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Calorimetric study of skutterudite ($CoAs_{2.92}$) and heazlewoodite (Ni_3S_2)

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Abstract

Nickel and cobalt arsenides, sulfarsenides, and sulfides occur in many hydrothermal ore deposits, but their thermodynamic properties are not well known, in some cases not known at all. In this work, we determined a full set of thermodynamic properties for heazlewoodite and skutterudite. Both phases were synthesized in evacuated silica tubes at elevated temperatures, and electron microprobe analyses gave their compositions as Ni_3S_2 and $CoAs_{2.92}$, respectively. Enthalpies of formation were measured by high-temperature oxide-melt solution calorimetry. The reference phases were pure elements, thus eliminating any systematic errors related to such phases. The enthalpies of formation at $T = 298.15$ K and $P = 10^5$ Pa are –216.0 ± 8.4(2σ) and –88.2 ± 6.1 kJ·mol^{-1} for Ni_3S_2 and $CoAs_{2.92}$, respectively. Entropies were calculated from low-temperature heat capacity (C_P) data from relaxation (PPMS) calorimetry and are 133.8 ± 1.6 and 106.4 ± 1.3 J·mol^{-1}·K^{-1}, respectively. The calculated Gibbs free energies of formation are –210.0 ± 8.4 and –79.9 ± 6.2 kJ·mol^{-1} for Ni_3S_2 and $CoAs_{2.92}$, respectively. The PPMS C_P data, together with a set of differential scanning calorimetry measurements, were used to derive C_P polynomials up to 700 K with the Kieffer model based on previously published frequencies of acoustic and optic modes. Equilibrium constants for selected reactions with an aqueous phase were calculated up to 700 K. Geochemical modeling in these systems, however, should await until more reliable data for other phases from the system Co-Ni-As-S are available.

Keywords: Heazlewoodite, skutterudite, enthalpy, entropy, geochemical modeling