:1:1 according to different authors [4, 5].

In the present work the solubility of ancylite in aqueous solutions was studied under systematically varied conditions of acidity and partial pressure of carbon dioxide. The experimental data obtained were thermodynamically analysed in order to establish the stoichiometric formula and the standard Gibbs energy of formation of this basic lanthanum carbonate. Moreover, by varying the ionic strength the applicability of the Pitzer model was tested.

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Experimental

1. Materials

Basic lanthanum carbonate, $La(OH)_m(CO_3)_q \cdot rH_2O$, of the ancylite type was prepared by homogeneous precipitation according to Akinc and Sordelet [4]. The X-ray data of the compound thus obtained agreed reasonably with those listed in [4]. By chemical and thermogravimetric analyses the ratios of $La:OH:CO_3:H_2O$ in ancylite were established to be $1:(0.8 \pm 0.1):(1.10 \pm 0.05):(0.1 \pm 0.02)$. Pure carbon dioxide ($\geq 99.99\%$) and carbon dioxide/nitrogen mixtures (ca. 50%, 20%, 10%, 5%, 2%, 1% and 0.07% CO_2) were taken from cylinders. Sodium perchlorate (GR Merck) was recrystallized at 60 °C. All other reagents were of reagent grade quality and used without further purification.

2. Procedure

The solubility measurements were carried out at 25 °C essentially as described in [1]. However, p_{CO_2} was varied over at least two orders of magnitude, so as to obtain reliable additional information on the ratio of $La:CO_3$. Thus, solutions S_0 ($[H^+] = H$ mol kg^{-1}, $[Na^+] = (I - H)$ mol kg^{-1}, $[ClO_4^{-1}] = I$ mol kg^{-1}) were equilibrated with solid $La(OH)_m(CO_3)_q \cdot rH_2O$

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at partial pressures of CO_2 ranging from 0.9 to 0.009 atm [1]. In the resulting solutions S the total molality of La(III) was determined by EDTA titration.

The hydrogen ion molality was followed using the galvanic cell described in [1]. At constant ionic strength the measured e.m.f. may be written as

$$E = E^\circ + \frac{RT \ln 10}{F} \log [H^+] + E_j , \qquad (1)$$

where the liquid junction potential is essentially proportional to $[H^+]$:

$$E_j = -k[H^+] . \qquad (2)$$

For constant ionic medium junctions, E_j can be determined experimentally or, as in the pertinent case, calculated by an approximate form of the Henderson equation (3) [6, 7]; the limiting ionic conductivities λ^0_B were taken from [8].

The e.m.f. was measured with a digital pH meter (ORION 940). The electrode system was calibrated with solutions S_0, and values of E^0 were obtained after correcting for E_j according to the equation

$$E_j = -[H^+] \frac{RT}{F} \left\{ \frac{\lambda^0_{H^+} - \lambda^0_{Na^+}}{I(\lambda^0_{Na^+} + \lambda^0_{ClO_4^-})} \right\} . \qquad (3)$$

Usually after 48 hours of intimate contact between the solid lanthanum carbonate and the solutions constant e.m.f. readings were obtained, indicating equilibration. Occasionally the solid material recovered from equilibrated solutions was checked by X-ray powder diffraction, so as to make sure that no phase transition had occurred.

Results

Solubility measurements of samples from different batches agreed within the experimental error. The pertinent data are listed in Table I. The entries of column 5, $[La^{3+}]^{calc}$, have been calculated from the charge balance.

$$3[La^{3+}]^{calc} + [Na^+] + [H^+] = [ClO_4^-] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] . \qquad (4)$$

It follows from the composition of solutions S_0 that $[ClO_4^-] - [Na^+] = H$. In the pH range of the pertinent solubility equilibria it can be shown that $2[CO_3^{2-}] \ll [HCO_3^-]$ and $[OH^-] \ll [H^+]$, thus (4) leads to

$$[La^{3+}]^{calc} = \tfrac{1}{3}(H - [H^+] + K^I_{pa_1} \cdot p_{CO_2} \cdot [H^+]^{-1}), \qquad (5)$$

where $K^I_{pa_1}$ is defined by

$$\log K^I_{pa_1} = \log \left\{ \frac{[HCO_3^-] \cdot [H^+]}{p_{CO_2}} \right\} . \qquad (6)$$

$[La^{3+}]^{calc}$ and $[La^{3+}]^{exp}_{tot}$ in columns 5 and 6 of Table I are in fair agreement. Thus, under the conditions of this work the aqua ion, $La^{3+}(aq)$, predominates, while complex La(III) species can be neglected. This was also confirmed by calculations using the equilibrium constants given by Millero [10] and Pitzer parameters from [11].

According to the overall dissolution reaction of basic lanthanum carbonates

$$La(OH)_m(CO_3)_q \cdot r H_2O + 3H^+ \rightleftharpoons La^{3+} + q CO_2 + (m+q+r) H_2O$$

a stoichiometric solubility constant is introduced by

$$\log^* K^I_{pso} = \log [La^{3+}] + q \log p_{CO_2} - 3 \log [H^+] . \qquad (7)$$

Plots of $\log [La^{3+}][H^+]^{-3}$ versus $\log p_{CO_2}$ and plots of $\log [La^{3+}] p^q_{CO_2}$ versus $\log [H^+]$ should fall on straight lines with slopes q and -3, respectively. Indeed both plots were linear with average slopes of $q = -1.11 \pm$

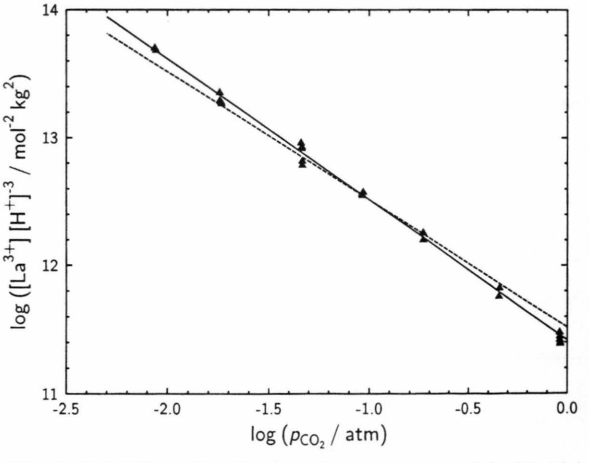

Fig. 1. Solubility of $La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\ H_2O$ in (H, Na) ClO_4 media at $I = 1.0$ mol kg^{-1} and 25 °C. – ▲ exp. data, solid line La:CO_2 = 1:1.1 ($q = 1.1$), dashed line La:CO_2 = 1:1 ($q = 1$). The deviation of the exp. data from the straight line with slope $q = 1$ is obviously significant, however a wide range of $\log(p_{CO_2}/\text{atm})$ has to be covered to ascertain the actual value of the slope $q = 1.1$.

[1] 1 atm = 1.01325×10^5 Pa.

Table I. Solubility of $La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\,H_2O$ at 25 °C.

I / mol kg^{-1}	p_{CO_2} / atm	$10^3 \times H$ / mol kg^{-1}	$10^6 \times [H^+]$ / mol kg^{-1}	$10^3 \times [La^{3+}]^{calc}$ / mol kg^{-1}	$10^3 \times [La^{3+}]^{exp}_{tot}$ / mol kg^{-1}	$\log {}^*K^I_{ps0}$
0.10	0.4597	5.01	18.16	1.87	1.85	11.12
	0.4518	4.98	18.11	1.86	1.91	11.13
	0.4551	4.98	18.84	1.85	1.91	11.08
	0.1842	5.01	13.43	1.78	1.80	11.06
	0.1821	5.01	13.18	1.78	1.81	11.08
	0.0927	5.01	10.00	1.74	1.75	11.11
	0.0924	5.01	10.00	1.74	1.78	11.11
	0.0463	5.01	7.29	1.72	1.73	11.18
	0.0457	5.01	7.50	1.72	1.74	11.14
	0.0181	5.01	5.71	1.70	1.72	11.05
	0.0182	5.01	5.89	1.69	1.75	11.02
	0.0088	5.00	4.21	1.68	1.71	11.10
	0.0089	5.00	4.02	1.68	1.73	11.17
0.25	0.4611	10.18	20.94	3.59	3.71	11.24
	0.4614	10.18	20.65	3.60	3.70	11.25
	0.1847	10.18	14.55	3.51	3.60	11.26
	0.1822	10.18	13.93	3.52	3.58	11.31
	0.0928	10.18	10.47	3.47	3.52	11.35
	0.0933	10.18	10.64	3.47	3.54	11.34
	0.0454	10.18	8.02	3.44	3.50	11.35
	0.0459	10.18	8.49	3.44	3.53	11.29
	0.0088	10.18	4.39	3.41	3.53	11.36
	0.0087	10.18	4.48	3.41	3.49	11.33
1.00	0.9241	9.93	24.21	3.66	3.63	11.37
	0.9192	9.93	23.44	3.67	3.67	11.41
	0.9178	9.93	22.91	3.68	3.68	11.45
	0.1857	9.95	12.27	3.46	3.40	11.46
	0.1857	9.95	12.88	3.45	3.46	11.41
	0.0935	9.95	9.62	3.41	3.41	11.45
	0.0926	9.95	9.79	3.40	3.39	11.42
	0.0922	9.95	9.71	3.40	3.39	11.43
	0.0467	9.95	7.93	3.37	3.34	11.36
	0.0463	9.93	7.43	3.37	3.45	11.46
	0.0460	9.93	7.11	3.37	3.35	11.50
	0.0184	9.95	5.61	3.35	3.34	11.37
	0.0183	9.95	5.55	3.35	3.33	11.38
	0.0180	9.95	5.26	3.35	3.37	11.45
	0.0180	9.95	5.51	3.35	3.33	11.38
	0.9224	104.21	52.36	34.88	35.80	11.36
	0.9191	104.21	51.17	34.89	35.92	11.39
	0.4557	99.24	36.73	33.18	33.74	11.46
	0.4526	99.24	38.64	33.09	33.70	11.39
	0.0467	99.24	17.70	33.10	34.47	11.33
	0.0465	99.24	15.74	33.10	33.73	11.47
	0.0464	99.24	18.58	33.10	34.56	11.27[a]
	0.0088	99.24	8.79	33.09	33.45	11.43
	0.0087	99.24	8.67	33.09	33.51	11.45
2.00	0.4642	98.57	34.67	32.94	33.17	11.53
	0.4632	98.57	34.99	32.94	33.12	11.52
	0.1844	98.74	22.86	32.96	33.25	11.64
	0.1818	98.74	22.96	32.96	33.51	11.63
	0.0923	98.57	17.82	32.89	32.96	11.63
	0.0919	98.57	18.11	32.89	33.19	11.61
	0.0457	98.74	13.24	32.93	33.35	11.68
	0.0455	98.74	13.37	32.93	33.34	11.67
	0.0087	98.57	7.78	32.86	33.13	11.58
	0.0087	98.57	7.71	32.86	33.25	11.60
4.00	0.4610	96.72	31.55	32.28	32.29	11.64
	0.1849	96.72	20.18	32.27	32.08	11.79
	0.1843	96.72	20.23	32.27	32.28	11.78
	0.0926	97.41	16.44	32.49	32.18	11.72
	0.0925	97.41	17.38	32.48	32.59	11.66
	0.0465	97.41	13.12	32.48	32.33	11.69
	0.0462	97.41	12.68	32.48	32.39	11.73
	0.0089	97.21	7.36	32.41	32.28	11.65
	0.0088	97.21	7.50	32.41	32.29	11.63
	0.0088	97.41	7.64	32.47	32.44	11.60
	0.0086	96.72	6.58	32.24	32.27	11.78

[a] This value differs more than three times the standard deviation from the mean value, therefore it was excluded from the averaging procedure.

Table II. Auxiliary parameters for the determination of ancylite, $La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\ H_2O$, solubilities (25 °C).

I / mol kg^{-1}	k / V kg mol^{-1}	$\frac{d \log \{[La^{3+}][H^+]^{-3}\}}{d \log p_{CO_2}}$	$\frac{d \log \{[La^{3+}] p_{CO_2}^{1.1}\}}{d \log [H^+]}$	$-\log K^I_{pa_1}$
0.10	0.656	-1.10 ± 0.02	-2.98 ± 0.06	7.61
0.25	0.262	-1.15 ± 0.02	-2.86 ± 0.04	7.55
1.00	0.066	-1.11 ± 0.01	-2.98 ± 0.03	7.55
2.00	0.033	-1.13 ± 0.03	-2.91 ± 0.07	7.67
4.00	0.016	-1.07 ± 0.04	-3.18 ± 0.10	7.95

Table III. Solubility constants of $La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\ H_2O$ (25 °C).

I/mol kg^{-1}	$\log^* K^I_{ps0}$	$\log(\gamma_{La^{3+}} \gamma_{H^+}^{-3})$	$2 \log a_{H_2O}$	$\log^* K^0_{ps0}$
0.10	11.10 ± 0.05	-0.659	-0.003	10.43_8
0.25	11.32 ± 0.04	-0.789	-0.007	10.52_4
1.00	11.42 ± 0.04	-0.906	-0.029	10.47_5
2.00	11.63 ± 0.03	-0.964	-0.059	10.60_7
4.00	11.70 ± 0.06	-0.984	-0.124	10.62_2

0.03 (see Fig. 1 and Table II) and -2.98 ± 0.12 (see Table II). Thus, in addition to chemical and thermogravimetric analyses the formula of ancylite was ascertained to be $La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\ H_2O$ by thermodynamic analysis of $\log[La^{3+}]$, $\log[H^+]$ and $\log p_{CO_2}$ data at solid-aqueous solution equilibria.

Auxiliary parameters necessary for the calculation of solubility constants (k-values obtained from (3), slopes derived from data of Table I, and $-\log K^I_{pa_1}$ calculated with the Pitzer parameters given in [9]) are listed in Table II; errors quoted are standard deviations.

The solubility constant according to (8) was indeed found to be about one order of magnitude higher than that of lanthanite. Therefore the value determined by Jordanov and Havezov [2] presumably refers to ancylite, whereas the data reported by Firsching and Mohammadzadel [3] still remain puzzling.

$$La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\ H_2O(s) + 3\ H^+(aq) \rightleftharpoons La^{3+}(aq) + 1.1\ CO_2(g) + 2\ H_2O(aq) \quad (8)$$

In Fig. 2, $\log^* K^I_{ps_0}$ values of $La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\ H_2O$ and for comparison of $La_2(CO_3)_3 \cdot 8\ H_2O$ [1] are plotted versus $I^{1/2}$. The experimental results up to $I = 1.0$ mol kg^{-1} (Na)ClO_4 fall on the solid curves calculated with ${}^S\theta_{Na,La}$ and ψ_{Na,La,ClO_4} given by Kim and Frederick [12]. The dashed curve is obtained when these ternary mixing parameters are neglected. In this case, however, calculated and experimental data agree only up to $I = 0.25$ mol kg^{-1}. The ancylite curve extrapolates to

$$\log^* K^0_{ps_0} = \log \{([La^{3+}] p_{CO_2}^{1.1} [H^+]^{-3}) \cdot (\gamma_{La^{3+}} \gamma_{H^+}^{-3})\, a^2_{H_2O}\} = 10.48 \pm 0.08\,.$$

Experimental solubility constants, their standard deviations and the terms containing activity coefficients and water activities calculated with the Pitzer equations including ${}^S\theta_{Na,La}$ and ψ_{Na,La,ClO_4} are listed in Table III. Note that for the sake of exactness $\log a^2_{H_2O}$

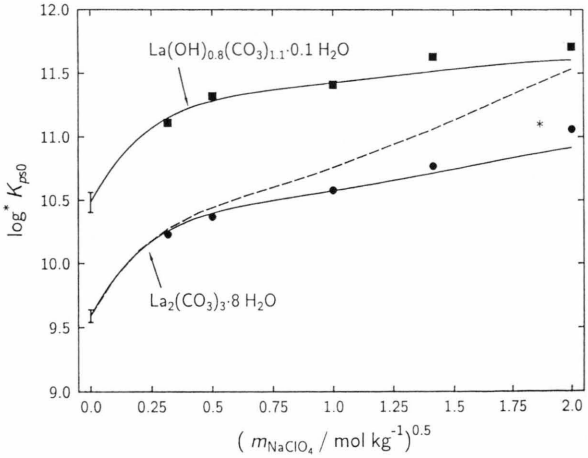

Fig. 2. Extrapolation of $\log^* K_{ps0}$ of $(La(OH)_{0.8}(CO_3)_{1.1} \cdot 0.1\ H_2O)$ and $(La_2(CO_3)_3 \cdot 8\ H_2O)$ to infinite dilution. – ● exp. data lanthanite [1], * recalculated from [17], $I = 3.47$ mol kg^{-1}, ■ exp. data ancylite, both error bars refer to extrapolated $\log^* K^0_{ps0}$ values. The solid curves were calculated with ${}^S\theta_{Na,La}$ and ψ_{Na,La,ClO_4} given by Kim and Frederick [12]. The dashed curve is obtained when these ternary mixing parameters are neglected.

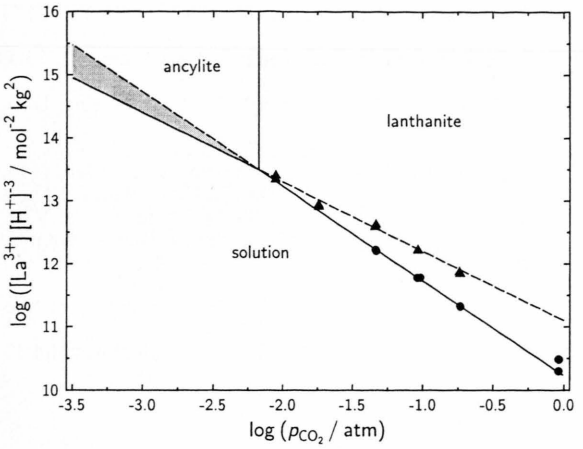

Fig. 3. Predominance diagram, of La-carbonates at 25 °C, $I = 0.1$ mol kg^{-1}. ● exp. data of lanthanite, ▲ exp. data of ancylite, solid lines: Stable range, dashed lines: Metastable range. Under the conditions indicated by the shaded area ancylite can be precipitated, whereas starting from solutions it should not be possible to form even a metastable lanthanite.

is always taken into account, although this term exceeds the experimental error only at the highest ionic strengths investigated.

With the standard potential of La^{3+}/La taken from Nugent [13] (whose value agrees closely with that of Johnson [14]) and the CODATA values [15] for $\Delta_f G^\ominus_{CO_2}$ and $\Delta_f G^\ominus_{H_2O}$ the Gibbs energy of formation $\Delta_f G^\ominus_{La(OH)_{0.8}(CO_3)_{1.1}\cdot 0.1\,H_2O}$ can be calculated. Note that the experimental error in $\ln {}^*K^0_{ps0}$ contributes only ca. ± 0.5 kJ mol^{-1} to the overall uncertainty.

$$\begin{aligned}\Delta_f G^\ominus_{La(OH)_{0.8}(CO_3)_{1.1}\cdot 0.1\,H_2O} = {} & \Delta_f G^\ominus_{La^{3+}} \\ & + 1.1\,\Delta_f G^\ominus_{CO_2} + 2\,\Delta_f G^\ominus_{H_2O} \\ & + RT \ln {}^*K^0_{ps0} \\ = {} & -1531.5 \text{ kJ mol}^{-1}.\end{aligned}$$

The stability fields of lanthanum carbonates can efficiently be depicted by predominance area diagrams. In Fig. 3, $\log\{[La^{3+}][H^+]^{-3}/\text{mol}^{-2}\,\text{kg}^2\}$ is plotted versus $\log(p_{CO_2}/\text{atm})$. Ancylite becomes the stable phase below $\log(p_{CO_2}/\text{atm}) \approx -2.2$. The exact value depends on the ionic strength. According to the solubility constant of $La(OH)_3$ given by Baes and Mesmer [6], the ancylite to lanthanum hydroxide phase transition occurs only far below the atmospheric CO_2 partial pressure.

Discussion

This study confirms conclusions obtained previously [1, 16]: 1) The Pitzer equations are useful to extrapolate solubility constants ${}^*K^I_{ps0}$ to zero ionic strength, particularly in simple cases where only one species as e.g. the aqua ion controls the overall solubility of the metal. 2) ${}^*K^0_{ps0}$ values thus obtained lead to accurate Gibbs energies of formation. 3) Measurements carried out in a constant ionic medium may be used to calculate the respective value of the solubility at infinite dilution provided the ionc strength is not higher than ca. 1 mol kg^{-1}, because up to this concentration range the Pitzer equations are particularly successful. 4) Ternary Pitzer parameters needed to predict solubilities at higher ionic strengths have been taken from the literature unaltered, so as to check on their applicability. A better fit than in Fig. 2 would doubtless have been obtained with parameters refined by taking into account the experimental results of this work. Solubility data can in general be used to optimize Pitzer parameters. Once this has been achieved systematically, a wealth of already existing experimental information can be made to contribute to thermodynamic data banks.

The predominance area diagram in Fig. 3 shows paradigmatically the efficiency of thermodynamics under favourable conditions. All data on ancylite leading to its standard Gibbs function have been obtained in the metastable range. Moreover, guided by Fig. 3, a CO_2/N_2 mixture (0.07% CO_2) was bubbled through a lanthanum(III) perchlorate solution and slowly alkalized by NH_3 in order to remain in the stability field of ancylite preferably in the shaded area. It should be emphasized that the compositional range useful for preparing ancylite was predicted by thermodynamic arguments only, and indeed beautifully pure crystals of this substance have thus been obtained.

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