Solid-Solute Phase Equilibria in Aqueous Solutions, VIII: The Standard Gibbs Energy of La$_2$(CO$_3$)$_3$·8H$_2$O**,**

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Summary. The solubilities of lanthanum carbonate La$_2$(CO$_3$)$_3$·8H$_2$O in solutions $S_o ([H^+] = H$ mol kg$^{-1}$, $[Na^+] = (I - H)$ mol kg$^{-1}$, $[ClO_4^-] = I$ mol kg$^{-1}$) at various fixed partial pressures of CO$_2$ have been investigated at 25.0 °C. The hydrogen ion molality and the total molality of La(III) ion in equilibrium with the solid phase were determined by e.m.f. and analytical methods, respectively. The stoichiometric solubility constants

$$\log K_{p0} = \log \left\{ \frac{[La^{3+}]^{3/2} [H^+]^{-3}}{p_{CO_2} \gamma_{La^{3+}} \gamma_{H^+} \gamma_{H_2O}} \right\}$$

according to the overall reaction

$$\frac{1}{2} La_2(CO_3)_3 \cdot 8H_2O + 3H^+ \rightleftharpoons La^{3+} + 3/2CO_2 + 11/2H_2O$$

have the values 10.23, 10.37, 10.58, 10.77 and 11.06 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 “thermo-dynamic” solubility constant:

$$\log K_{p0}^0 = \log \left\{ \frac{([La^{3+}]^{3/2} [H^+]^{-3})}{(p_{CO_2} \gamma_{La^{3+}} \gamma_{H^+} \gamma_{H_2O})^{1/2}} \right\} = 9.57 \pm 0.05.$$  

This in turn led to the Gibbs energy of lanthanite, La$_2$(CO$_3$)$_3$·8H$_2$O, formation:

$$\Delta_f G^0_{298} = -5048.4 \text{ kJ mol}^{-1}.$$  

Keywords. Lanthanum carbonate; Pitzer model; Solubility.
Molalität der La(III)-Ionen im Gleichgewicht mit der festen Phase wurden potentiometrisch bzw. analytisch bestimmt. Für die stöchiometrischen Löslichkeitskonstanten
\[
\log *K_p^{\text{f}} = \log \left\{ \frac{[La^{3+}]^{3/2} [H^+]^{-3}}{p_{CO_2}} \right\}
\]
entsprechend der Gesamtreaktion
\[
\frac{1}{2}La_2(CO_3)_3 \cdot 8H_2O + 3H^+ \rightleftharpoons La^{3+} + 3/2CO_2 + 11/2H_2O
\]
wurden bei \( I = 0.1, 0.25, 1.0, 2.0 \) und \( 4.0 \) mol kg\(^{-1}\) (Na)ClO\(_4\), folgende Werte gefunden: \( 10.23, 10.37, 10.58, 10.77 \) und \( 11.06 \). Die Extrapolation auf unendliche Verdünnung mit Hilfe der Pitzer-Gleichungen führte zu einer „thermodynamischen“ Löslichkeitskonstante von:
\[
\log *K_p^{\text{f}} = \log \left\{ \frac{[La^{3+}]^{3/2} [H^+]^{-3}}{p_{CO_2}} \right\} = 9.57 \pm 0.05.
\]
Mit dieser ergab sich die freie Bildungsenthalpie von Lanthanit \( La_2(CO_3)_3 \cdot 8H_2O \) zu:
\[
\Delta G_{298}^0 = -5048.4 \text{ kJ mol}^{-1}.
\]

Introduction
Solubility studies of sparingly soluble metal carbonates contribute to fundamental as well as applied chemical research. Firstly, Gibbs energies of formation can be derived by appropriate combination of solubility constants and standard potentials, when both are measured in the same ionic medium [2] or extrapolated to infinite dilution. Secondly, thermodynamic information obtained thereby is since many decades used to predict the behaviour of the respective substances in industrially important reactions [3].

For the approach originally suggested by Schindler [4, 5] to be applicable, reversible electrode potentials must be experimentally accessible in aqueous solutions of appropriate ionic strengths. However, only few metals meet this condition. Fortunately, the method of extrapolation can be improved considerably with the aid of the Pitzer equations [6]. Recently this was shown in the systems \( Na^+-Y^{3+}-ClO_4^- -CO_2-H_2O \) [7] and \( Na^+-Mg^{2+}-ClO_4^- -CO_2-H_2O \) [8].

In the present work it was attempted to determine the solubility constant of lanthanite \( La_2(CO_3)_3 \cdot 8H_2O \) at systematically varying ionic strengths. To avoid complications of side reactions, conditions were selected so as to minimize complex formation between lanthanum(III) ion and carbonate species. Information on solubility constants taken from the papers of Jordanov and Havezov [9], Ciavatta et al. [10], Ferri and Salvatore [11] and Firsching and Mohammadzadel [12] were compared with the results obtained in this work. Calculations were carried out with the Gibbs energy minimization program ChemSage [13] which uses the Pitzer model in the version of Harvie et al. [14] and, in addition, was recently improved by a general optimization routine [15].

Experimental
Lanthanite, \( La_2(CO_3)_3 \cdot 8H_2O \) (99.99%), was either purchased from ABCR (Germany) and used directly, or lanthanum oxide (99.99% ABCR) was taken as starting material for its preparation following the procedure of Fischer et al. [16]. According to the latter, well crystallized \( La_2(CO_3)_3 \cdot 8H_2O \) was prepared by adding slowly \( NH_4HCO_3 \) solution into the appropriate volume of \( 0.0067 \) mol kg\(^{-1}\) \( La(NO_3)_3 \) solution at 0 °C, in a molar ratio \( La^{3+}:HCO_3^- = 1:0.75 \). These lanthanum nitrate solutions