

Calorimetric study of skutterudite (CoAs_{2.92}) and heazlewoodite (Ni₃S₂)

JURAJ MAJZLAN^{1,*}, STEFAN KIEFER¹, KRISTINA LILOVA², TAMILARASAN SUBRAMANI²,
ALEXANDRA NAVROTSKY², MAREK TUHÝ^{3,4,†}, ANNA VYMAZALOVÁ³, DMITRIY A. CHAREEV^{5,6,7},
EDGAR DACHS⁸, AND ARTUR BENISEK⁸

¹Institute of Geosciences, Friedrich-Schiller University, Burgweg 11, 07749 Jena, Germany

²School of Molecular Sciences and Center for Materials of the Universe, Arizona State University, Tempe, Arizona 85287, U.S.A.

³Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic

⁴Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 00 Prague

⁵Institute of Experimental Mineralogy (IEM RAS), 142432 Chernogolovka, Moscow Region, Russia

⁶Ural Federal University, Ekaterinburg 620002, Russia

⁷Dubna State University, Dubna 141982 Russia

⁸Department of Chemistry and Physics of Materials, University of Salzburg, Jakob-Haringer-Strasse 2a, 5020 Salzburg, Austria

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 Ni₃S₂ 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 $-216.0 \pm 8.4(2\sigma)$ and -88.2 ± 6.1 kJ·mol⁻¹ for Ni₃S₂ 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 Ni₃S₂ 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