

A calorimetric and thermodynamic investigation of the synthetic analogs of cobaltomenite, $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$, and ahlfeldite, $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$

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ABSTRACT

Thermophysical and thermochemical calorimetric investigations were carried out on synthetic analogs of two minerals: cobaltomenite ($\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$) and ahlfeldite ($\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$). The synthesis was realized by mixing of aqueous solutions of cobalt and nickel nitrates, accordingly, and sodium selenite, acidified with the help of a solution of nitric acid and characterized by X-ray powder diffraction and FTIR spectroscopy methods. The low-temperature heat capacities of $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$ were measured using adiabatic calorimetry between 8 and 340 K, and the third-law entropies were determined. Values of S° (298 K, $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$, cr.) = 183.2 ± 1.0 J/(mol·K) and S° (298 K, $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$, cr.) = 172.9 ± 1.0 J/(mol·K) are obtained with an uncertainty of 0.5%. The enthalpies of formation for $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$ were determined by solution calorimetry with H_2SO_4 solution as the solvent and giving $\Delta_f H^\circ$ (298 K, $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$, cr.) = -1135.3 kJ/mol, $\Delta_f H^\circ$ (298 K, $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$, cr.) = -1133.3 kJ/mol. The Gibbs energy of formation for $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$ at $T = 298$ K, 1 atm can be calculated on the basis on $\Delta_f H^\circ$ and $\Delta_f S^\circ$: $\Delta_f G^\circ$ (298 K, $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$, cr.) = -937.4 kJ/mol and $\Delta_f G^\circ$ (298 K, $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$, cr.) = -932.4 kJ/mol. Smoothed $C_p^\circ(T)$ values between $T = 0$ K and $T = 320$ K for $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ (cr.) and $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$ (cr.) are presented along with values for S° and the functions $[H^\circ(T) - H^\circ(0)]$ and $[G^\circ(T) - H^\circ(0)]$. These results motivate a re-evaluation of the natural conditions under which selenites, and selenates replace selenides, and sulfides in the oxidation zones of sulfide ore deposits or upon weathering of technologic waste. The values of $\Delta_f G^\circ$ for $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$ were used to calculate the Eh-pH diagrams of the Co-Se- H_2O and Ni-Se- H_2O systems. These diagrams have been constructed for the average contents of these elements in acidic waters of the oxidation zones of sulfide deposits. The behavior of selenium, cobalt, and nickel in surface environments have been quantitatively explained by variations of the redox potential and the acidity–basicity of the mineral-forming medium. Precisely these parameters determine the migration ability of selenium compounds and its precipitation in the form of various solid phases.

Keywords: Cobaltomenite, ahlfeldite, heat capacity, entropy, enthalpy of formation, Gibbs energy of formation