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Solid–solute phase equilibria in aqueous solutions XV [1]. Thermodynamic analysis of the solubility of nickel carbonates

Harald Wallner, Wolfgang Preis, Heinz Gamsjäger*

Institut für Physikalische Chemie, Montanuniversität Leoben, A-8700 Leoben, Austria

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Abstract

The aqueous solubilities of hellyerite, $NiCO_3 \cdot 6H_2O$, and gaspéite, $NiCO_3$, were thermodynamically analyzed to obtain the respective standard molar quantities of formation $\Delta_f G_m^\ominus$ and $\Delta_f H_m^\ominus$. For the molar entropy, $S_m^\ominus$ ($NiCO_3 \cdot 6H_2O$), no direct calorimetric measurements are available, so it was derived from solubility data also. Solubility constants extrapolated to infinite dilution using the specific ion-interaction theory and the Pitzer equations, respectively, agreed with each other within the experimental uncertainty. All calculations were carried out with the ChemSage optimizer and based on auxiliary quantities which were either recommended by CODATA or recently critically evaluated. The following set of thermodynamic data for $NiCO_3 \cdot 6H_2O$ and $NiCO_3$ (numerical values of the latter in brackets) were obtained at $T = 298.15\,K$: solubility constant, $\log^* K_{ps0}^0 = [Ni^{2+}] \times p_{CO_2} \times [H^+]^{-2} = 10.64 \pm 0.10\,(7.12 \pm 0.18)$; standard Gibbs energy of formation, $\Delta_f G_m^\ominus\,(kJ\,mol^{-1}) = -2039.2 \pm 1.1\,(-636.5 \pm 1.4)$; standard enthalpy of formation, $\Delta_f H_m^\ominus\,(kJ\,mol^{-1}) = -2456.7 \pm 3.1\,(-713.4 \pm 1.6)$; standard entropy, $S_m^\ominus(NiCO_3 \cdot 6H_2O)\,(J\,mol^{-1}\,K^{-1}) = 343 \pm 10$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nickel carbonates; Gaspéite; Hellyerite; Solubility; Thermodynamic data

1. Introduction

It was shown recently in a short communication that data obtained from $NiCO_3 \cdot 6H_2O$, hellyerite, were erroneously ascribed to $NiCO_3$, gaspéite [1], whereas measurements on the latter phase never made their way into compilations of thermodynamic quantities [2,3]. Nickel carbonates are used in industry as catalysts and occur as minerals in various natural deposits [4–6]. For modeling potential risks of nickel contamination in aquatic systems a reliable thermodynamic data base of nickel carbonates is still lacking.

This work reports solubility data of $NiCO_3 \cdot 6H_2O$ and $NiCO_3$. The pH variation method was employed to investigate the temperature and ionic strength dependence of the solubility constants defined by Eqs. (1) and (2), where I designates the ionic medium predominantly consisting of $NaClO_4$:

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

$$NiCO_3(s) + 2H^+(I) \rightleftharpoons Ni^{2+}(I) + CO^2(g) + H_2O(I) \quad (2)$$

Solubility measurements are especially valuable for the determination of internally consistent sets of thermodynamic data for these carbonates, because other

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* Corresponding author. Fax: +43-3842-40-2335.
E-mail address: gamsjaeg@unileoben.ac.at (H. Gamsjäger).

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methods turned out to be less convenient. Thus at the low transition temperature of the reaction due to Eq. (3) the equilibrium pressure of decomposition is difficult to obtain:

$$\mathrm{NiCO_3 \cdot 6H_2O(s) \rightleftharpoons NiO(s) + CO_2(g) + 6H_2O(g)} \tag{3}$$

From the hydrothermal *T*, *P* decomposition curve of the reaction according to Eq. (4) $\Delta_f G_m^\ominus$ and $\Delta_f H_m^\ominus$ of gaspéite were calculated [7]. The respective values are 8–10 kJ mol^{-1} higher than those derived from solubility studies, where pure synthetic $NiCO_3$ was investigated [2,3]. A detailed description of the material used for the decomposition experiments is lacking:

$$\mathrm{NiCO_3(s) \rightleftharpoons NiO(s) + CO_2(g)} \tag{4}$$

Furthermore, the calorimetric determination of dissolution enthalpies according to Eqs. (1) and (2) are bound to be inaccurate, because the results depend to a high extent on the state of carbon dioxide and it is

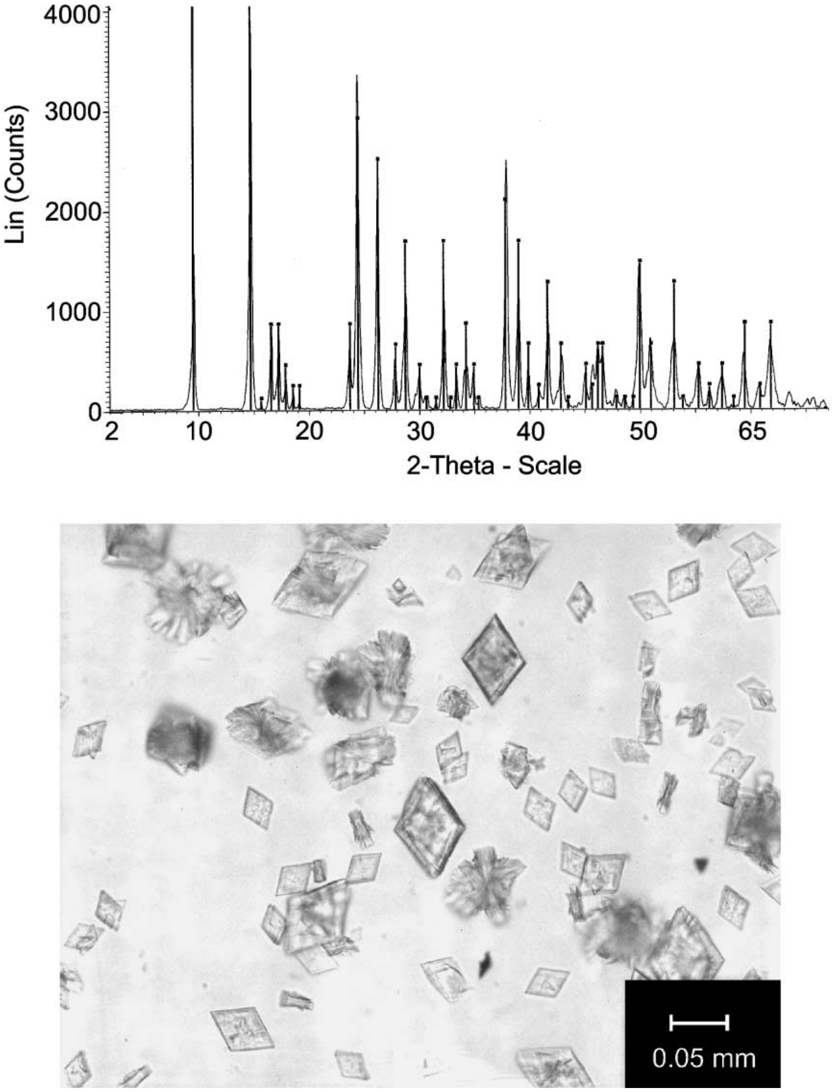

Fig. 1. X-ray diagram (Cu Kα radiation) and photomicrograph of crystalline hellyerite. Thin line: X-ray data of our sample; thick line: X-ray data of JCPDS-ICDD card 12-276.

quite difficult to keep CO_2 quantitatively either in solution or in the gas phase [8].

The ChemSage optimizer routine was utilized for a comprehensive thermodynamic analysis [9] of all experimental data and their comparison with literature values [10,11].

2. 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.

2.1. Synthesis of hellyerite

The first preparation of artificial hellyerite was described by Rossetti-François [12]. With this method tiny and partially amorphous particles were obtained. Therefore, a new method was developed: 100 g of an aqueous solution containing 1.5 mol kg^{-1} Na_2CO_3 were added dropwise to 700 g of 0.25 mol kg^{-1} $NiCl_2$ solution at 0 °C. A pale green amorphous precipitate formed rapidly and was transformed to bluish green hellyerite by bubbling carbon dioxide for 3 days through the solution thermostatted to 0 °C. Still larger crystals formed in solutions of 0.5 mol kg^{-1} Ni^{2+} and 0.1 mol kg^{-1} $NaHCO_3$ after a treatment prolonged for 3 weeks. The mother liquor was sucked off and the precipitate washed free of chloride with water. After removing most of the water, the crystals were dried in a desiccator over silica gel at room temperature. At higher temperatures (above 50 °C) the well crystallized hellyerite decomposed to apple green amorphous carbonates. The X-ray data of hellyerite prepared by the new method agreed satisfactorily with those given in the JCPDS-ICDD card 12-276 (see Fig. 1).

2.2. Solubility

Solubility data of $NiCO_3$ at $I = 1.0$ and 0.20 mol kg^{-1} $NaClO_4$ at $T = 348.15, 358.15,$ and 363.15 K were taken from previous work and are listed in Table 1 [13,14].

Solubility measurements of hellyerite were carried out at different ionic strengths of $NaClO_4$ ($I = 0.5$, 1.0, 2.0, and 3.0 mol kg^{-1}) at 25 °C. In addition, the solubility was also determined at an ionic strength of

Table 1
Solubility data of $NiCO_3$ from Reiterer [13]

T (K)	I (mol kg^{-1})	p_{CO_2} (bar)	$10^3 \times H^a$ (mol kg^{-1})	$10^5 \times [H^+]$ (mol kg^{-1})	$10^3 \times [Ni^{2+}]_{tot}^{exp}$ (mol kg^{-1})	$\log^* K_{ps0}^I$
348.15	1.0	0.5934	30.0	2.9242	15.210	7.023
	1.0	0.5632	10.0	1.6982	5.921	7.063
	1.0	0.5618	3.0	0.9727	2.210	7.118
	1.0	0.5603	1.0	0.9638	1.352	6.911
	1.0	0.0574	30.0	0.9333	15.080	6.997
	1.0	0.0575	3.0	0.2500	1.723	7.200
358.15	1.0	0.3961	100.0	4.9431	50.120	6.910
	1.0	0.3947	30.0	2.2699	15.240	7.067
	1.0	0.3882	10.0	1.4997	5.520	6.979
363.15	1.0	0.2816	100.0	3.9264	50.370	6.964
	1.0	0.2882	30.0	2.3933	15.420	6.890
	1.0	0.2763	10.0	1.1614	5.561	7.057
	1.0	0.2803	3.0	0.8609	2.331	6.945
	1.0	0.2724	1.0	0.7798	2.133	6.980
	1.0	0.0283	100.0	1.0789	50.940	7.093
	1.0	0.0274	3.0	2.6792	1.743	6.823
	1.0	0.0275	1.0	0.1644	0.873	6.964
	0.2	0.272	30.0	2.2909	13.030	6.822
	0.2	0.267	1.0	0.6607	0.598	6.557
	0.2	0.253	10.0	1.9498	4.828	6.496

[a] H designates the initial H^+ molality.

1.0 mol kg^{-1} and different temperatures (5, 15, 35 and 40 °C). The pH variation method was used to study the dissolution reaction according to Eq. (1). The galvanic cell for pH measurement can be represented as

$$\mathrm{Ag|AgCl|0.10\,mol\,kg^{-1}\;NaCl,\;0.90\,mol\,kg^{-1}\;NaClO_4|1.00\,mol\,kg^{-1}\;NaClO_4|test\;solution\;[\mathit{I}_c = 1.00\,mol\,kg^{-1}\;(Na)ClO_4]|GE}$$

where GE is a glass electrode (Schott H 1180). The AglAgCl reference electrodes of thermal-electrolytic type were home made and employed with Wilhelm-type salt bridges [15]. Details of the potentiometric measurements and the electrode calibration are given in [16]. The concentration of Ni^{2+} was determined by complexometric titration. The crystals used were X-rayed before and after the dissolution experiment, but always only the characteristic peaks of hellyerite were found (see Fig. 1).

Table 2
Solubility of $NiCO_3 \cdot 6H_2O$

T (K)	I (mol kg^{-1})	p_{CO_2} (bar)	$10^3 \times H^a$ (mol kg^{-1})	$10^7 \times [H^+]$ (mol kg^{-1})	$10^3 \times [Ni^{2+}]_{tot}^{exp}$ (mol kg^{-1})	$\log^* K_{ps0}^I$
298.15	0.5	0.1845	10.0	1.8549	20.970	11.050
	0.5	0.0926	5.0	1.1866	15.718	11.014
	0.5	0.9131	10.0	5.1431	33.080	11.057
	0.5	0.9226	100.0	8.4644	73.031	10.995
	1.0	0.9200	10.0	5.8264	32.450	10.945
	1.0	0.9183	3.0	5.0254	30.270	11.040
	1.0	0.9249	0.0	5.0690	28.880	11.017
	1.0	0.9236	100.0	7.7109	70.060	11.036
	1.0	0.0921	10.0	1.1117	17.750	11.120
	1.0	0.0922	50.0	1.8126	41.641	11.067
	1.0	0.9255	100.0	7.6809	70.228	11.042
	1.0	0.0933	3.0	1.0430	14.740	11.101
	1.0	0.1852	10.0	1.8197	21.042	11.070
	2.0	0.1832	10.0	1.7283	17.198	11.023
	2.0	0.0919	10.0	0.8712	12.690	11.186
	2.0	0.9240	100.0	6.5426	69.231	11.174
	2.0	0.9286	10.0	4.3139	30.390	11.181
	3.0	0.9180	10.0	3.5800	27.630	11.296
	3.0	0.1851	10.0	1.2862	17.631	11.295
	3.0	0.9266	100.0	6.0312	66.513	11.229
	3.0	0.0926	0.0	0.7754	12.212	11.274
278.15	1.0	0.9440	100.0	9.4779	72.250	10.880
	1.0	0.1901	10.0	2.2943	20.779	10.875
	1.0	0.9492	10.0	6.5108	35.801	10.904
	1.0	0.0937	0.0	1.2740	14.415	10.920
288.15	1.0	0.0938	10.0	1.2311	16.890	11.019
	1.0	0.0936	100.0	2.4217	56.681	10.956
	1.0	0.9244	0.0	5.3327	27.120	10.945
	1.0	0.0283	10.0	0.5569	12.001	10.775
308.15	1.0	0.9017	0.0	4.2794	29.620	11.163
	1.0	0.1803	3.0	2.0773	29.070	11.110
	1.0	0.0888	10.0	1.2211	15.364	10.966
	1.0	0.8885	100.0	6.7011	70.890	11.140
313.15	1.0	0.8758	30.0	4.8620	37.400	11.142
	1.0	0.8883	0.0	4.7213	22.370	10.950
	1.0	0.0874	3.0	1.1290	11.290	10.889
	1.0	0.8824	100.0	6.6130	72.561	11.166

[a] H designates the initial H$^+$ molality.

3. Results and discussion

Driven by an intrinsic tendency to enhance the low crystal symmetry hellyerite forms predominantly twin crystals. Therefore, its crystal structure remains still unclear, as the indexing of the X-ray peaks proposed by Threadgold [6] seems to be doubtful. Special methods are necessary to solve such structural problems which in the present case are further complicated by the fact that the nuclei of most of the larger crystals (0.1 mm) are turbid. Hellyerite is probably build up by alternating layers consisting of ions (Ni^{2+}, $CO_3{}^{2-}$) and H_2O, respectively [6]. This layer structure with its unknown arrangement of H_2O molecules is

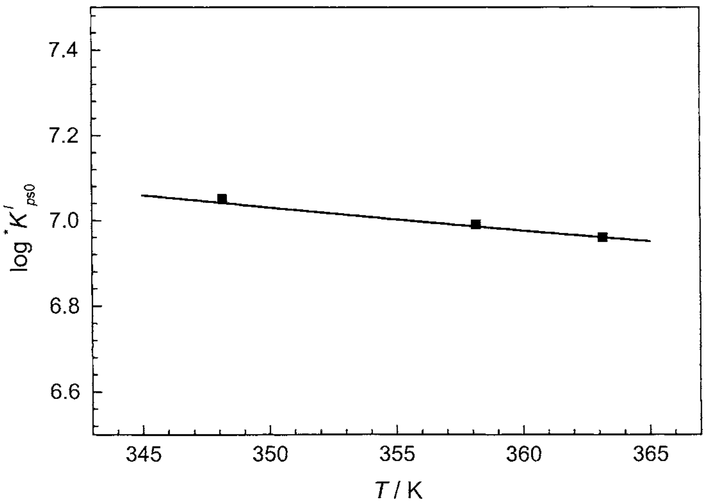

Fig. 2. Temperature dependence of gaspéite ($NiCO_3$) solubility: $I = 1.0\,mol\,kg^{-1}$ $NaClO_4$, $\theta = 75, 85, 90\,°C$. Solid line: calculated with optimized thermodynamic quantities (■ Experimental data).

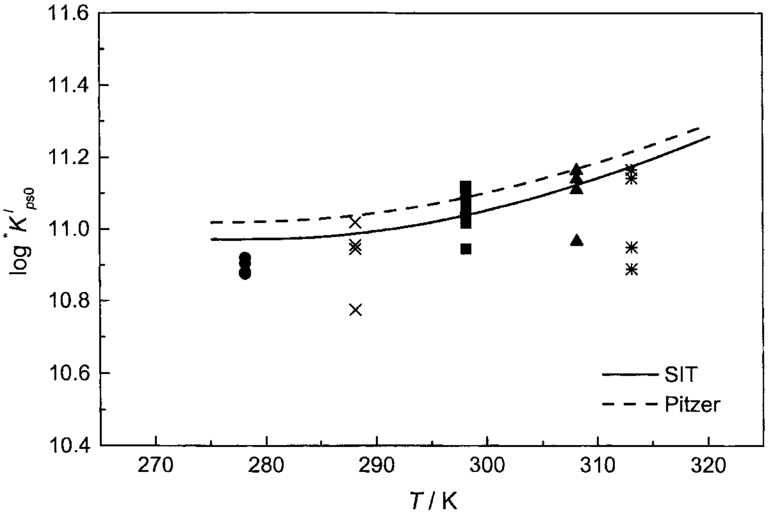

Fig. 3. Temperature dependence of hellyerite solubility: $I = 1.0\,mol\,kg^{-1}$ $NaClO_4$, (●) 5 °C, (×) 15 °C, (■) 25 °C, (▲) 35 °C, (∗) 40 °C. Solid line: specific ion-interaction formalism [27]; dashed line: Pitzer model [22].

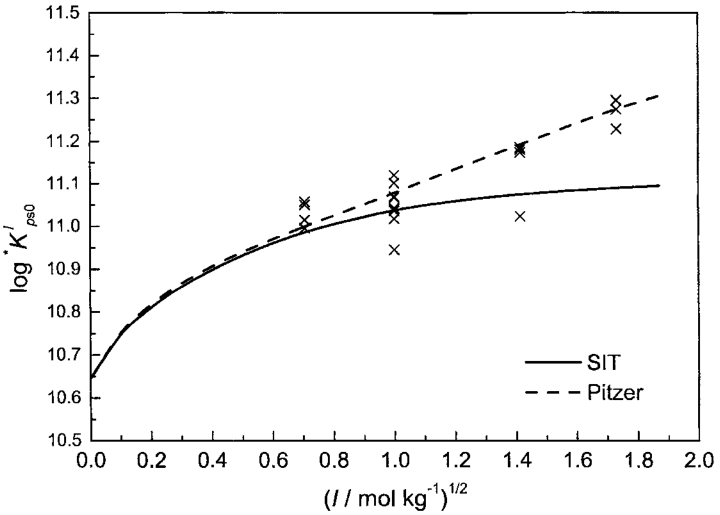

Fig. 4. Ionic strength dependence of hellyerite solubility: $\theta = 25\,°C$. Ionic medium: $I = 0.5–3.0\,mol\,kg^{-1}$ $NaClO_4$, solid line: specific ion-interaction formalism [27]; dashed line: Pitzer model [22]; (x) experimental data.

presumably responsible for chemical analyses of hellyerite resulting in a stoichiometric formula of $NiCO_3·5.5H_2O$ instead of $NiCO_3·6H_2O$ [1]. Crystallographic investigations to solve the hellyerite structure definitively are in progress.

The thermodynamic calculations of this work are based on the conventional formula $NiCO_3·6H_2O$ which is generally accepted. The experimental data for the solubilities of hellyerite are listed in Table 2. Data of $\log\{[Ni^{2+}]_{tot} \times p_{CO_2}\}$ plotted versus p[H] fell on straight lines with slopes of approximately −2.0 for all temperatures[1] [1]. From the weak temperature dependence of the solubility constants, $\log^* K_{ps0}$, of gaspéite (see Fig. 2) and hellyerite (see Fig. 3) $\Delta_f H_m^{\ominus}(NiCO_3)$, $\Delta_f H_m^{\ominus}(NiCO_3 \cdot 6H_2O)$ and $S^{\ominus}(Ni\ CO_3 \cdot 6H_2O)$ were calculated using the ChemSage optimizing routine [9]. Thermodynamic auxiliary data of H_2O, CO_2 and Ni^{2+} were taken from CODATA [17] and the NBS tables [18], respectively. A critical re-evaluation of thermodynamic quantities of Ni^{2+} led to essentially the same values [19]. Nickel hydroxo complexes are negligible in the pH ranges where these experiments were carried out [20]. Fig. 4 shows the solubility constant of $NiCO_3·6H_2O$ plotted as a function of ionic strength at 298.15 K. Both the Pitzer equations [21–23] and the specific ion-interaction theory (SIT) [24] were applied to model the ionic strength dependence of $\log^* K_{ps0}$. Whereas the Pitzer equations seem to predict the ionic strength dependence of the solubility constant more accurately than the SIT approach, the experimental data as a function of temperature coincide best with the latter, see Fig. 3.

A plot of log $\{a(Ni^{2+})a(H_2O)^7 a(H^+)^{-2}\}$ versus $\log p[CO_2]$ shown in Fig. 5 describes the thermodynamic analysis of the data presented in [10,11] and this work in comparison with the optimized line (slope = −1.00). The activities of Ni^{2+} and H^+ were calculated by using the SIT model. This result reveals a ratio of $n[Ni]/n[CO_2]$ close to 1 in the solid phase, as it is expected for $NiCO_3·6H_2O$. A re-evaluation of the experimental data of Ageno and Valla [10] as well as Müeller and Luber [11] resulted in $\log^* K_{ps0} = 10.54 \pm 0.1$ compared with $\log^* K_{ps0} = 10.64 \pm 0.1$ calculated from experimental data of this work. All uncertainties correspond to 2σ. Thus, it can be concluded that Ageno and Valla studied $NiCO_3·6H_2O$ and not $NiCO_3$ $\log^* K^0_{ps0} = 7.12 \pm 0.18$).

A consistent set of thermodynamic quantities of hellyerite and gaspéite are listed in Table 3. The standard entropy of $NiCO_3$ is based on the heat capacity function between 0 and 298.15 K [25]. The standard entropy of hellyerite is derived from solubility measurements at various temperatures and ionic

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

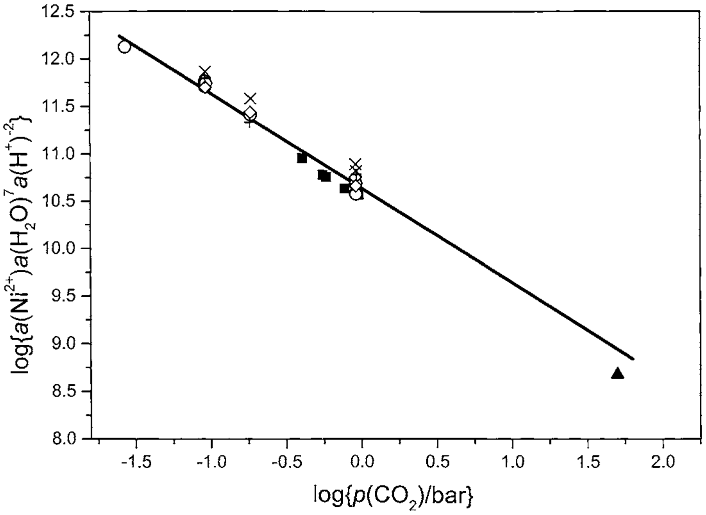

Fig. 5. Thermodynamic analysis of hellyerite solubility at 25 °C. Data of Ageno and Valla [10]: (■), data of Mueller and Luber [11]: (▲), this work: (◇) $I = 0.5\,\text{mol}\,\text{kg}^{-1}$ $NaClO_4$, (○) $I = 1.0\,\text{mol}\,\text{kg}^{-1}$ $NaClO_4$, (+) $I = 2.0\,\text{mol}\,\text{kg}^{-1}$ $NaClO_4$, (×) $I = 3.0\,\text{mol}\,\text{kg}^{-1}$ $NaClO_4$. Solid straight line: calculated with thermodynamic quantities optimized with experimental data of this work.

Table 3
Thermodynamic properties of $NiCO_3$ and $NiCO_3{\cdot}6H_2O$

$T_0 = 298.15\,\text{K}$	$NiCO_3$	Ref.	$NiCO_3{\cdot}6H_2O$	Ref.
$\log^* K^0_{ps0}$	7.12 ± 0.18	[2]	10.64 ± 0.10	This work
$\Delta_f G^\ominus$ (kJ mol^{-1})	−636.5 ± 1.4	[3]	−2039.2 ± 1.1	This work
$\Delta_f H^\ominus$ (kJ mol^{-1})	−713.4 ± 1.6	This work	−2456.7 ± 3.1	This work
$S^\ominus$ (J mol^{-1} K^{-1})	85.4 ± 2.0	[28]	343 ± 10	This work

strengths. The result presented in this work agrees reasonably well with $S^\ominus(NiCO_3 \cdot 6H_2O) = 328\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$ estimated according to Latimer [26].

4. Conclusion

The solubility constant of hellyerite $\log^* K_{ps0}$ was determined as a function of temperature and ionic strength by employing the pH variation method. The results were analyzed with the SIT as well as the Pitzer model in order to compare the solubility constants of hellyerite and gaspéite at infinite dilution and 298.15 K. These constants differ by 3.5 orders of magnitude.

Thus this work presents a further example that solubility data measured at different temperatures and ionic strengths provide a useful basis for the calculation of thermodynamic quantities when and only when the solid samples investigated are analytically and structurally unambiguously characterized. Moreover, a careful thermodynamic analysis showed that the experimental information of rather old solubility studies contributed almost equivalently to the optimized set of thermodynamic properties obtained [10,11]. Care has to be taken that reliable—preferably CODATA recommended—auxiliary variables are used throughout the critical evaluation of data.

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