

Thermodynamic Analysis of Solubility Measurements on Sparingly Soluble Ionic Solids with Basic Anions

Heinz Gamsjäger ^{a)}

^{a)}*Lehrstuhl für Physikalische Chemie, Montanuniversität Leoben, Leoben, Austria*

The solubility of sparingly soluble ionic solids with basic anions, such as metal oxides, hydroxides, basic salts, sulphides and carbonates, in water is thermodynamically characterized by the solubility product. Hydroxides, for example, of divalent metals dissolve according to



The equilibrium constant of this dissolution process is called solubility product:

$$K_{s0}^\circ = a(\text{M}^{2+}) \cdot a^2(\text{OH}^-),$$

it is connected to the standard molar Gibbs energy and the standard molar enthalpy of reaction (1), respectively, by

$$\Delta_{r1}G_m^\circ = -RT \ln K_{s0}^\circ \text{ and } \Delta_{r1}H_m^\circ = RT^2 (\partial \ln K_{s0}^\circ / \partial T)$$

The determination of the solubility product is in principle a straight forward method to evaluate the standard molar Gibbs energy of formation and the standard molar enthalpy of formation.

$$\begin{aligned} \Delta_f G_m^\circ(\text{M(OH)}_2, \text{cr}) &= \Delta_f G_m^\circ(\text{M}^{2+}, \text{aq}) + 2 \Delta_f G_m^\circ(\text{OH}^-, \text{aq}) - \Delta_{r1} G_m^\circ \\ \Delta_f H_m^\circ(\text{M(OH)}_2, \text{cr}) &= \Delta_f H_m^\circ(\text{M}^{2+}, \text{aq}) + 2 \Delta_f H_m^\circ(\text{OH}^-, \text{aq}) - \Delta_{r1} H_m^\circ \end{aligned}$$

For a methodological review of the experimental determination of solubilities of sparingly soluble ionic solids in aqueous solutions see ref.¹

Two prerequisites for obtaining reliable thermodynamic data from solubility measurements *i.e.* solubility products will be discussed.

- (1) The solid phase should be synthesized and characterized properly before and after the solubility measurement.

Case study: basic tin(II) chloride, $\text{Sn}_{21}\text{Cl}_{16}(\text{OH})_{14}\text{O}_6$, abhurite.

- (2) Effects of particle size on solubilities should be considered. The dissolution behaviour of nanodispersed particles is of current research interest.

Case study: nickel hydroxide, $\beta\text{-Ni(OH)}_2$, theophrastite.

¹H. Gamsjäger, E. Königsberger. *Solubility, of Sparingly Soluble Ionic Solids in Liquids*. In G. T. Hefter and R. P. T. Tomkins(Eds). *The Experimental Determination of Solubilities*. Wiley, Chichester, UK (2003), pp. 315-358.