Thermodynamic Analysis and Application of Metal Carbonate Solubilities

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

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From Solubilities to Thermodynamic Quantities of Metal Carbonates

- **$\Delta_f G°(MCO_3$, s, 298.15 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

$$CdCO_3(s) + 2H^+(aq) = Cd^{2+}(aq) + CO_2(g) + H_2O(l) \qquad (1)$$

$$\lg{}^*K_{ps0} = \lg\{[Cd^{2+}]\cdot p(CO_2)\cdot[H^+]^{-2}\}$$

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

2) Electrode Potential

$$\mathrm{Cd^{2+}(aq) + H_2(g) + (sat)\ Hg(l) = Cd(Hg)_{sat} + 2H^+(aq)} \qquad (2)$$

$$E°(\mathrm{Cd^{2+}|\ Cd(Hg)_{sat}}) = \{\mathrm{R}T\ \ln(10) / 2\mathrm{F}\}\mathrm{lg}\{[\mathrm{H^+}]^2\cdot[\mathrm{Cd^{2+}}]^{-1}\}$$

$$\mathrm{Cd(cr) + (sat)\ Hg(l) = Cd(Hg)_{sat}} \qquad (3)$$

$$\Delta_\mathrm{f}G°\ (\mathrm{Cd(Hg)_{sat}}) = 2\mathrm{F}\cdot E°(\mathrm{Cd\ |\ Cd(Hg)_{sat}})$$

$$\mathrm{Cd^{2+}(aq) + H_2(g) = Cd(cr) + 2H^+(aq)} \qquad (4)$$

$$\Delta_\mathrm{f}G°\ (\mathrm{Cd^{2+}}) = 2\mathrm{F}\cdot\{E°(\mathrm{Cd^{2+}|\ Cd(Hg)_{sat}}) - E°(\mathrm{Cd\ |\ Cd(Hg)_{sat}})\}$$

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.

$$\mathrm{Cd(cr) + C(gr) + 1.5O_2(g) = CdCO_3(cr)} \qquad (5)$$

$$\boldsymbol{\Delta_\mathrm{f}G°(\mathrm{CdCO_3}) = \Delta_\mathrm{f}G°\ (\mathrm{Cd^{2+}}) + \Delta_\mathrm{f}G°(\mathrm{CO_2}) + \Delta_\mathrm{f}G°(\mathrm{H_2O}) - \Delta_\mathrm{sol}G°}$$

Measurements of $\Delta_\mathrm{f}G°(\mathrm{Cd^{2+}})$ and $\Delta_\mathrm{sol}G°(\mathrm{CdCO_3})$, re-evaluated by the SIT model, resulted in Table 1 and the following mean value (± 2σ):

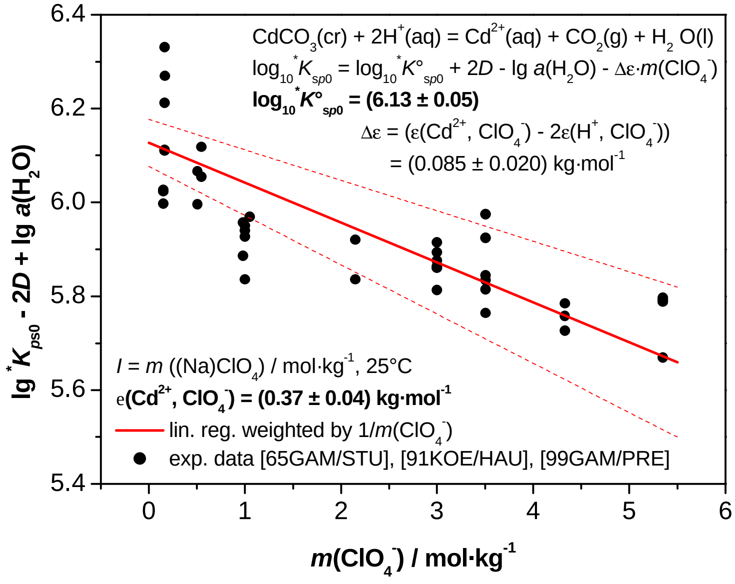
Table 1: Standard Gibbs energies of formation, eqs.(4, 5), and reaction, eq. (1), at 25°C

I / mol·kg^{-1}	$\Delta_\mathrm{f}G°$ ($\mathrm{Cd^{2+}}$) / kJ·mol^{-1}	- $\Delta_\mathrm{sol}G°$ / kJ·mol^{-1}	$\Delta_\mathrm{f}G°(\mathrm{CdCO_3})$ / kJ·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

$$\boldsymbol{\Delta_\mathrm{f}G°(\mathrm{CdCO_3}) = -\ (674.4 \pm 0.5)\ \mathrm{kJ\cdot mol^{-1}}}$$

- **$\Delta_\mathrm{f}H°(\mathrm{MCO_3}$, s, 298.15 K):** The solubility of otavite, $\mathrm{CdCO_3}$, is almost independent of temperature. The SIT analysis of (I, lg$^*K_{ps0}$) data at 25°C (see Figure 1) results in
  lg$^*K_{ps0}$($\mathrm{CdCO_3}$, 25°C, I = 1.0 mol·kg^{-1} $\mathrm{NaClO_4}$) = 6.45 ± 0.05.
  A least squares analysis of (T, lg$^*K_{ps0}$) data at I = 1.0 mol·kg^{-1} $\mathrm{NaClO_4}$ leads to
  lg$^*K_{ps0}$($\mathrm{CdCO_3}$, 25 – 75°C, I = 1.0 mol·kg^{-1} $\mathrm{NaClO_4}$) = 6.39 ± 0.14.

Fig. 1: SIT analysis of $CdCO_3$(cr) solubility



$\Delta_{sol}H°$ vanishes within the experimental uncertainty.

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

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

$\mathbf{\Delta_f H°(CdCO_3) = \Delta_f H°(Cd^{2+}) + \Delta_f H°(CO_2) + \Delta_f H°(H_2O) - \Delta_{sol} H°}$

$\Delta_f H°(CdCO_3) = - (755.3 \pm 5.6)\ kJ \cdot mol^{-1}$

- **$S°(MCO_3$, s, 298.15 K):** The standard entropy of $CdCO_3$ can also be estimated from this information.With CODATA values for $S°$ (Cd^{2+}), $S°(CO_2)$ and $S°(H_2O)$ one obtains

  $S°(CdCO_3) = S°\ (Cd^{2+}) + S°(CO_2) + S°(H_2O) - \Delta_{sol}S°$

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

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

  $S°(CdCO_3) = (103.9 \pm 0.2)\ J \cdot mol^{-1} \cdot K^{-1}$ [96ARC]
- **Recommended set of thermodynamic quantities:**

  $\mathbf{\Delta_f G°(CdCO_3) = -(674.4 \pm 0.5)\ kJ \cdot mol^{-1}}$

  $\mathbf{\Delta_f H°(CdCO_3) = -(752.3 \pm 0.5)\ kJ \cdot mol^{-1}}$

  $\mathbf{S°(CdCO_3) = (103.9 \pm 0.2)\ J \cdot mol^{-1} \cdot K^{-1}}$

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 $NiCO_3$(s). Reiterer synthesized neutral anhydrous nickel carbonate by a hydrothermal autoclave method. Thus well crystallized pure nickel carbonate, $NiCO_3$(cr), gaspéite, was obtained and investigated by the pH variation method (Fig. 2). Gamsjäger et al. synthesized $NiCO_3 \cdot 5.5H_2O$, 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:

$NiCO_3$, cr, 298.15 K	**$NiCO_3 \cdot 5.5H_2O$, cr, 298.15 K**
$\Delta_f G^\circ$ / kJ·mol^{-1} = – (636.4 ± 1.3)	**$\Delta_f G^\circ$ / kJ·mol^{-1} = – (1920.9 ± 1.0)**
$\Delta_f H^\circ$ / kJ·mol^{-1} = – (713.3 ± 1.4)	**$\Delta_f H^\circ$ / kJ·mol^{-1} = – (2313.0 ± 3.1)**
	S° / J·mol^{-1}·K^{-1} = (311.1 ± 10.0)

Fig. 2: Solubility of nickel carbonates

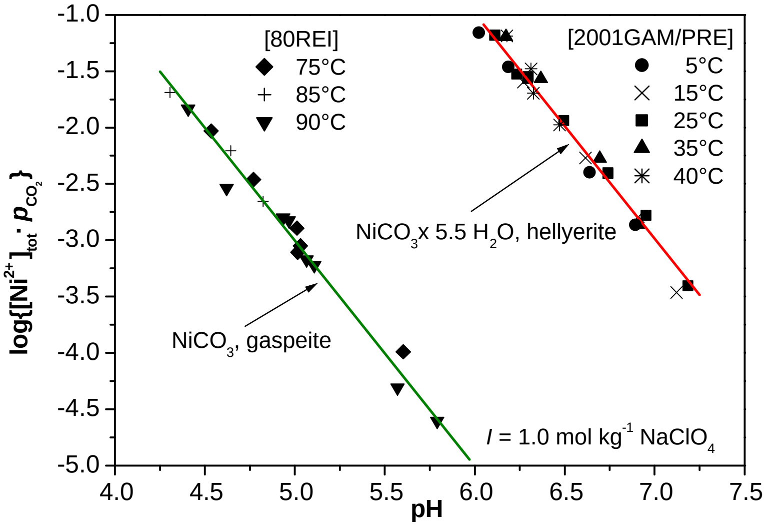


Fig. 3: Thermodynamic analysis of $NiCO_3 \cdot 5.5H_2O$ solubility

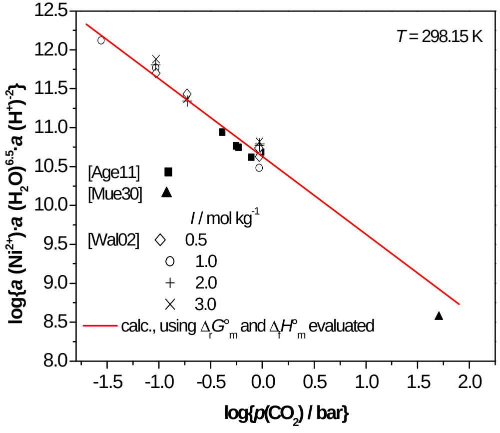
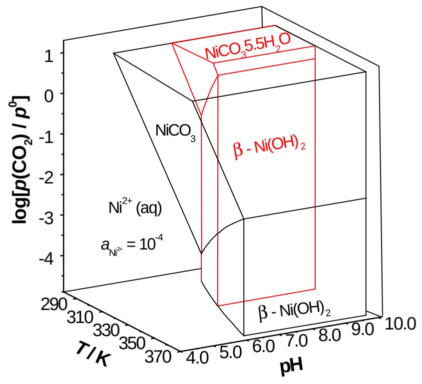


Fig. 4: Three-dimensional predominance diagram for the system Ni^{2+}-CO_2-H_2O



Solubility Measurements and/or Critical Evaluations are available for:

Formula	Mineral Name	Thermodynamic Analysis $\delta\log\{[M^{2+}] \cdot [H^+]^{-2}\} / \delta\log p(CO_2)$
$MnCO_3$	Rhodochrosite	-1.0
$FeCO_3$	Siderite	-1.0
$CoCO_3$	Spherocobaltite	-1.0
$NiCO_3$	Gaspéite	-1.0
$NiCO_3 \cdot 5.5H_2O$	Hellyerite	-1.0
$CuCO_3$	****	-1.0
$Cu_2(OH)_2CO_3$	Malachite	-1/2
$Cu_3(OH)_2(CO_3)_2$	Azurite	-2/3
$ZnCO_3$	Smithsonite	-1.0
$Zn_5(OH)_6(CO_3)_2$	Hydrozincite	-2/5
$CdCO_3$	Otavite	-1.0