Monatshefte für Chemie 132, 411–415 (2001)

Monatshefte für Chemie
Chemical Monthly

Short Communication

Solid-Solute Phase Equilibria in Aqueous Solutions XIV [1]. Thermodynamic Analysis of the Solubility of Hellyerite in Water

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Summary. The solubility of hellyerite, $NiCO_3 \cdot 6H_2O$, in water was studied at different temperatures. From the experimental data obtained, a preliminary set of the thermodynamic quantities $\Delta_f G^\ominus$, $\Delta_f H^\ominus$, and $S^\ominus$ for hellyerite was derived using the ChemSage optimizer routine.

Keywords. Nickel carbonates; Hellyerite; Solubility; Thermodynamic data.

Introduction

Nickel carbonates are simple chemical compounds of industrial and geochemical importance. Consequently, one would expect that their thermochemical quantities are sufficiently well known. However, a closer look into the literature shows that this view is too optimistic. The *Gibbs* energies of formation, $\Delta_f G^\ominus$, of $NiCO_3$, gaspèite, listed in compilations of thermodynamic data [2–4] and derived from solubility measurements [5, 6] differ by 17 to $34\,kJ \cdot mol^{-1}$. Seemingly, the solubility of $NiCO_3$ was studied by *Ageno* and *Valla* for the first time [7]; however, in their preliminary communication the authors described no attempt to characterize the chemical and physical state of the samples investigated. Regardless of this uncertainty the result was ascribed to anhydrous $NiCO_3$ and found its way into thermodynamic compilations [8, 9]. *Müller* and *Luber* [10] determined a single value of the solubility of nickel carbonate hydrate, $NiCO_3 \cdot 6H_2O$, at $p(CO_2) = 50\,atm$ without giving the temperature of equilibration explicitly. When it is tentatively assumed that the experiment was carried out at 25°C, their result agrees fairly well with data given in Ref. [7], indicating that the same nickel carbonate phases have been used in both studies. On the other hand, the solubilities of synthetic gaspèite, $NiCO_3$, determined by *Gamsjäger et al.* [5, 6] are at least three orders of magnitude lower and confirm the suspicion that data related to $\Delta_f G^\ominus(NiCO_3 \cdot 6H_2O)$ have erroneously been employed to determine $\Delta_f G^\ominus(NiCO_3)$.

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To clarify the situation, hellyerite was synthesized and its solubility as a function of temperature was determined. Based on the formula $NiCO_3 \cdot 6H_2O$, a preliminary set of the thermodynamic quantities $\Delta_f G^\ominus$, $\Delta_f H^\ominus$, and $S^\ominus$ for hellyerite is proposed.

Results and Discussion

Synthesis of hellyerite

Williams et al. [11] and *Threadgold* [12] have described natural hellyerite, $NiCO_3 \cdot 6H_2O$, and synthesized it artificially using the method of *Rossetti-François* [13]. This method resulted in tiny and partially amorphous particles. The amorphous particles were dissolved, and larger crystals ($d = 0.1$ mm) were obtained when Ni^{2+} was kept in excess and the solution was slowly acidified by CO_2. This new method is described in detail in the experimental section.

The stoichiometric composition of hellyerite is not yet quite clear. The X-ray density according to the unit cell proposed by *Threadgold* [12] results in $\varrho = 2.04\,\mathrm{g \cdot cm^{-3}}$, whereas a value of $1.97\,\mathrm{g \cdot cm^{-3}}$ is found experimentally. This discrepancy can probably be explained by a stoichiometric formula of $NiCO_3 \cdot 5.5H_2O$ instead of $NiCO_3 \cdot 6H_2O$ [11]. This agrees with the chemical analysis of our hellyerite samples, which gave mass fractions $w(\mathrm{NiO}) = 0.3468$ (0.3430)[1], $w(\mathrm{CO_2}) = 0.2021$ (0.2023), and $w(\mathrm{H_2O}) = 0.4482$ (0.4549). The thermodynamic calculations of this work are based on the conventional formula $NiCO_3 \cdot 6H_2O$ which is apparently generally accepted [14]. It should be noted, however, that presently neither the structure nor the stoichiometry of hellyerite are definitively known. A study to elucidate this aspects has been initiated.

Solubility constant of hellyerite

X-Ray diffractograms of hellyerite samples taken before and after solubility measurements confirmed that no other phase was formed during the experiments. The solubility constant, ${}^*K^{I}_{ps0} = [\mathrm{Ni}^{2+}] \cdot p_{\mathrm{CO_2}} \cdot [\mathrm{H}^+]^{-2}$, of hellyerite according to Eq. (1) exceeds the solubility constant of gaspèite, $NiCO_3$, by almost three and a half orders of magnitude. The experimental values for the solubilities of hellyerite and gaspèite are depicted in Fig. 1.

$$\mathrm{NiCO_3 \cdot 6H_2O(s) + 2H^+}(I) \rightleftharpoons \mathrm{Ni^{2+}}(I) + \mathrm{CO_2(g) + 7H_2O}(I) \qquad (1)$$

Data of $\log([\mathrm{Ni}^{2+}]_{\mathrm{tot}} \cdot p_{\mathrm{CO_2}})$ plotted *vs.* p[H] fall on almost the same straight line with the theoretical slope of −2, although the temperatures were varied between 75 to 90°C for nickel carbonate and between 5 to 40°C for nickel carbonate hexahydrate[2]. From the weak temperature dependence of the solubility constants (Fig. 2) $\Delta_f H^\ominus$ and $S^\ominus$ of hellyerite were estimated using the ChemSage optimizing routine [16]. In this procedure, data on the ionic strengths dependence not shown in this

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[1] Numbers in parentheses refer to $NiCO_3 \cdot 5.5H_2O$

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

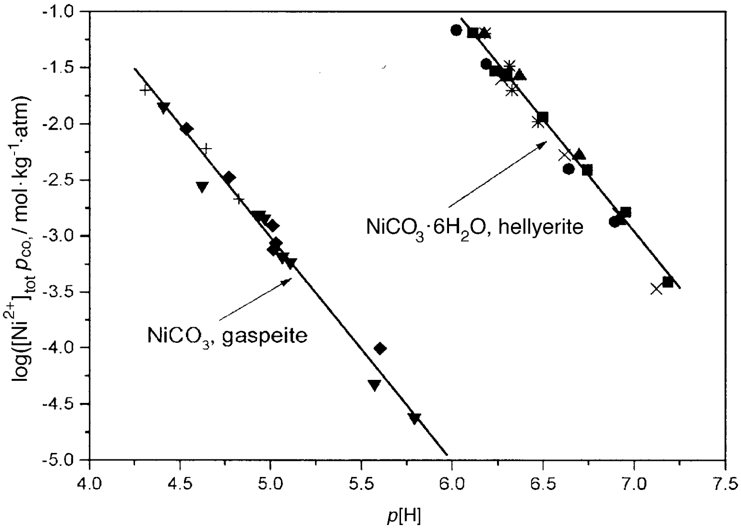

Fig. 1. Solubility of nickel carbonates, $I = 1.0\,\mathrm{mol \cdot kg^{-1}}$ $NaClO_4$; *Reiterer* [15]: ◆ 75°, + 85°C, ▼ 90°C; this work: ● 5°, × 15°, ■ 25°, ▲ 35°, * 40°C; solid lines: slope $= -2$; the mole fractions of carbon dioxide in the CO_2/N_2 gas mixtures varied between 0.01 and 1.00

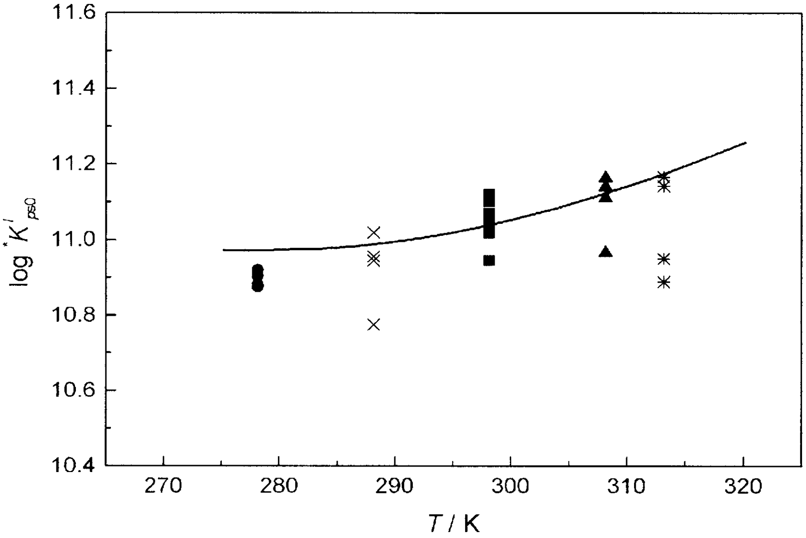

Fig. 2. Temperature dependence of $NiCO_3 \cdot 6H_2O$ solubility; $I = 1.0\,\mathrm{mol \cdot kg^{-1}}$ $NaClO_4$; ● 278, × 288, ■ 298, ▲ 308, * 313 K. solid curve: calculated according to the SIT model [19] with the interaction parameter $\epsilon(Ni^{2+}, ClO_4^-) = 0.36$ derived from osmotic coefficient data of $Ni(ClO_4)_2$-H_2O solutions [20]

paper were also included. Thermodynamic auxiliary data of H_2O and CO_2 were taken from CODATA [17], whereas data of Ni^{2+} were taken from the NBS tables [18]. It turned out that the presence of Ni hydroxo complexes could be neglected in the *pH* range considered. The preliminary set of thermodynamic properties given in Table 1 is recommended for $NiCO_3$ and $NiCO_3 \cdot 6H_2O$. If $\Delta_f G^\ominus(NiCO_3)$ in data

Table 1. Thermodynamic properties of $NiCO_3$ and $NiCO_3 \cdot 6H_2O$

$T_0/K = 298.15$	$NiCO_3$	Ref.	$NiCO_3 \cdot 6H_2O$	Ref.
$\log {}^*K^0_{ps0}$	7.12 ± 0.18	[5]	10.64 ± 0.10	this work
$\Delta_{sol}H^\ominus/kJ \cdot mol^{-1}$	–	–	8.3 ± 3.0	this work
$\Delta_f G^\ominus/kJ \cdot mol^{-1}$	-636.5 ± 1.4	[6]	-2039.2 ± 1.1	this work
$\Delta_f H^\ominus/kJ \cdot mol^{-1}$	-713.4 ± 1.6	this work	-2456.7 ± 3.1	this work
$S^\ominus/J \cdot mol^{-1} \cdot K^{-1}$	85.4 ± 2.0	[21]	343 ± 10	this work

compilations can be traced back to experimental information given in Refs. [7] and/or [10], it should be replaced by the value of Table 1.

Experimental

Analytical grade reagents, bidistilled water, and prehumidified high purity (99.996%) CO_2 gas or defined CO_2/N_2 mixtures were employed throughout. Solubility measurements were performed by the *pH* variation method at a constant ionic strength of $1.0\,mol \cdot kg^{-1}$ $NaClO_4$ in glass jacketed cells [22, 23] thermostatted to ±0.03 at 5 to 40°C. The galvanic cell can be represented as

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

$$1.00\,mol \cdot kg^{-1}\ NaClO_4|\ \text{test solution}\ [I_c = 1.00\,mol \cdot kg^{-1}\ NaClO_4]|GE$$

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 [24]. Details of the potentiometric measurements and the electrode calibration are given in Ref. [25]. The concentration of Ni^{2+} was determined by complexometric titration.

The preparation of hellyerite was achieved by dropwise addition of 100 g of $1.5\,mol \cdot kg^{-1}$ Na_2CO_3 to 700 g of $0.25\,mol \cdot kg^{-1}$ $NiCl_2$ at 0°C. A pale green amorphous precipitate formed rapidly and was transformed at 0°C to bluish green hellyerite by bubbling carbon dioxide for three days through the solution. The mother liquor was sucked off *via* a glass filter funnel, the precipitate was washed free of chloride with water, and most of the remaining water was removed with ethanol. Finally, the crystals were dried to constant weight in a desiccator over silica gel at room temperature (*ca*. 23°C). The purity of the hellyerite was checked by chemical and X-ray diffraction analyses.

Acknowledgements

The authors would like to sincerely thank Ms. *W. Dolezel* (Veitsch-Radex AG, Leoben) and Mr. *H. Mülhans* (University of Leoben) for the X-ray diffraction analyses. We are also grateful to Dr. *Hans Wanner* (*Paul Scherrer* Institute, Villigen, Switzerland) for valuable comments.

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Received January 16, 2001. Accepted January 18, 2001