Calorimetric study of skutterudite (CoAs$_{2.92}$) and heazlewoodite (Ni$_3$S$_2$)

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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$_3$S$_2$ and CoAs$_{2.92}$, respectively. Enthalpies 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 $216.0 \pm 8.4$ (Ni$_3$S$_2$) and $-88.2 \pm 6.1$ kJ·mol$^{-1}$ for Ni$_3$S$_2$ and CoAs$_{2.92}$, respectively.

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

**Introduction**

Nickel and cobalt arsenides, sulfarsenides, and sulfides occur in many hydrothermal ore deposits (Dolansky 2007; Belkin and Luo 2008; Ahmed et al. 2009; Gervilla et al. 2012; Kreissl et al. 2018; Scharrer et al. 2019; Tourneur et al. 2021; Horn et al. 2021). They are found especially in orthomagmatic Cu-Ni-PGE ores (Naldrett 2004), hydrothermal ores, commonly of the “five-element association” (Burisch et al. 2017), or in stratiform Cu-Co ores (Dewaele et al. 2006). They represent a large and complex group of minerals, with sulfides, disulfides, mono-, di- and tri-arsenides, and sulfarsenides [a list of the minerals with further references can be found in Table 1 in Hem (2006)]. In addition to Co, Ni, and As, many of these minerals show the As-Sb substitution, for example, in the gersdorffite-ullmanite (NiAsS-NiSbS$_5$) series (Števko and Sejkora 2020). Occasionally, minerals like gersdorffite may contain economically interesting concentrations of gold or platinum-group elements (e.g., Pašava et al. 2013; Cabri et al. 2017). The presence of reduced arsenic is likely to drive gold incorporation in the sulfarsenide minerals (Pokrovski et al. 2021). Arsenides also commonly form in serpentinization processes at high $T$-$P$ in subduction zones and may be important carriers of As and PGE in such settings (González-Jiménez et al. 2021). Some of the compositions show polymorphism, for example, NiAs$_3$ is known as the minerals rammelsbergite, pararammelsbergite, and krutovite. Structural variations are encountered even within one mineral species; gersdorffite, for example, can have an ordered structure (space group $P2_1_3$) or two disordered structures (space groups $P2_1_3$ and $P1$) (Bayliss and Stephenson 1967, 1968; Steger et al. 1974; Bayliss 1982).

Experimental work on dry systems [Klemm 1965; Maurel and Picot 1974; Hem and Makovicky 2004a, 2005b; see also Table 2 in Hem (2006)] showed that complete solid solutions can be expected at temperatures above 500 °C but such high temperatures were rarely encountered during the formation of the ores with Co-Ni arsenides and sulfarsenides (Scharrer et al. 2019). Thermodynamic properties of the Co-Ni-As-S phases are mostly not well constrained or unknown. For the obvious reason of their abundance, more attention was paid to the Fe-dominant