

Studies on Metal Carbonate Equilibria. 6. On the Solubility Equilibria of Rare-earth Carbonates: The Lanthanum Carbonate, $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}(\text{s})$

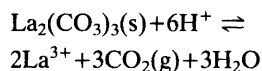
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A general method for the accurate evaluation of the solubility equilibria of rare-earth carbonates from emf measurements is proposed. Its application to $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}(\text{s})$ is described in detail and the equilibrium constant

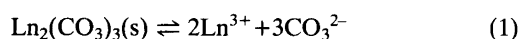
$$K = [\text{La}^{3+}]^2 [\text{H}^+]^{-6} P_{\text{CO}_2}^3 = 10^{(22.65 \pm 0.03)}$$

for the reaction



is determined in 1 M $\text{La}(\text{ClO}_4)_3$ medium, at 25 °C.

Equilibria of the type



have usually been investigated by solubility measurements.¹ The attainment of equilibrium is the critical stage when studying heterogeneous equilibria. The time for equilibration is often several days long, particularly if an initially amorphous phase recrystallizes. Thus serious effort has to be devoted to ascertain that true equilibrium is reached.

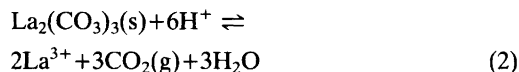
The attainment of a constant solubility value is certainly a simple equilibrium criterium, but a tedious one because of the manipulations involved.

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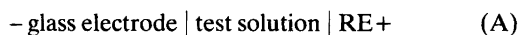
In this communication, we have chosen the lanthanum carbonate system to describe how the emf method can conveniently ensure the reliable attainment of equilibrium and the accurate evaluation of the solubility equilibria.

METHOD

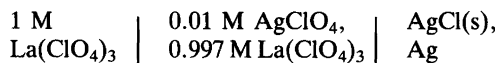
The equilibrium constant of the reaction



has been determined at 25 °C in 1 M $\text{La}(\text{ClO}_4)_3$ by measuring the emf of the cell



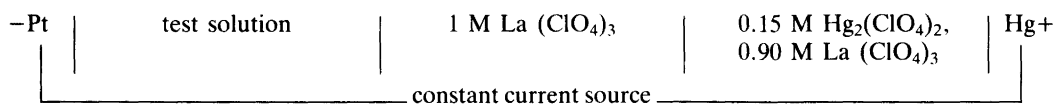
where RE is the reference half cell



The emf of cell (A) can be written

$$E = E_o - 59.16 \log h + E_j \quad (3)$$

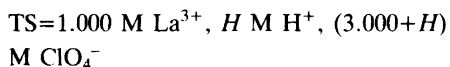
In (3) h is the proton concentration. E_j is the liquid junction potential between the test solution and 1 M $\text{La}(\text{ClO}_4)_3$ which was considered negligible. Actually E_j did not exceed 0.1 mV, since the initial h was always smaller than 10^{-2} M. E_o is a constant determined in the initial part of



Scheme 1.

the experiments. These were carried out as titrations, where the total lanthanum concentration was kept constant, whereas the analytical concentration excess of protons, H^+ , was varied by stepwise reduction on a Pt gauze by means of the coulometric circuit (Scheme 1). In order to avoid local formation of lanthanum oxide on the cathode, current densities lower than $1 \cdot 10^{-3} \text{ A/cm}^2$ were used.

The test solutions had the general composition



In the first part of the titration, H was only varied within the range where $h=H$ can be assumed, *i.e.* no appreciable hydrolysis of La^{3+} takes place.

E_0 could thus be determined from the $E(H)$ data by using eqn. (3) and the relation

$$H = H_0 - w/V \quad (4)$$

In (4) H_0 is the initial analytical concentration excess of protons and $V \text{ (dm}^3\text{)}$ the volume of the test solution; w represents the total number of mol of protons removed after each step of electrolysis.

Then a stream of $\text{CO}_2\text{-N}_2$ gas of known composition, presaturated with the proper H_2O vapour pressure (0.0276 atm) by equilibration with 1 M $\text{La}(\text{ClO}_4)_3$, was passed through TS. H was decreased in a single step to a value where the incipient formation of a solid phase, recognized as $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$, was observed. The electrolysis was then discontinued. Equilibrium was reached in a few days as indicated by the emf of cell (A) which eventually reached a value that remained constant within 0.1 mV for several days.

* The analytical variable H is equal to the analytical concentration of HClO_4 at the beginning of the titration minus the total OH^- concentration coulometrically generated.

Table 1. $h(P_{\text{CO}_2})$ data at $[\text{La}^{3+}] = 1.000 \text{ M}$.

P_{CO_2} (atm)	$h \cdot 10^3$ (M)	$\log K_s$ (eqn. 6)
0.978	0.164	22.68
0.099 ₅	0.052	22.69
0.298 ₅	0.093	22.62
0.995	0.168	22.64

The equilibrium was also re-established in a few days, when the $\text{CO}_2\text{-N}_2$ mixture was replaced with another of different partial pressure of carbon dioxide, P_{CO_2} . Experiments performed by letting P_{CO_2} span repeatedly the values 1, 0.1, 0.3, 1 atm indicate that the emf of cell (A) is the same within the experimental errors on approaching equilibrium both from supersaturated and undersaturated solutions. Thus true equilibrium is attained.

From the $h(P_{\text{CO}_2})$ data, K can easily be calculated with a high degree of accuracy, as shown in the next section.

CALCULATIONS

Determination of K. The coulometric alkalinification of the test solution is carried out until the incipient precipitation of the solid phase. Only a negligible fraction of the lanthanum ion is thus removed from the solution to enable the formation of $\text{La}_2(\text{CO}_3)_3(\text{s})$. In addition from the $h(P_{\text{CO}_2})$ data (see Table 1), we can deduce that the concentration of the hydroxo³ and carbonate² complex species in the test solutions equilibrated with the solid $\text{La}_2(\text{CO}_3)_3$ are always several orders of magnitude lower than the total metal concentration.

Consequently, no loss of accuracy is introduced by assuming that the concentration of non-bound lanthanum stays constant at the 1 M level throughout the experiment, *i.e.*

$$[\text{La}^{3+}] = 1.000 \text{ M} \quad (5)$$

From the $h(P_{\text{CO}_2})$ data and from (5), we can calculate

$$K = [\text{La}^{3+}]^2 P_{\text{CO}_2}^3 \text{ h}^{-6} \quad (6)$$

From a series of measurements of which a sample is reported in Table 1, we obtained

$$\log K = 22.65 \pm 0.03$$

The error represents the maximum deviation from the mean.

Extrapolation of the results. The value of K for reaction (2) determined above refers to a 1 M $\text{La}(\text{ClO}_4)_3$ medium.

The medium dependence of equilibrium constants is usually evaluated by estimating the activity factors of the species involved.

The specific interaction (SI) theory has satisfactorily been used^{4,5} for this purpose. Its application is shown here to the calculation of the constant of reaction (2) at infinite dilution, K_0 , from its value valid in 1 M $\text{La}(\text{ClO}_4)_3$. The relation between K and K_0 expressed in molal units is given by

$$\log K_0 = \log K + \log (\gamma_{\text{La}^{3+}}^2 \cdot \gamma_{\text{H}^+}^{-6}) - 4 \log(d - 0.4373) \quad (7)$$

where γ_i is the molal activity coefficient of species i at the molality m_i , $d = 1.328 \text{ g cm}^{-3}$ is the density of 1 M $\text{La}(\text{ClO}_4)_3$ at 25 °C and 0.4373 is the weight of 1 mmol of $\text{La}(\text{ClO}_4)_3$. The activity coefficients ratio in (7) can be evaluated by applying the SI theory:

$$\log (\gamma_{\text{La}^{3+}}^2 \cdot \gamma_{\text{H}^+}^{-6}) = -6.131 \sqrt{I} (1 + 1.5 \sqrt{I})^{-1} + [2\varepsilon(\text{La}^{3+}, \text{ClO}_4^-)_I - 6\varepsilon(\text{H}^+, \text{ClO}_4^-)_I] m_{\text{ClO}_4^-} \quad (8)$$

where I is the ionic strength of the solution and $\varepsilon(i, K)_I$ is the interaction coefficient at ionic strength I of the species i with the species K at the molality m_K .

In (8) the terms accounting for the interaction between La^{3+} and H^+ with HCO_3^- and CO_3^{2-} have been neglected because of the very low values attained by $m_{\text{HCO}_3^-}$ and $m_{\text{CO}_3^{2-}}$ in this study. By introducing in (8) the values

$$\varepsilon(\text{H}^+, \text{ClO}_4^-)_{6,7} = 0.16 \text{ kg mol}^{-1}$$

$$\varepsilon(\text{La}^{3+}, \text{ClO}_4^-)_{3,5} \approx \varepsilon(\text{La}^{3+}, \text{ClO}_4^-)_{6,7} = 0.47 \text{ kg mol}^{-1}$$

evaluated from osmotic coefficients reported in the literature,^{6,7} we obtain

$$\log(\gamma_{\text{La}^{3+}}^2 \cdot \gamma_{\text{H}^+}^{-6}) = -3.3 \pm 0.2 \quad (9)$$

Consequently,

$$\log K_0 = 19.15 \pm 0.2 \quad (10)$$

The errors in (9) and (10) have been estimated by varying the interaction coefficients within $\pm 10\%$. The magnitude of K_0 in molar units obviously coincides with the value given in (10).

Further evidence for the convenience of the emf method for the evaluation of solubility equilibria will be given in a forthcoming paper on the yttrium carbonate system.⁸ This extensive study carried out at several ionic strengths also corroborates the numerical treatment illustrated above.

EXPERIMENTAL

Lanthanum, carbon and water in a sample of the air-dried precipitate were analysed using elemental analytical techniques. The results showed ratios corresponding to $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}(\text{s})$. In addition, X-ray powder diffraction data, compared with those reported by Wakita,⁹ also indicated $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}(\text{s})$.

The details of the emf measurements as well as the methods of preparation and analysis of solutions have been described elsewhere.^{2,3}

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