



Thermodynamic Analysis and Application of Metal Carbonate Solubilities

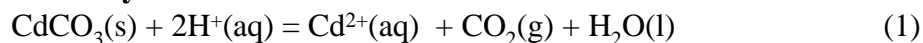
(Solubility data of compounds relevant to mobility of metals in the
environment)

Heinz Gamsjäger, Erich Königsberger, M. Clara Magalhães
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From Solubilities to Thermodynamic Quantities of Metal Carbonates

- $\Delta_f G^\circ(\text{MCO}_3, \text{s}, 298.15 \text{ K})$: The determination of standard Gibbs energies of formation of sparingly soluble metal carbonates can be based on solubility and electrode potential measurements. The same ionic medium is employed as solvent when both solubility and redox equilibria are studied. The first metal carbonate investigated by this method was otavite, CdCO_3 .

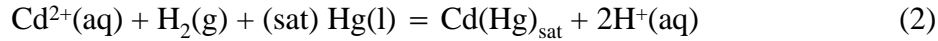
1) Solubility



$$\lg^* K_{ps0} = \lg\{[\text{Cd}^{2+}] \cdot p(\text{CO}_2) \cdot [\text{H}^+]^{-2}\}$$

$$\Delta_{\text{sol}} G^\circ = -RT \ln(10) \cdot \lg^* K_{ps0}$$

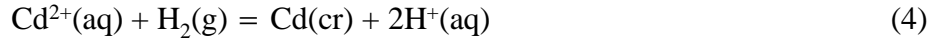
2) Electrode Potential



$$E^\circ(\text{Cd}^{2+} | \text{Cd}(\text{Hg})_{\text{sat}}) = \{RT \ln(10) / 2F\} \lg\{[\text{H}^+]^2 \cdot [\text{Cd}^{2+}]^{-1}\}$$

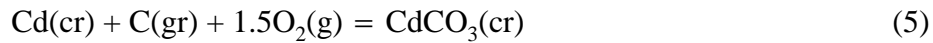


$$\Delta_f G^\circ(\text{Cd}(\text{Hg})_{\text{sat}}) = 2F \cdot E^\circ(\text{Cd} | \text{Cd}(\text{Hg})_{\text{sat}})$$



$$\Delta_f G^\circ(\text{Cd}^{2+}) = 2F \cdot \{E^\circ(\text{Cd}^{2+} | \text{Cd}(\text{Hg})_{\text{sat}}) - E^\circ(\text{Cd} | \text{Cd}(\text{Hg})_{\text{sat}})\}$$

When equilibria of Reactions (1) and (2) are studied in the same ionic medium the standard Gibbs energy of the metal carbonate formation becomes accessible without any non-thermodynamic assumptions.



$$\Delta_f G^\circ(\text{CdCO}_3) = \Delta_f G^\circ(\text{Cd}^{2+}) + \Delta_f G^\circ(\text{CO}_2) + \Delta_f G^\circ(\text{H}_2\text{O}) - \Delta_{\text{sol}} G^\circ$$

Measurements of $\Delta_f G^\circ(\text{Cd}^{2+})$ and $\Delta_{\text{sol}} G^\circ(\text{CdCO}_3)$, re-evaluated by the SIT model, resulted in Table 1 and the following mean value ($\pm 2\sigma$):

Table 1: Standard Gibbs energies of formation, eqs.(4, 5), and reaction, eq. (1), at 25°C

$I / \text{mol} \cdot \text{kg}^{-1}$	$\Delta_f G^\circ(\text{Cd}^{2+}) / \text{kJ} \cdot \text{mol}^{-1}$	$-\Delta_{\text{sol}} G^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f G^\circ(\text{CdCO}_3) / \text{kJ} \cdot \text{mol}^{-1}$
0.0000	-77.75	34.97	-674.29
1.0515	-79.38	36.72	-674.17
3.5034	-79.25	36.39	-674.38
2.2124	-78.93	35.82	-674.62

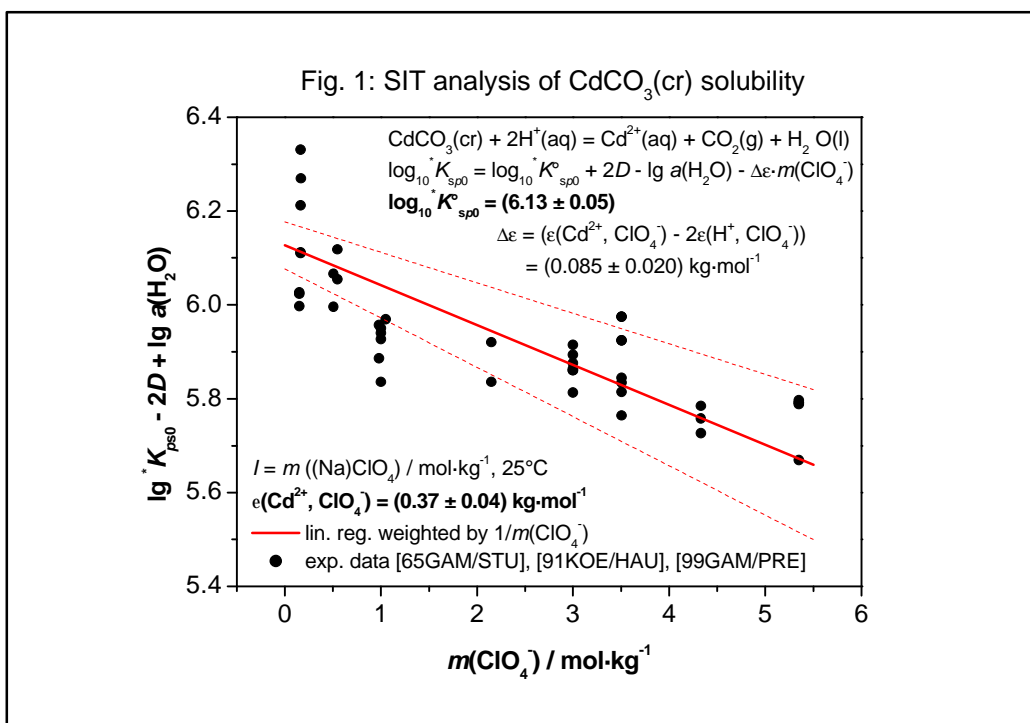
$$\Delta_f G^\circ(\text{CdCO}_3) = - (674.4 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$$

➤ $\Delta_f H^\circ(\text{MCO}_3, \text{s}, 298.15 \text{ K})$: The solubility of otavite, CdCO_3 , is almost independent of temperature. The SIT analysis of ($I, \lg^* K_{ps0}$) data at 25°C (see Figure 1) results in

$$\lg^* K_{ps0}(\text{CdCO}_3, 25^\circ\text{C}, I = 1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4) = 6.45 \pm 0.05.$$

A least squares analysis of ($T, \lg^* K_{ps0}$) data at $I = 1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4$ leads to

$$\lg^* K_{ps0}(\text{CdCO}_3, 25 - 75^\circ\text{C}, I = 1.0 \text{ mol} \cdot \text{kg}^{-1} \text{ NaClO}_4) = 6.39 \pm 0.14.$$



$\Delta_{\text{sol}}H^\circ$ vanishes within the experimental uncertainty.

$$\Delta_{\text{sol}}H^\circ = -R \cdot \ln(10) \cdot \delta(\lg^* K_{ps0}) / \delta(1/T)$$

$$= (0.0 \pm 5.6) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{f}}H^\circ(\text{CdCO}_3) = \Delta_{\text{f}}H^\circ(\text{Cd}^{2+}) + \Delta_{\text{f}}H^\circ(\text{CO}_2) + \Delta_{\text{f}}H^\circ(\text{H}_2\text{O}) - \Delta_{\text{sol}}H^\circ$$

$$\Delta_{\text{f}}H^\circ(\text{CdCO}_3) = -(755.3 \pm 5.6) \text{ kJ}\cdot\text{mol}^{-1}$$

- **$S^\circ(\text{MCO}_3, \text{s}, 298.15 \text{ K})$:** The standard entropy of CdCO_3 can also be estimated from this information. With CODATA values for $S^\circ(\text{Cd}^{2+})$, $S^\circ(\text{CO}_2)$ and $S^\circ(\text{H}_2\text{O})$ one obtains

$$S^\circ(\text{CdCO}_3) = S^\circ(\text{Cd}^{2+}) + S^\circ(\text{CO}_2) + S^\circ(\text{H}_2\text{O}) - \Delta_{\text{sol}}S^\circ$$

$$= (93 \pm 18) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

Low-temperature heat capacity data result in a more precise value

$$S^\circ(\text{CdCO}_3) = (103.9 \pm 0.2) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ [96ARC]}$$

- **Recommended set of thermodynamic quantities:**

$$\Delta_{\text{f}}G^\circ(\text{CdCO}_3) = -(674.4 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{f}}H^\circ(\text{CdCO}_3) = -(752.3 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$$

$$S^\circ(\text{CdCO}_3) = (103.9 \pm 0.2) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

Exceptionally Deviating Solubilities Indicate Different Metal Carbonate Phases

Originally the solubility of solid nickel carbonate was studied without trying to characterize the chemical and physical state of the samples. The result was ascribed to $\text{NiCO}_3(\text{s})$. Reiterer synthesized neutral anhydrous nickel carbonate by a hydrothermal autoclave method. Thus well crystallized pure nickel carbonate, $\text{NiCO}_3(\text{cr})$, gaspéite, was obtained and investigated by the pH variation method (Fig. 2). Gamsjäger et al. synthesized $\text{NiCO}_3 \cdot 5.5\text{H}_2\text{O}$, hellyerite, and studied its solubility by the same method (Fig. 2). The quantities below were obtained by thermodynamic analysis (Fig. 3).

Recommended set of thermodynamic quantities:

$\text{NiCO}_3, \text{cr}, 298.15 \text{ K}$

$$\Delta_f G^\circ / \text{kJ}\cdot\text{mol}^{-1} = - (636.4 \pm 1.3)$$

$$\Delta_f H^\circ / \text{kJ}\cdot\text{mol}^{-1} = - (713.3 \pm 1.4)$$

$\text{NiCO}_3 \cdot 5.5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}$

$$\Delta_f G^\circ / \text{kJ}\cdot\text{mol}^{-1} = - (1920.9 \pm 1.0)$$

$$\Delta_f H^\circ / \text{kJ}\cdot\text{mol}^{-1} = - (2313.0 \pm 3.1)$$

$$S^\circ / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = (311.1 \pm 10.0)$$

