Short Communication

Solid-Solute Phase Equilibria in Aqueous Solutions XVII [1].
Solubility and Thermodynamic Data of Nickel(II) Hydroxide

Heinz Gamsjäger*, Harald Wallner, and Wolfgang Preis
Institut für Physikalische Chemie, Montanuniversität Leoben, A-8700 Leoben, Austria

Summary. The solubility of nickel(II) hydroxide (theophrastite) in water was determined as a function of temperature and ionic strength by the pH variation method. In each experiment the inert electrolyte medium was made up with sodium perchlorate. The experimental data were thermodynamically analyzed, and the standard solubility constant was extrapolated to zero ionic strength with the specific ion-interaction equation. Furthermore, the standard molar Gibbs energy and the enthalpy of formation for theophrastite, β-Ni(OH)₂, were evaluated. For all calculations, ChemSage and its optimizer routine were used.

Keywords. Nickel hydroxide; Theophrastite; Solubility; Thermodynamic data.

Introduction

Recently, Plyasunova et al. have critically evaluated the thermodynamics of hydrolysis reactions and hydroxocomplexes of Ni²⁺ [2]. This review includes Nickel(II) hydroxide, and it is pointed out that the determination of its solubility product is a straightforward method to evaluate the standard Gibbs energy of formation, ΔfG°(Ni(OH)₂(cr)). This is in principle correct; however, it presumes that indeed the solubility product or any appropriate solubility constant (as for example defined by Eq. (1)) of the respective phase has been determined.

\[
\text{Ni(OH)}_2(\text{cr}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Ni}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \tag{1}
\]

Actually, most solubility data of Ni(OH)₂ reported so far suffer from an uncertainty in the physical state of the solid investigated [3–11]. This is surprising, because in a comprehensive review on nickel(II) hydroxide it has been clearly pointed out that, apart from the well defined β-Ni(OH)₂ named theophrastite thereafter [12], a number of basic salts of changing composition exist [13]. When nickel hydroxide is

* Corresponding author. E-mail: gamsjaeg@unileoben.ac.at
precipitated from aqueous NiCl₂, Ni(NO₃)₂, or NiSO₄ with NaOH or KOH solutions it is always contaminated with basic salts. The solubility of the latter varies depending on the anion and the molar ratio OH/Ni. This means that solubility studies on poorly defined nickel hydroxide or the respective basic salts are useless as an experimental basis to derive accurate thermodynamic functions of nickel(II) hydroxide. The most careful solubility study reported was carried out by Mattigod et al., but according to their preparative method the respective results refer to a microcrystalline probably chloride containing $\beta$-Ni(OH)₂ [14].

As this solid phase is of considerable importance for the deposition and remobilization of nickel, an effort to obtain reliable thermodynamic data of pure, well crystallized theophrastite was made in this work. Thus, $\beta$-Ni(OH)₂ was synthesized by an improved method, and its solubility was measured at varying temperatures and ionic strengths. This task turned out more difficult than expected, because the solutions approaching saturation with solid Ni(OH)₂ are poorly buffered by solute species, whereas buffering by the solid–liquid equilibrium is ineffective as it is attained only slowly due to the notorious inertness of Ni²⁺ at 25°C. The solubility was measured at elevated temperatures (35–80°C) to speed up equilibration; thus, a consistent set of the thermodynamic quantities $\Delta_f G^\ominus$ and $\Delta_f H^\ominus$ for theophrastite can be proposed.

Results and Discussion

In a first series of solubility experiments on theophrastite the temperatures were varied between 35 to 80°C, and the ionic strength was kept constant at 1.0 mol·kg⁻¹ NaClO₄. Figure 1 shows results typical for the pH-variation method [15]. Data of log [Ni²⁺]ₕν plotted vs. $p[H]^1$ fall on straight lines with the theoretical slope of −2.0.

At 50°C a second series of solubility measurements was carried out at different ionic strengths varying from 0.5 to 3.0 mol·kg⁻¹ NaClO₄. The Specific Ion-Interaction Theory (SIT, [16]) was applied to extrapolate log$^*$K$^{0}$₀ defined by Eq. (1) to infinite dilution. In Fig. 2, the solubility constant log$^*$K$^{0}$₀ is plotted as a function of temperature. It is quite obvious that i) the scatter of the published data at $\theta \leq 25^\circ$C exceeds the usual experimental error by orders of magnitude and ii) solubility measurements carried out with carefully prepared theophrastite lead to closer error limits and a more reliable prediction of thermodynamic quantities. $\Delta_f G^\ominus$ and $\Delta_f H^\ominus$ of $\beta$-Ni(OH)₂ (cr) were estimated using the Bayesian algorithm implemented in the ChemSage optimizing routine [17]. The data measured at 25°C were given a lower weight, because even after an equilibration period of more than 5 weeks the pH readings remained noisy. Thermodynamic auxiliary data of H₂O were taken from CODATA [18], whereas data of Ni²⁺ were taken from the NBS tables [19] rather than from Plyasunova et al. [2], because the latter quantities agree anyway within the error limits given with the former. It turned out that Ni hydroxo complexes were negligible in the pH range considered. In Table 1 the thermodynamic properties of Ni(OH)₂ obtained in this work and by Plyasunova

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1 The square brackets of $p[H]$ indicate that in fact H⁺-ion molalities were measured with the calibration system used