A calorimetric and thermodynamic investigation of the synthetic analogs of cobaltomenite, CoSeO₃·2H₂O, and ahlfeldite, NiSeO₃·2H₂O

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ABSTRACT

Thermophysical and thermochemical calorimetric investigations were carried out on synthetic analogs of two minerals: cobaltomenite (CoSeO₃·2H₂O) and ahlfeldite (NiSeO₃·2H₂O). 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 CoSeO₃·2H₂O and NiSeO₃·2H₂O were measured using adiabatic calorimetry between 8 and 340 K, and the third-law entropies were determined. Values of S°(298 K, CoSeO₃·2H₂O, cr.) = 183.2 ± 1.0 J/(mol·K) and S°(298 K, NiSeO₃·2H₂O, cr.) = 172.9 ± 1.0 J/(mol·K) are obtained with an uncertainty of 0.5%. The enthalpies of formation for CoSeO₃·2H₂O and NiSeO₃·2H₂O were determined by solution calorimetry with H₂SO₄ solution as the solvent and giving ΔHf°(298 K, CoSeO₃·2H₂O, cr.) = −1135.3 kJ/mol, ΔHf°(298 K, NiSeO₃·2H₂O, cr.) = −1133.3 kJ/mol. The Gibbs energy of formation for CoSeO₃·2H₂O and NiSeO₃·2H₂O at T = 298 K, 1 atm can be calculated on the basis of ΔHf° and ΔS°:ΔG°(298 K, CoSeO₃·2H₂O, cr.) = −937.4 kJ/mol and ΔG°(298 K, NiSeO₃·2H₂O, cr.) = −932.4 kJ/mol. Smoothed Cg‴(T) values between T = 0 K and T = 320 K for CoSeO₃·2H₂O (cr.) and NiSeO₃·2H₂O (cr.) are presented along with values for S° and the functions [Hf‴(T)−Hf‴(0)] and [G‴(T)−G‴(0)]. These results motivate a re-evaluation of the natural conditions under which selenium, and selenates replace selenides, and sulfides in the oxidation zones of sulfide ore deposits or upon weathering of technologic waste. The values of ΔG° for CoSeO₃·2H₂O and NiSeO₃·2H₂O were used to calculate the Eh-pH diagrams of the Co-Se-H₂O and Ni-Se-H₂O 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

INTRODUCTION

Since the discovery of the toxic properties and biological significance of selenium, there have been continuous studies of the geological occurrence and geochemistry of this element in oxygenated aqueous environments. Drainage from mineralized and mined areas may have high concentrations of dissolved selenium. This is of major concern as waterflows, soils, and plants in the vicinity of ore bodies containing Se-bearing sulfides and selenides are prone to be the low-temperature oxidizing environments for the natural sources of Se (Lonar 2004). Most selenites are formed by chemical weathering of ores by oxygenated waters, establishing conditions of increased Eh and low or neutral pH (with seasonal fluctuations of temperatures and atmospheric pressure). These parameters define the migration of selenium, and its precipitation in the form of selenite minerals [chalcomenite CuSeO₃·2H₂O, cobaltomenite CoSeO₃·2H₂O, ahlfeldite NiSeO₃·2H₂O, mandarinoite Fe₂(SeO₄)₃·6H₂O, molybdemenite PhSeO₄]. Eh-pH diagrams of the Me-Se-H₂O systems (Me = Co, Ni, Fe, Cu, Zn, Pb) have been published, which make it possible to estimate the conditions for the near-surface formation of Se minerals (selenites) (Krivovichiev et al. 2011).

The analysis of the thermodynamic data for calculation of mineral equilibria involving selenites and selenides of Fe, Cu, Zn, Pb, Co, and Ni (Seby et al. 2001; Olin et al. 2005; Charykova et al. 2010) showed that, even in cases when it is possible to find corresponding parameters in the literature, they frequently raise questions and need specification. In particular, this is true for the standard thermodynamic functions of ahlfeldite, NiSeO₃·2H₂O, and cobaltomenite, CoSeO₃·2H₂O. Their standard enthalpies