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Evaluation of Solubility and Thermodynamic Properties of Synthetic Nickel Hydroxide Carbonate

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Abstract

Knowledge of the values of the thermodynamic functions of natural minerals of transition elements has important applications in the study of the processes of their formation and geochemical migration with groundwater; when developing methods to prevent corrosion of non-ferrous alloys in fresh and sea water; when immobilizing heavy metals in mine drainage and industrial waters, etc. Also, these values are in demand when calculating reactions and developing methods for producing synthetic analogs of minerals, many of which exhibit magnetic, catalytic, photochemical, and other properties. However, in scientific literature, there is a lack of detailed data on the thermodynamic properties of nickel hydroxysalts. A sample of basic nickel carbonate with the theoretical formula $Ni_3[CO_3](OH)_4{\cdot}3H_2O$ was obtained using the hydrothermal synthesis method. The structure of the compound was verified by X-ray diffraction and infrared spectroscopy. Experiments were carried out on sample dissolution in order to measure the solubility constant (solubility product): $\log_{10} K_{SP} = -45.8 \pm 1.8$. Based on the data obtained, the thermodynamic parameters of the reaction of dissolution of the compound were determined and the main thermodynamic functions were determined: Gibbs free energy of formation $\Delta_f G^\circ = -1554 \pm 6$ kJ·mol^{-1}; enthalpy of formation $\Delta_f H^\circ = -1798 \pm 9$ kJ·mol^{-1}; standard entropy $S^\circ = 260.6 \pm 7.8$ J·mol^{-1}·K^{-1}.

Keywords Nickel hydroxycarbonate · Solubility product · Thermodynamic functions · Enthalpy of formation · Gibbs free energy of formation

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1 Introduction

Thermodynamic parameters of oxidized minerals of transition metals (copper, zinc, nickel, etc.) are important when studying minerals in the oxidation zone of ore deposits [1], corrosion of non-ferrous metal alloys [2], immobilization of heavy metals in environment [3], obtaining new materials [4–6], etc.

Layered nickel compounds of this kind have unusual magnetic properties, thus, the structure of nickel hydroxysulfate at T_N 29 K transforms from paramagnetic to a canted antiferromagnetic state, the magnetic moments of which are not completely antiparallel. Resulting compensated structure of the arrangement of moments within one layer includes one ferromagnetic and three antiferromagnetic superexchange interactions between nickel atoms [7].

In addition, layered metal hydroxides are promising materials for water splitting and the development of energy storage devices. Bifunctional electrocatalyst with Co–Ni carbonate hydroxides exhibits an excellent catalytic activity and good stabilities, and achieves very low overpotentials [8]. The specific capacity of hierarchical structures with nickel carbonate hydroxide achieves more than 200–300 mAh/g and suitable as materials for supercapacitor electrodes [9, 10]; high electrochemical capacity, energy density, and cyclic stability allow their using in electrochemical energy storage application [11, 12].

Questions about formation and reactivity require knowledge of the physicochemical properties of these compounds. However, for a number of compounds, solubility products and basic thermodynamic functions have not yet been determined. At present time, in scientific literature, there is a lack of detailed data on the thermodynamic properties of nickel hydroxo salts. One of the ways to obtain self-consistent thermodynamic data for sparingly soluble compounds is to study their dissolution processes at different temperatures.

In this work, we studied synthetic nickel hydroxycarbonate obtained by hydrothermal synthesis. The processes of solubility of the compound at various temperatures were studied and thermodynamic data on its physicochemical properties were obtained.

2 Materials and Methods

2.1 Materials

To carry out the synthesis of nickel hydroxycarbonate, nickel sulfate heptahydrate $NiSO_4 \cdot 7H_2O$ and urea $(NH_2)_2CO$ were used as starting materials (Table 1). The reagents are classified as "chemically pure" and contain at least 98% of the main substance. Before synthesis, the starting substances were recrystallized twice and then dried in a desiccator over a sulfuric acid solution with a concentration of 20 wt% to ensure a residual water vapor content of 15 mm Hg at 293 K.

2.2 X-ray Diffraction

The powder X-ray diffraction study of the synthesized samples was carried out on a diffractometer Empyrean X-ray (Malvern Panalytical Ltd). The diffractometer is equipped

Table 1 Origin, CAS registry number, and mass fraction purity of the chemicals

Component	Formula	CAS reg. no	Suppliers	Mass fraction	Analysis method
Nickel sulfate heptahydrate	$NiSO_4 \cdot 7H_2O$	10101-98-1	Kupavnareaktiv LLP	$> 0.98^{a}$	TA^{b}
Urea (carbamide)	$(NH_2)_2CO$	57-13-6	Kupavnareaktiv LLP	$> 0.993^{c}$	TA
Nickel hydroxycarbonate hydrate	$Ni_3[CO_3](OH)_4 \cdot 3H_2O$	12244-51-8	synthetic	> 0.97	GA^{d}

[a] According to GOST 4465-2016

[b] Titration analysis

[c] According to GOST 2081-2010

[d] Gravimetric analysis

with an X-ray tube with a copper anode ($K\alpha_1 = 1541874$ Å). The measurements were carried out at room temperature in the 2θ angle range from 0° to 90° in step-by-step scanning mode with a step of 0.013 degrees.

2.3 IR Spectroscopy

Infrared spectra were recorded on a Fourier spectrometer FSM-1201 (Infraspek Ltd). Samples for IR spectroscopic studies were prepared in the form of tablets compressed from 2 mg of the test substance and 300 mg of potassium bromide KBr. The sample was crushed in an agate mortar, and then it was pressed at a force up to 80 kN. The tablet had a diameter of 13 mm and a thickness of 1 mm. The spectra were recorded in the transmission mode in the range from 400 to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1} at room temperature.

2.4 Dissolution Experiments

To study the thermodynamic characteristics of the compound, dissolution experiments were performed at different temperatures. Weights of the sample were placed in 500-mL volumetric flasks with ground-in stoppers and topped up with distilled water to the mark. The sample weight was 200 ± 2 mg to ensure equilibrium dissolution conditions. The flasks were placed in three thermostats at temperatures of 293, 323, and 353 K with an accuracy of ± 1 K and kept for several weeks with periodic stirring. To determine the concentration of nickel ions in the solution, a sample was taken from the flasks for analysis once every few days. Samples in a volume of 1 mL were taken from the flask through a 0.45 μm nylon filter. To compensate the thermal expansion of water, the volume of the aliquots was increased by 1% at temperature 50 °C, and by 3% at temperature 80 °C. After sampling, distilled water was added to the flask in an appropriate amount.

Experiments were carried out until a stable concentration in the solution occurred, determined by the agreement of the results of the last three analyses within the standard deviation.

2.5 Spectrophotometric Analysis

The analysis of the nickel content in the solution (1 mL probe) was carried out by the method of absorption photometry by the dimethylglyoxime method [13]. The analysis of experimental solutions was carried out in triplicate on a photoelectric spectrophotometer KFK-3 (JSC «ZOMZ»). To a probe of the test solution, 1 mL of a 20% potassium-sodium tartrate solution, 2 mL of a 10% solution of $NH_2OH{\cdot}HCl$, and 2 mL of 1% dimethylglyoxime solution are added, and bringing the solution with ammonia up to pH 9. The solution is extracted with two portions of chloroform in a separatory funnel. The resulting extracts are washed with diluted ammonia solution and nickel is reextracted with 0.5 $mol{\cdot}L^{-1}$ hydrochloric acid. The solution is placed in 50-mL volumetric flask, adding 1 mL of 1% dimethylglyoxime solution, 2 mL of 4% ammonium persulfate solution, 5 mL of concentrated ammonia solution, and up to the mark with distilled water. The absorbance of the resulting solution is measured at 445 nm using distilled water as a reference solution.

3 Synthesis and Characterization

3.1 Hydrothermal Synthesis

The ratio of starting substances during the synthesis was 0.02 mol of nickel sulfate and 4 mol of urea per 2 L of distilled water. The synthesis was carried out in a dismountable autoclave, consisting of an internal fluoroplastic vessel with a lid and an outer steel case secured with a threaded connection. The reaction mixture was poured into the vessel, which was sealed in the steel case. The assembled design was placed in a Nabertherm N7/H oven and kept at a temperature of 363 ± 1 K for 1 h. The resulting microcrystalline precipitates were filtered off on a paper filter and washed with distilled water, and then with ethyl alcohol and acetone for drying.

3.2 X-ray Phase Analysis

Processing of diffractometry data (Fig. 1) and searching for individual phases were carried out using the Match! v.2.3 program [14] and the PDF-2 powder diffraction database [15]. The compound profiles were refined by means of the Rietveld method using the PowderCell v.2.4 program [16].

A noticeable broadening of the reflections in the diffraction pattern indicates a fairly small size of the sample crystallites, at a level of 10 nm according to Scherrer. The resulting compound is structurally similar to compounds from the hydrotalcite group [6, 17–20]. When refining the profiles, the structural parameters of the takovite mineral were taken as a basis [21]. The best refinement results ($R_p = 7.22\%$, $R_{wp} = 9.35\%$) were obtained using the theoretical formula $Ni_3[CO_3](OH)_4 \cdot 3H_2O$. The unit cell parameters obtained as a result of full-profile analysis are given in Table 2.

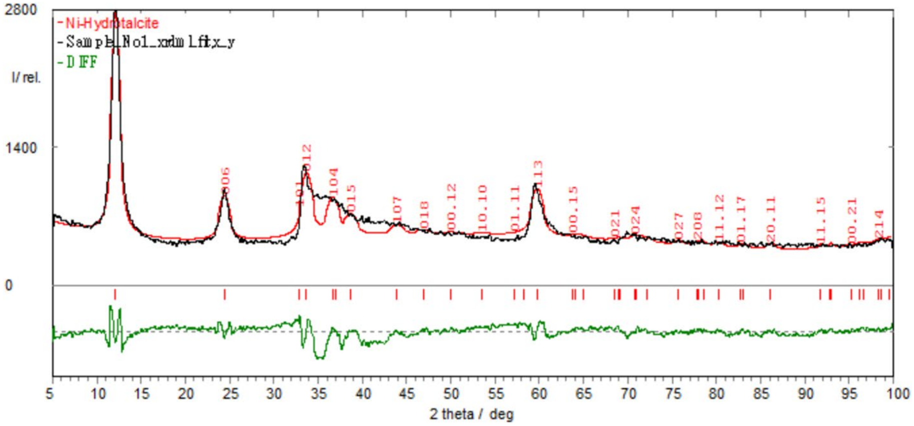

Fig. 1 Experimental (thick black line), theoretical (thin red line), and difference (green line below) diffraction patterns of the synthetic sample of nickel hydroxycarbonate (Color figure online)

Table 2 Crystal lattice parameters of a nickel hydroxycarbonate sample

Lattice parameters	$Ni_3[CO_3](OH)_4\cdot 3H_2O$ synth
Space group	R^{-3} m
a (Å)	3.167(3)
c (Å)	21.89(1)

3.3 Infrared Spectra

Experimental IR spectra were processed using the PeakFit 4.12 program [22]. In the smoothed spectrum, the main peaks were identified, after which hidden peaks were identified. To obtain a smoothed spectrum, the Lorentz-Gaussian variation of the peak shape parameter was used. Smoothing was performed until a correlation coefficient of at least 0.995 was obtained.

The main absorption bands of the synthetic sample of nickel hydroxycarbonate (Fig. 2) mainly correspond to the infrared spectra of similar compounds [3, 5, 23].

Intense lines in the region of 3600–3700 cm^{-1} refer to stretching vibrations of OH groups included in the structure of hydroxycarbonate. The lines at 1361, 1398, and 1444 cm^{-1} belong to antisymmetric stretching vibrations of C–O bonds. The splitting of this vibration band into a triplet indicates a distortion of the shape of the carbonate ion in the structure of the compound. Lines at 950–1200 cm^{-1} correspond to symmetrical stretching vibrations of C–O bonds. The lines at 810–940 cm^{-1} correspond to symmetrical bending vibrations of the O–C–O bond angles. The lines in the region of 640–780 cm^{-1} belong to bending vibrations of hydroxyl groups. The lines at 464 and 482 cm^{-1} correspond to bending vibrations of the carbonate ion. The line at 399 cm^{-1} refers to vibrations of the Ni–O bonds.

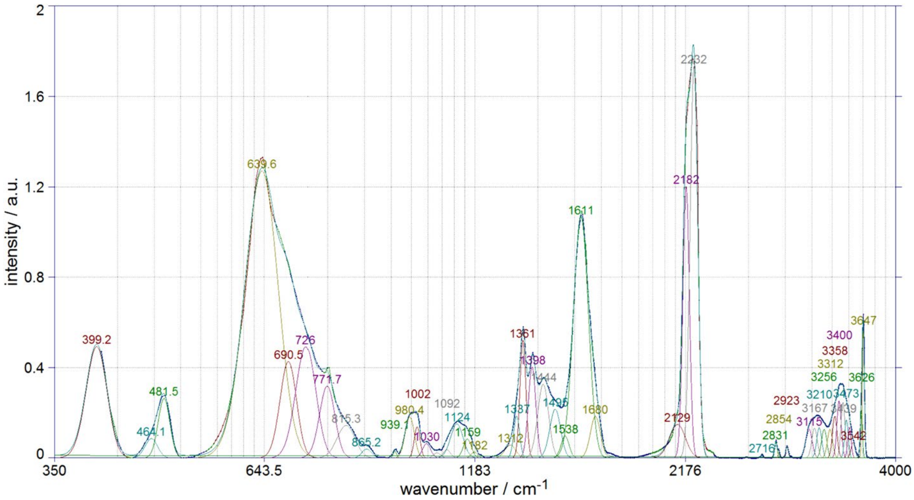

Fig. 2 Infrared spectrum and individual absorption bands of the synthetic nickel hydroxycarbonate

The spectrum contains a band at 2100–2250 cm^{-1}, which is due to the total combination of torsional and deformation vibrations of water molecules and can be attributed to vibrations of crystalline hydrate water. The bands in the regions at 1500–1700 cm^{-1} and 3100–3500 cm^{-1} correspond to vibrations of free and weakly bound water, which indicates the presence of some amount of adsorbed water in the sample.

4 Results and Discussion

As a result of the experiments, data were obtained on changes in the concentration of nickel ions upon dissolution of the synthesized sample (Fig. 3). The increase in the concentration of nickel ions occurs quite quickly and approaches a certain limiting value corresponding to the equilibrium concentration of nickel in the solution. The resulting sets of experimental data were smoothed by a dependence equation of the form $y = x/(a + bx)$, which has an asymptotic limit. The asymptotic values of this function were taken as the equilibrium concentrations of nickel ions in solution.

The dissolution process of nickel hydroxycarbonate is described by the following equations:

$$\mathrm{Ni_3}\left[\mathrm{CO_3}\right](\mathrm{OH})_4 \cdot 3\mathrm{H_2O(s)} \leftrightarrow \mathrm{Ni_3}\left[\mathrm{CO_3}\right](\mathrm{OH})_4\mathrm{(s)} + 3\mathrm{H_2O(aq)}, \tag{1}$$

$$\mathrm{Ni_3}\left[\mathrm{CO_3}\right](\mathrm{OH})_4\mathrm{(s)} \leftrightarrow 3\left[\mathrm{Ni^{2+}}\right]\mathrm{(aq)} + \left[\mathrm{CO_3^{2-}}\right]\mathrm{(aq)} + 4[\mathrm{OH^-}]\mathrm{(aq)}, \tag{2}$$

where symbols in square brackets indicate equilibrium concentrations. In this case, the concentrations of ions in the solution are equal to each other, taking into account the stoichiometric coefficients. The parameters of reaction 1 are difficult to estimate because the species involved have generally constant concentrations and the thermal effect of the reaction is quite small [24]. Assuming the concentration of the solid substance to be a constant value equal to 1, the expressions for the equilibrium constant of reaction 2, in accordance with the law of mass action, in simple and logarithmic form have the form:

$$K_{\mathrm{SP}} = \left\{\mathrm{Ni^{2+}}\right\}^3 \cdot \left\{\mathrm{CO_3^{2-}}\right\} \cdot \{\mathrm{OH^-}\}^4, \tag{3}$$

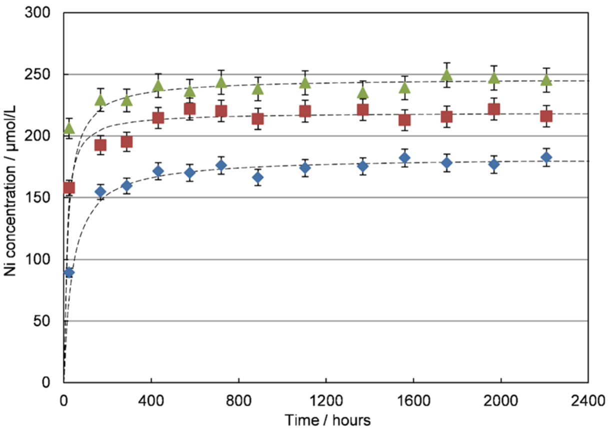

Fig. 3 Change in the concentration of nickel ions in solution during experiments on dissolving a sample of nickel hydroxycarbonate at different temperatures. From bottom to top: diamonds—293 K; squares—323 K; triangles—353 K

Table 3 Equilibrium concentrations of nickel ions in solution and equilibrium constants

Temperature, K	C_{Cu}, μmol/L	K_{SP}	$\log_{10} K_{\mathrm{SP}}$
293	182.8 ± 9.9	1.26×10^{-46}	-45.9 ± 1.8
323	219.2 ± 11.3	5.37×10^{-46}	-45.3 ± 2.2
353	246.9 ± 12.2	1.38×10^{-45}	-44.9 ± 2.8

Uncertainties of concentration measurements are standard uncertainties (level of confidence = 0.67); for derived values the common mathematic methods of uncertainty calculation were used

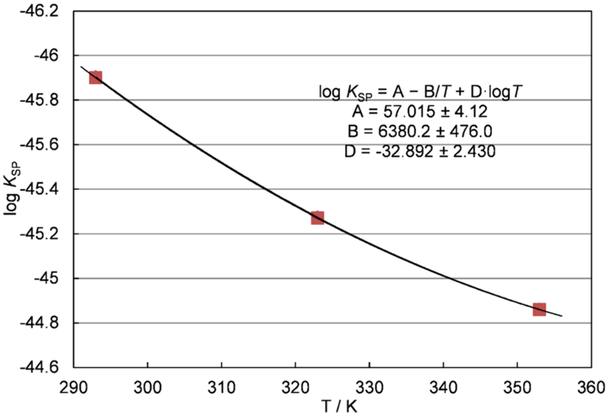

Fig. 4 Temperature dependence of the decimal logarithm of the dissolution constant of synthetic nickel hydroxycarbonate and the coefficients of the smoothing equation

$$\log_{10} K_{\mathrm{SP}} = 3 \log_{10} \left\{\mathrm{Ni}^{2+}\right\} + \left\{\mathrm{O}_3^{2-}\right\} + 4 \log_{10} \left\{\mathrm{OH}^-\right\}, \tag{4}$$

where the designations in curly brackets express the activities of ions in solution, which in extremely dilute solutions become almost equal to equilibrium concentrations. The final averaged experimental values of the equilibrium concentrations of nickel ions in solutions and ionic products at various temperatures calculated using formulas 3 and 4 are shown in Table 3.

The temperature dependence of the dissolution constant under equilibrium conditions is described by the equation

$$\log_{10} K_{\mathrm{SP}} = A - B/T + D \cdot \log_{10} T. \tag{5}$$

The temperature dependence of this function is shown in Fig. 4. Based on the available data set, the coefficients of Eq. 5 were calculated and their uncertainties were estimated. Using the smoothed curve, the value of the dissolution constant for nickel hydroxycarbonate at a standard temperature of 298.15 K and its uncertainty were calculated: $\log_{10} K_{SP} = -45.8 \pm 1.8$.

Thermodynamic functions of the reaction of dissolution of compounds are related to the coefficients of Eq. 5 by the following relations:

$$\Delta_{\mathrm{r}} G^{\circ} = -2.3026 RT \log_{10} K_{\mathrm{SP}}, \tag{6}$$

$$\Delta_{\mathrm{r}} C_{\mathrm{p}}^{\circ} = DR, \tag{7}$$

Table 4 Standard thermodynamic functions for the reactions of dissolution and formation of synthetic nickel hydroxycarbonate (temperature $T=298.15$ K)

Function	Value	Units
$\Delta_r G°$	261.3 ± 5.5	kJ·mol^{-1}
$\Delta_r H°$	40.61 ± 9.0	kJ·mol^{-1}
$\Delta_r S°$	− 740.1 ± 4.8	J·mol^{-1}·K^{-1}
$\Delta_f G°$	− 1554 ± 6	kJ·mol^{-1}
$\Delta_f H°$	− 1798 ± 9	kJ·mol^{-1}
$S°$	260.6 ± 7.8	J·mol^{-1}·K^{-1}

Uncertainties of the values are calculated from standard uncertainties of concentration measurements in accordance with the common mathematic methods (level of confidence = 0.67)

$$\Delta_r H^\circ = 2.3026RB + T\Delta_r C_p^\circ \tag{8}$$

$$\Delta_r S^\circ = 2.3026RA + 2.3026T\Delta_r C_p^\circ \log_{10} T + \Delta_r C_p^\circ, \tag{9}$$

where $R=8.31446$ J·mol^{-1}·K^{-1} is the universal gas constant. Based on formulas 6–9, standard values were calculated for Gibbs free energy $\Delta_r G°$, heat capacity $\Delta_r C°_p$, entropy $\Delta_r S°$, and enthalpy $\Delta_r H°$ of synthetic nickel hydroxycarbonate dissolution reaction 1, 2 and their uncertainties.

Next, the values of the Gibbs free energy of formation $\Delta_f G°$, the enthalpy of formation $\Delta_f H°$, and the standard entropy $S°$ of the compound were calculated in accordance with Hess's law by the following expressions:

$$\Delta_f G^\circ = 3\Delta_f G^\circ_{\mathrm{Ni}^{2+}} + \Delta_f G^\circ_{\mathrm{CO}_3^{2-}} + 4\Delta_f G^\circ_{\mathrm{OH}^-} - \Delta_r G^\circ, \tag{10}$$

$$\Delta_f H^\circ = 3\Delta_f H^\circ_{\mathrm{Ni}^{2+}} + \Delta_f H^\circ_{\mathrm{CO}_3^{2-}} + 4\Delta_f H^\circ_{\mathrm{OH}^-} - \Delta_r H^\circ, \tag{11}$$

$$S^\circ = 3S^\circ_{\mathrm{Ni}^{2+}} + S^\circ_{\mathrm{CO}_3^{2-}} + 4S^\circ_{\mathrm{OH}^-} - \Delta_r S^\circ \tag{12}$$

The values of the thermodynamic functions of individual ions required for calculation using Eqs. 10–12 were taken from the base reference book on the thermodynamic properties of minerals [25].

The final standard values of the main thermodynamic functions of synthetic nickel hydroxycarbonate are given in Table 4.

The obtained values of the thermodynamic functions of nickel hydroxycarbonate are in satisfactory agreement with the calculated data, and also coincide in order of magnitude with the experimental data for similar compounds [26].

5 Conclusion

A synthetic sample of nickel hydroxycarbonate was obtained using the hydrothermal method, for which its structure was confirmed. The processes of sample dissolution were studied, and based on the experimental results, solubility constants were determined, as well as the main thermodynamic functions and their errors. The obtained values are in satisfactory agreement with the calculated data.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10953-024-01406-3.

Author Contributions D. Gogol contributed toward methodology, supervision, and writing—review & editing. A. Makasheva contributed toward formal analysis and writing—original draft. D. Sadyrbekov contributed toward data curation and resources. L. Dyussembayeva contributed toward investigation. I. Rozhkovoy contributed toward validation and conceptualization. I. Ishmiev contributed toward investigation. O. Zemskiy contributed toward investigation and software. S. Aldabergenova contributed toward investigation and visualization.

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Data Availability No datasets were generated or analyzed during the current study.

Declarations

Competing Interests The authors declare no competing interests.

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