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Short Communication

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

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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 Ni^{2+} [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, $\Delta_f G^\ominus(Ni(OH)_2(cr))$. 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.

$$Ni(OH)_2(cr) + 2H^+(aq) \rightleftharpoons Ni^{2+}(aq) + 2H_2O(l) \qquad (1)$$

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

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precipitated from aqueous $NiCl_2$, $Ni(NO_3)_2$, or $NiSO_4$ 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 β-$Ni(OH)_2$ [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, β-$Ni(OH)_2$ 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 Ni^{2+} 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 $1.0\,mol \cdot kg^{-1}$ $NaClO_4$. Figure 1 shows results typical for the *pH*-variation method [15]. Data of $\log\,[Ni^{2+}]_{tot}$ 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 $3.0\,mol \cdot kg^{-1}$ $NaClO_4$. The Specific Ion-interaction Theory (SIT, [16]) was applied to extrapolate $\log{}^*K^0_{s0}$ defined by Eq. (1) to infinite dilution. In Fig. 2, the solubility constant $\log{}^*K^0_{s0}$ is plotted as a function of temperature. It is quite obvious that *i*) the scatter of the published data at $\theta \leq 25$°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 β-$Ni(OH)_2$ (cr) were estimated using the *Bayes*ian 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 H_2O were taken from CODATA [18], whereas data of Ni^{2+} 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

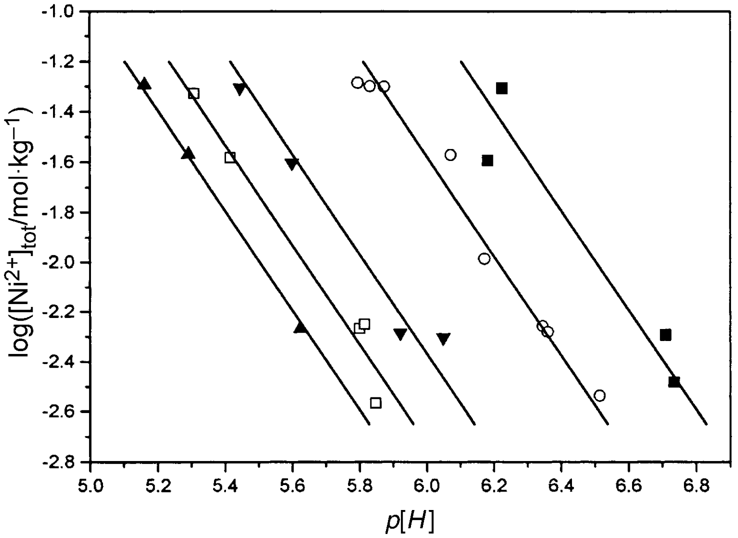

Fig. 1. Solubility of theophrastite as determined by the pH variation method; θ/°C: 80 ▲, 70 □, 60 ▼, 50 ○, 35 ■; solid straight lines: calculated with mean values of $\log{}^{*}K^{I}_{s0}$ and theoretical slope $= -2.0$; $I = 1.0\,\mathrm{mol \cdot kg^{-1}}$ $NaClO_4$

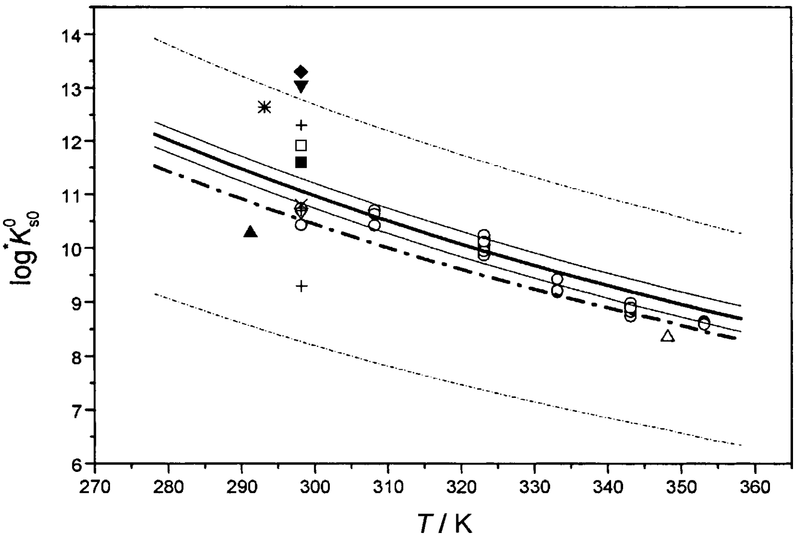

Fig. 2. Solubility constant of $Ni(OH)_2$ as a function of temperature; thick solid curve: optimized from experimental data of this work; thin solid curves: corresponding error limits; thick dash-dot curve: calculated according to Ref. [2]; thin dash-dot curves: corresponding maximal error limits; ○: this work, ▽: Ref. [4], ×: Ref. [7] (aged), □: Ref. [14], +: Ref. [10] (high value: slow, low value: fast precipitation), ▲: Ref. [3], ■: Ref. [5], ∗: Ref. [8], ▼: Ref. [9], ◆: Ref. [7] (freshly prepared), △: Ref. [6]

et al. are compared. The latter authors overlooked a direct calorimetric determination of $S^{\ominus}$ of $Ni(OH)_2$ (cr) [20] which found its way into the recommended thermodynamic data of nickel compounds [21]. For the iterative optimization algorithm of this work, the calorimetrically measured $S^{\ominus}$ (β-($Ni(OH)_2$)/$\mathrm{J \cdot mol^{-1} \cdot}$

Table 1. Thermodynamic properties of $Ni(OH)_2$

$T_0/\mathrm{K} = 298.15$	$Ni(OH)_2^a$	Ref.	β-$Ni(OH)_2^b$	Ref.
$\log{}^*K^0_{s0}$ (Eq. (1))	10.5 ± 1.3	[2]	11.1 ± 0.2	this work
$\Delta_{sol}H^{\ominus}/\mathrm{kJ \cdot mol^{-1}}$	-78.7 ± 10.2	[2]	-84.1 ± 1.0	this work
$\Delta_{sol}S^{\ominus}/\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	-63.1 ± 10.4	[2]	-69.0 ± 3.0	this work
$\Delta_f G^{\ominus}/\mathrm{kJ \cdot mol^{-1}}$	-459.7 ± 6.9	[2]	-456.4 ± 3.5	this work
$\Delta_f H^{\ominus}/\mathrm{kJ \cdot mol^{-1}}$	-547.1 ± 9.9	[2]	-541.6 ± 2.7	this work
$S^{\ominus}/\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	73 ± 10	[2]	80.0 ± 0.4	[20, 21]

[a] Uncertainties are taken from *Plyasunova et al.* [2]; [b] uncertainties based on $\Delta\log{}^*K^I_{s0} = \pm 0.2(2\sigma)$ as estimated from the experiments

$\mathrm{K^{-1}} = 80.0$ was kept fixed and $S^{\ominus}$ $(Ni^{2+})/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = -130.0 \pm 3.0$ were taken as starting value and error limits, respectively [2, 21]. The latter value was changed only insignificantly (-130.7) by the optimization procedure. Thus, based on solubility data, the precision and reliability of $\Delta_f G^{\ominus}$ and $\Delta_f H^{\ominus}$(β-$Ni(OH)_2$) can be improved considerably.

The synthesis and characterization of β-$Ni(OH)_2$ is described in more detail in Ref. [22], where all numerical values of the solubility data can be found as well.

Experimental

Analytical grade reagents, bidistilled H_2O, and prehumidified high purity (99.999%) N_2 gas, high purity $Ni(ClO_4)_2 \times 6\ H_2O$, and NaOH were employed throughout. Solubility measurements were performed at constant ionic strength of $1.0\,\mathrm{mol \cdot kg^{-1}}$ $NaClO_4$ in glass jacketed cells [23, 24] thermostatted to ± 0.03 at 25 to 80°C. In addition, the solubility was also determined at 50°C and different ionic strengths (0.5, 1.0, 2.0, 3.0 $\mathrm{mol \cdot kg^{-1}}$ $NaClO_4$). The galvanic cell can be represented as

$$\mathrm{Ag}\ |\mathrm{AgCl}|\ 0.10\,\mathrm{mol \cdot kg^{-1}}\ \mathrm{NaCl}, 0.90\,\mathrm{mol \cdot kg^{-1}}\ \mathrm{NaClO_4}|$$

$$1.00\,\mathrm{mol \cdot kg^{-1}}\ \mathrm{NaClO_4}|\text{test solution } (I_c = 1.00\,\mathrm{mol \cdot kg^{-1}} (\mathrm{Na})\mathrm{ClO_4})|\mathrm{GE}$$

where GE is a glass electrode (Schott H 1180). The Ag | AgCl reference electrodes of thermal-electrolytic type were home-made and employed with *Wilhelm*-type salt bridges [25]. Details of the potentiometric measurements and the electrode calibration are given in Ref. [26]. The concentration of Ni^{2+} was determined by complexometric titration.

For the preparation of theophrastite the method of *Scholder* and *Giesler* was modified [27]. In a teflon flask, 152 g NaOH and 48 g H_2O were heated to 140°C. When all NaOH pellets were melted an aqueous solution prepared of 10 g $Ni(ClO_4)_2 \times 6\ H_2O$ and 6 g H_2O was added dropwise. A pale-green amorphous precipitate formed rapidly and was transformed into olive-green crystals by keeping the solution at 140°C for 24 h. The teflon flask was equipped with a reflux condenser and an electromagnetic stirrer. The use of teflon was necessary because the mixture corrodes the conventional laboratory glassware rapidly. When the reaction is finished, an olive-green coarse-crystalline precipitate can be located on the bottom of the flask. The major part of the molten NaOH is removed, and well crystallized $Ni(OH)_2$ with crystal sizes of about 0.1 mm is obtained by boiling the reaction product in H_2O for 24 h. The mother liquor was sucked off, and the precipitate was washed free of NaOH with water. After removing most of the H_2O with EtOH, the crystals were dried in a hot-air cabinet at 100°C. At higher temperatures (above 200°C) theophrastite decomposed to nickel oxide.

The X-ray data of β-$Ni(OH)_2$ prepared by the method described above were taken before and after the dissolution experiment and agreed closely with those given in the JCPDS-ICDD card 14–117.

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