



# Thermodynamic Analysis and Application of Metal Carbonate Solubilities

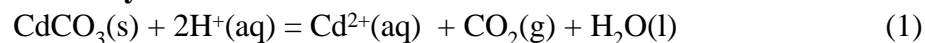
(Solubility data of compounds relevant to mobility of metals in the  
environment)

Heinz Gamsjäger, Erich Königsberger, M. Clara Magalhães  
Project No.: 2002-032-1-500

## 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,  $\text{CdCO}_3$ .

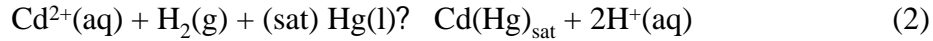
### 1) Solubility



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

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

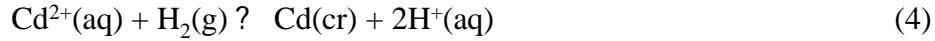
## 2) Electrode Potential



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

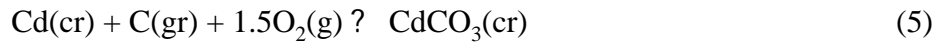


$$\Delta_f G^\circ(\text{Cd}(\text{Hg})_{\text{sat}}) = 2F \cdot E^\circ(\text{Cd} | \text{Cd}(\text{Hg})_{\text{sat}})$$



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

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 ( $\pm 2s$ ):

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

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

➤  $\Delta_f H^\circ(\text{CdCO}_3, \text{s}, 298.15 \text{ K})$ : The solubility of otavite,  $\text{CdCO}_3$ , 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

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



## 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:

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

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

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

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

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

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

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

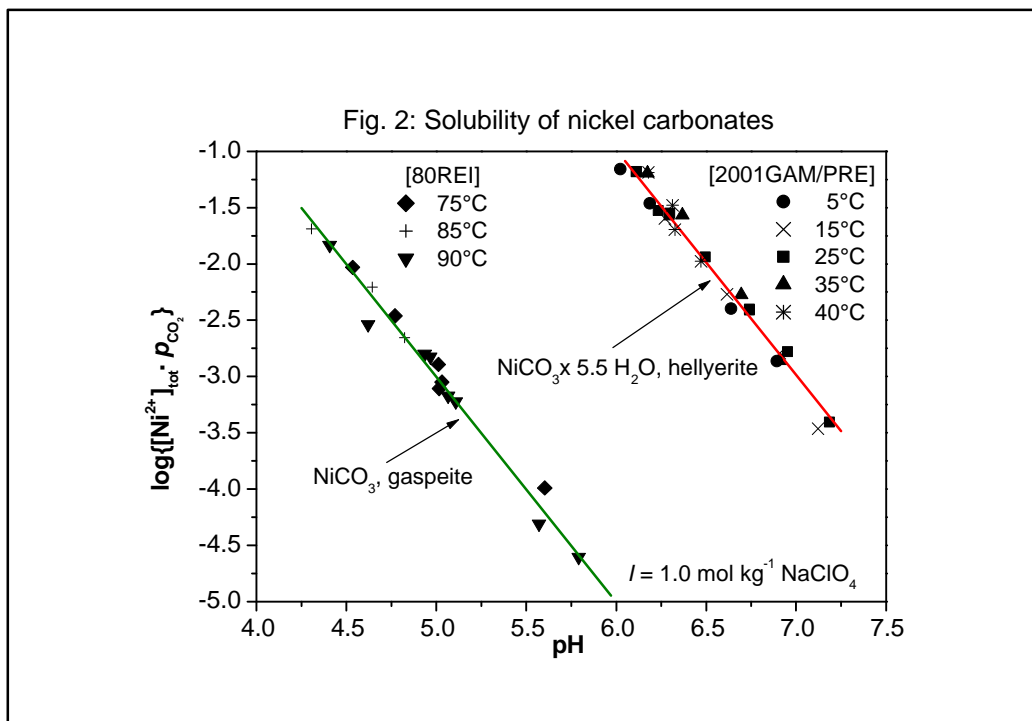


Fig. 3: Thermodynamic analysis of  $\text{NiCO}_3 \cdot 5.5\text{H}_2\text{O}$  solubility

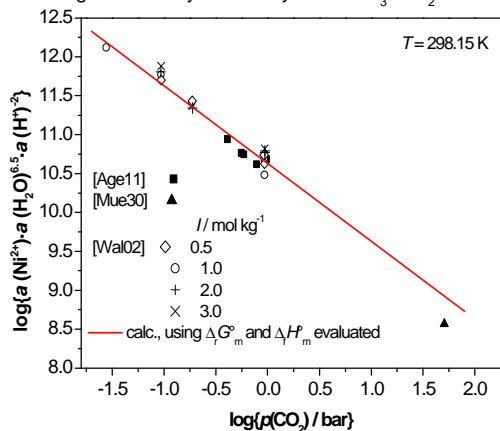
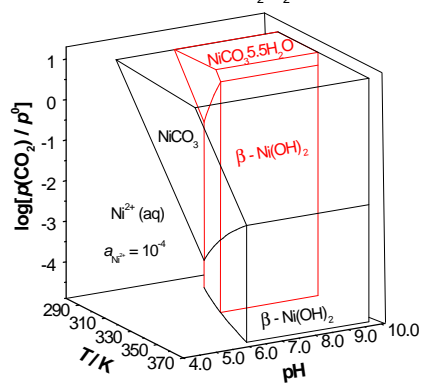


Fig. 4: Three-dimensional predominance diagram for the system  $\text{Ni}^{2+}\text{-CO}_2\text{-H}_2\text{O}$



**Solubility Measurements and/or Critical Evaluations are available for:**

Formula	Mineral Name	Thermodynamic Analysis $?\log\{[\text{M}^{2+}] \cdot [\text{H}^+]^{-2}\} / ? \log p(\text{CO}_2)$
$\text{MnCO}_3$	Rhodochrosite	-1.0
$\text{FeCO}_3$	Siderite	-1.0
$\text{CoCO}_3$	Spherochalcite	-1.0
$\text{NiCO}_3$	Gaspéite	-1.0
$\text{NiCO}_3 \cdot 5.5\text{H}_2\text{O}$	Hellyerite	-1.0
$\text{CuCO}_3$	****	-1.0
$\text{Cu}_2(\text{OH})_2\text{CO}_3$	Malachite	-1/2
$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	Azurite	-2/3
$\text{ZnCO}_3$	Smithsonite	-1.0
$\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$	Hydrozincite	-2/5
$\text{CdCO}_3$	Otavite	-1.0