

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

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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 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

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) 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, NiAs₂ 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 $P2_13$) or two disordered structures (space groups $Pa3$ 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

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members of arsenides and sulfides. For example, thermodynamic properties of löllingite (FeAs_2) were determined early by Barton (1969) from high-temperature equilibria and extrapolation to room temperature. A calorimetric measurement of heat capacity (C_p) of a synthetic löllingite sample and the resulting entropy by Pashinkin et al. (1991) deviated much from the datum in Barton (1969). In their compilation, Robie and Hemingway (1995) adopted the S° from Pashinkin et al. (1991). They also selected $\Delta_f G^\circ$ which is numerically equal to $\Delta_f H^\circ$ in Barton (1969) and adjusted their $\Delta_f H^\circ$ accordingly. The reasons behind this adjustment are not clear. Bessinger and Apps (2005) modified the $\Delta_f G^\circ$ from Barton (1969) slightly and took S° from Barton (1969), even though they referred to Pokrovski et al. (1996) as their data source. Perfetti et al. (2008) accepted S° from Pashinkin et al. (1991) and recalculated $\Delta_f H^\circ$ and $\Delta_f G^\circ$, based on their new solubility data and combustion calorimetry data of Stolyarova (1977). When reviewing the available source of thermodynamic data for löllingite, one notes differences of $40 \text{ kJ} \cdot \text{mol}^{-1}$ in $\Delta_f H^\circ$ and $40 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ in S° (see also Perfetti et al. 2008). Such differences are larger than expected experimental uncertainties in thermodynamic measurements. This example shows the difficulties and gaps in our understanding of these minerals, even though the Fe-As-S system received much more attention than the systems Co-As-S or Ni-As-S.

In this work, we have derived the thermodynamic properties of skutterudite (nominally CoAs_3) and heazlewoodite (nominally Ni_3S_2). Enthalpies of formation were measured by high-temperature oxide-melt solution calorimetry. The reference phases were pure elements, thus eliminating potential systematic errors from reference chemical compounds. This work was also meant as another test of this type of calorimetry on samples with highly volatile components (As, S). Flushing with oxygen maintains oxidative conditions, and all elements are converted rapidly and reproducibly to their highest oxidation state in the solvent (Majzlan 2017). The entropies were calculated from low-temperature heat capacities measured by relaxation calorimetry. Differential scanning calorimetry was used to measure C_p above the ambient temperature and the C_p data were extrapolated to higher temperatures using the appropriate treatment (Kieffer 1985). The data were then used to derive $\log K$ values for selected chemical reactions. These equilibrium constants can be used for geochemical modeling involving systems with Co-Ni sulfides and arsenides.

MATERIALS

The samples used in this study were prepared in evacuated silica tubes. The protocols described below are the results of many trials and errors, which were optimized to yield the desired products. Many other syntheses were carried out but did not run to completion, because they were contaminated by other minor sulfides/arsenides or oxygen.

A synthetic analog of heazlewoodite (Ni_3S_2) was prepared from a stoichiometric (3:2) mixture of pure elements (Ni 99.999%, S 99.999%) that were placed into a silica-glass tube. The tube with the charge was evacuated and sealed. The ampoule was placed into a preheated horizontal furnace, and the sample was tempered (200 °C for 32 days; 300 °C for 19 days). Afterward, the sample was quenched in a cold-water

bath, homogenized in an agate mortar, evacuated, sealed again, and heated (300 °C for two months). Finally, the sample was quenched, and the content purity and composition were checked using powder X-ray diffraction.

The synthetic analog of skutterudite was synthesized in evacuated silica-glass ampoules from pure elements (Co 99.9%, As 99.5%). The elements were weighed in an atomic ratio of 1:4 and placed in a silica-glass ampoule. The ampoule was evacuated, sealed, and placed in a horizontal tube furnace. The temperature of that part of the ampoule, in which the charge was located, was 500 °C. The temperature of the opposite part was 450 °C. The synthesis lasted 50 days. The excess arsenic condensed in the colder part of the ampoule and was easily separated. After that, the reacted mixture was removed, ground in an agate mortar under acetone, placed in another silica-glass ampoule, and heated at the same temperature for 30 days.

METHODS

Powder X-ray diffraction (PXRD) patterns of all compounds used in this work were collected using a Bruker D8 Advance DaVinci diffractometer (Institute of Geoscience of the University of Jena, Germany), employing $\text{CuK}\alpha$ radiation ($\lambda = 1.54058 \text{ \AA}$). The patterns were collected at room temperature between 5 and $90^\circ 2\theta$, with a step size of $0.02^\circ 2\theta$ and a time per step of 1 s. Lattice parameters and quantitative fractions of the studied phases were refined by a full-profile fit using the software suite JANA2006 (Petříček et al. 2014).

The powdery synthetic phases were embedded in a resin and polished. They were briefly examined for impurity phases or inhomogeneities by reflected-light microscopy. The phases were investigated by energy- and wavelength-dispersive (WDX) electron microprobe (EMP) analyses with the electron microprobe JEOL JXA-8230 Superprobe (Institute of Geoscience of the University of Jena, Germany). All samples were carbon-coated and measured with an accelerating voltage of 20 kV and 20 nA. The spot size was $1 \mu\text{m}$ and the measurement time on peak and on background 40 s. Peak overlap correction was used to avoid peak interference between the lines of S and Co. The elements were analyzed on the following emission lines, standards, with the estimated detection limits (in wt%): SbLa , InSb, 0.07; $\text{SK}\alpha$, pyrite, 0.04; $\text{FeK}\alpha$, pyrite, 0.04; $\text{AsK}\alpha$, arsenopyrite, 0.07; $\text{CuK}\alpha$, chalcocopyrite, 0.05; $\text{CoK}\alpha$, Co metal, 0.05; $\text{NiK}\alpha$, Ni metal, 0.04.

High-temperature oxide melt solution calorimetry has been described in detail by Navrotsky (1997, 2014). The experiments were performed at Arizona State University, U.S.A. The samples were dropped into a molten sodium molybdate

TABLE 1. Space groups, lattice parameters (a , c , unit-cell volume V), and chemical composition (wt%) of the synthetic phases used in this work

Nominal composition	Ni_3S_2	CoAs_3
Actual composition	Ni_3S_2	$\text{CoAs}_{2.92}$
Mineral name	heazlewoodite	skutterudite
Space group	$R\bar{3}2$	$Im\bar{3}$
a (Å)	5.7476(1)	8.2050(2)
c (Å)	7.1397(1)	
n	13	11
Sb	<DL	<DL
S	26.83(28)	0.06(1)
As	0.04(6)	78.21(87)
Co	<DL	21.07(27)
Cu	<DL	<DL
Ni	72.65(40)	<DL
Fe	<DL	0.04(2)
Total	99.54(38)	99.41(102)
Normalized to 1 Ni or Co atom		
S	0.676	
As		2.920
Co		1
Ni	1	

Notes: Chemical composition is recalculated to the molar ratio in the bottom part of the table. The numbers in parentheses are the uncertainties on the last significant digits. n = number of analyses averaged. <DL = below detection limit.

(3Na₂O·4MoO₃) solvent, maintained at 1073 K. Oxygen gas was flushed over the solvent at 90 mL·min⁻¹ and bubbled through it at 5 mL·min⁻¹. The choice of the calorimetric solvents is limited to a few compositions, namely sodium molybdate, lead borate, or alkali borate (see Navrotsky 1997). In the recent work of Abramchuk et al. (2020), sodium molybdate at 1073 K was used to dissolve a suite of elements, thus enabling it to close the thermochemical cycle without the need for reference phases. We used this advantage that also dictated the choice of the solvent and operation temperature.

Low-temperature heat capacity (C_p) was measured by relaxation calorimetry using a commercial Physical Properties Measurement System (PPMS, from Quantum Design, San Diego, California) at the University of Salzburg, Austria. With due care, accuracy can be within 1% at 5 to 300 K, and 5% at 0.7 to 5 K (Dachs and Bertoldi 2005; Kennedy et al. 2007). The powdered samples were wrapped in a thin Al foil and compressed to produce a ~0.5 mm thick pellet, which was then placed onto the sample platform of the calorimeter for measurement. Differential scanning calorimetry (DSC) was used to measure heat capacities near and above room temperature using a Perkin Elmer Diamond DSC. Samples were measured in a flow of dry argon. Further details of the method are described by Benisek et al. (2012). The entropy was calculated by integration of the C_p/T function in the interval from 0 to 298.15 K.

RESULTS

Characterization: Powder X-ray diffraction and chemical analysis

All samples used in this study were crystalline and consisted of a single phase. No indications of an amorphous impurity were found. The peaks were sharp, with their width (measured as FWHM) comparable with that of the LaB₆ standard. Refined lattice parameters of all phases are given in Table 1. The PXRD patterns are shown in Online Materials¹ Figures S1 and S2.

Examination with the electron microprobe confirmed that the samples consist of the elements of interest, either Ni-S or Co-As, with trace amounts of other elements (Table 1). Images in backscattered electrons (BSE) showed that the heazlewoodite and skutterudite samples were homogeneous. They were made of porous, angular aggregates, up to several hundreds of micrometers large, and their shape reflects the shape of the starting material (metal filing).

Chemical composition of the synthetic heazlewoodite sample corresponds to the nominal formula Ni₃S₂. For skutterudite, a slight deviation from the nominal formula was found. The composition, determined by EMP analyses, is CoAs_{2.92}. All thermodynamic data reported in this work are normalized to the molecular masses of Ni₃S₂ (240.2102 g·mol⁻¹) and CoAs_{2.92} (277.7043 g·mol⁻¹).

Determination of enthalpies of formation

Enthalpies of formation were determined via appropriate thermochemical cycles (Tables 2 and 3) from the experimentally measured drop solution enthalpies. No difficulties or anomalies were encountered during calorimetric experiments. The samples dissolved rapidly and reproducibly. The large drop solution enthalpies (Table 4) relate to the fact that the samples are oxidized and dissolved in the oxygen atmosphere in the active zone of the calorimeter. The large signals also cause larger uncertainties attached to the data; these uncertainties are expressed in calorimetry as two standard deviations of the mean. Relative to the magnitude of the signal, the uncertainties are smaller than usually encountered. They are only 0.09 and 0.24% for the drop solution enthalpies of Ni₃S₂ and CoAs_{2.92}, respectively, which is smaller than the usual precision of 1–2%. The resulting enthalpies of formation are given in Table 5.

TABLE 2. Thermochemical cycle used to calculate the enthalpies of formation for heazlewoodite (reaction # in parentheses)

Ni ₃ S ₂ (s, 298 K) + (2y + x/2)O ₂ (g, 1073 K) → xNi ²⁺ (sol, 1073 K) + xO ²⁻ (sol, 1073 K) + ySO ₄ ²⁻ (sol, 1073 K)	ΔH ₁	(1)
Ni (s, 298 K) + 0.5O ₂ (g, 1073 K) → Ni ²⁺ (sol, 1073 K) + O ²⁻ (sol, 1073 K)	ΔH ₂	(2)
S (s, 298 K) + 2O ₂ (g, 1073 K) → SO ₄ ²⁻ (sol, 1073 K)	ΔH ₃	(3)
xNi (s, 298 K) + yS (s, 298 K) → Ni ₃ S ₂ (s, 298 K) ^a	Δ _f H° = -ΔH ₁ + xΔH ₂ + yΔH ₃	
^a f_m , formation reaction of heazlewoodite.		

TABLE 3. Thermochemical cycle used to calculate the enthalpy of formation for skutterudite (reaction # in parentheses)

CoAs ₂ (s, 298 K) + (2z + 1/2)O ₂ (g, 1073 K) → Co ²⁺ (sol, 1073 K) + O ²⁻ (sol, 1073 K) + zAsO ₄ ³⁻ (sol, 1073 K)	ΔH ₄	(4)
Co (s, 298 K) + 0.5O ₂ (g, 1073 K) → Co ²⁺ (sol, 1073 K) + O ²⁻ (sol, 1073 K)	ΔH ₅	(5)
As (s, 298 K) + 2O ₂ (g, 1073 K) → AsO ₄ ³⁻ (sol, 1073 K)	ΔH ₆	(6)
Co (s, 298 K) + zAs (s, 298 K) → CoAs ₂ (s, 298 K) ^a	Δ _f H° = -ΔH ₄ + ΔH ₅ + zΔH ₆	
^a f_m , formation reaction of skutterudite.		

TABLE 4. Drop solution enthalpies of the samples and reference phases

Samples	
Ni ₃ S ₂	-1685.97 ^a ± 1.56 ^b (10) ^c
CoAs _{2.92}	-1424.46 ± 3.40 (10)
Reference phases	
Ni	-214.52 ± 2.06 (Hayun et al. 2020)
Co	-227.75 ± 2.18 (Hayun et al. 2020)
S	-629.18 ± 2.73 (Abramchuk et al. 2020)
As	-440.03 ± 1.57 (Abramchuk et al. 2020)

Notes: All values in kJ·mol⁻¹.

^a Mean.

^b Two standard deviations of the mean.

^c Number of measurements.

TABLE 5. Summary of thermodynamic data for heazlewoodite and skutterudite, obtained in this work

	Δ _f H° kJ·mol ⁻¹	S° J·mol ⁻¹ ·K ⁻¹	Δ _f G° kJ·mol ⁻¹	V° J·bar ⁻¹
Ni ₃ S ₂	-216.0 ± 8.4 -217.2 ± 1.6 ^a	133.8 ± 1.6 133.5 ± 0.7 ^a 133.89 ± 0.84 ^b 133.2 ^c	-210.0 ± 8.4 -211.2 ± 1.6 ^a	4.095
CoAs _{2.92}	-88.2 ± 6.1 -104.6 ^d	106.4 ± 1.3	-79.9 ± 6.2	4.159

Notes: Calculated enthalpies of formation are compared to the previously published literature values. Coefficients for the C_p polynomials are listed in Table 6.

^a Gamsjäger et al. (2005).

^b Weller and Kelley (1964).

^c Stølen et al. (1991).

^d Theoretically calculated for CoAs₃, <https://www.ctcms.nist.gov/~knc6/jsmol/JVASP-20306.html>, accessed on July 21, 2021.

Determination of low-temperature C_p and entropies

Heat capacity at temperatures between 2 and 303 K was measured for the synthetic heazlewoodite and skutterudite samples with the commercial PPMS system. The C_p data for both synthetic phases show no anomalies. Attempts to fit the low-temperature portion of the data ($T < 20$ K) with a Debye function ($C_p = A_3T^3$) or an extended Debye function ($C_p = A_3T^3 + A_5T^5 + A_7T^7$) failed. Satisfactory fits required the inclusion of a linear (A_1T) or quadratic (A_2T^2) term, probably reflecting the semi-conducting nature of the phases studied (see Gopal 1966). The data between 20 and 300 K were fitted by two orthogonal

polynomials. The adjustable parameters of these functions, together with the raw data and the results of integration, are available in the supporting electronic information. The calculated standard entropies (S° at $T = 298.15$ K) are listed in Table 5.

Determination of high-temperature C_p

Heat capacity above 280 K was measured by differential scanning calorimetry (DSC). In the region of overlap of the DSC and PPMS data, the agreement between the data sets was good. The deviation was 1.3% for heazlewoodite and 2.2% for skutterudite. Upon increasing temperature, the data became unusually scattered. At $T \approx 366$ K (skutterudite) or ≈ 466 K (heazlewoodite), the data were so erratic that the measurements were stopped. Even though the samples were measured in an inert atmosphere of purified argon, it has to be assumed that traces of oxygen caused partial oxidation of the samples. Of particular problem is sulfur or arsenic that coexists in the gas phase with the studied phases (see Leegaard and Rosenqvist 1964). With increasing temperature, more sulfur or arsenic is transferred into the gas phase and can rapidly react with small amounts of oxygen.

Extrapolation of C_p up to 700 K

To be able to use the presented data for geochemical models of hydrothermal systems, heat capacity must be determined up to higher temperatures than those that were reached experimentally in this work. For this purpose, the available experimental C_p data were augmented by heat capacities at constant volume (C_v) computed using a model proposed by Kieffer (1985, Eq. 60 therein)

$$C_v \propto S(x_i) + K(x_u, x_i) + E(x_E) \quad (7)$$

where $S(x_i)$ is the heat capacity function of a monatomic solid with a sine dispersion function, $K(x_u, x_i)$ refers to heat capacity of a continuum between frequencies x_u and x_i , and $E(x_E)$ is the heat capacity function of an Einstein oscillator. These functions and their prefactors are in detail defined by Equations 57–60 in Kieffer (1985) and will not be repeated here.

The frequencies necessary to calculate C_v according to function 7 can be determined experimentally or by a lattice-dynamic calculation. We emphasize that the function 7 is not a fit to data but is based purely on experimental or calculated frequencies of low- to high-frequency modes in a structure. The function 7, as used in this work, contains no adjustable parameters.

For the calculation for skutterudite, frequencies of the Raman bands were taken from <https://ruff.info/Skutterudite/R050593> (accessed on September 10, 2021). The frequencies for the acoustic branches were taken from Li and Mingo (2014) who performed first-principles calculations for the lattice dynamics of CoSb_3 skutterudite. For heazlewoodite, the Raman frequencies were taken from <https://ruff.info/Heazlewoodite> (accessed on September 10, 2021). The acoustic modes were characterized by first-principles calculations by Tian et al. (2021).

The isochoric heat capacity C_v can be used to calculate the isobaric heat capacity C_p as:

$$C_p = C_v + VT\alpha^2 B\kappa \quad (8)$$

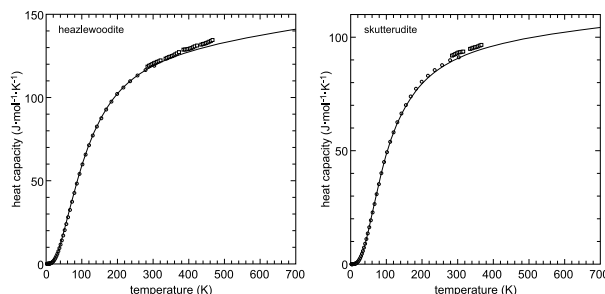


FIGURE 1. Experimental heat capacities from PPMS (circles) and DSC (squares) with the Kieffer model used to extrapolate C_p to higher temperatures. Note that this is not the fit used to determine entropy at $T = 298.15$ K.

where V is the molar volume, T is the thermodynamic temperature, α is the thermal expansion coefficient, and B is the bulk modulus. The variable κ is the only adjustable parameter that enters the calculations. It is necessary because the calculated C_p is slightly lower than the experimental C_p data. Such a situation can be encountered in these calculations and is corrected by κ , which can be regarded as an anharmonicity term in Equation 8.

For skutterudite, α was taken from Rogl et al. (2010) for CoSb_3 skutterudite, and B from Zouablia et al. (2020) for CoP_3 skutterudite. The value of κ was set to 2.4. For heazlewoodite, α was taken from Tian et al. (2021), B from Zhang et al. (2020), and κ was set to 2.4.

The fits are compared with the experimental data, and the extrapolations are shown in Figure 1. The results in the range of 280–700 K were refitted with polynomials accepted by the program SUPCRTBL (Johnson et al. 1992; Zimmer et al. 2016):

$$C_p = a + bT + cT^{-2} + dT^{-0.5}. \quad (9)$$

The coefficients a – d are listed in Table 6 in the format required by SUPCRTBL. Note that the values for the coefficients a , c , and d are to be used in SUPCRTBL as listed; the value of b should be multiplied by 10^{-5} before inserting into the Equation 9. The resulting C_p is in $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

DISCUSSION

Comparison of the data for heazlewoodite with earlier data

The enthalpies of formation of the two phases studied here can be compared with some previous results. The $\Delta_f H^\circ$ value for heazlewoodite (Table 5) is in excellent agreement with the value selected by Gamsjäger et al. (2005), based on the calorimetric work of Cemic and Kleppa (1986). They used reaction calorimetry with $\text{Ni}+\text{NiS}$ mixtures sealed in evacuated silica tubes. The entropy of heazlewoodite, derived in this work, is also in excellent agreement with the selection of Gamsjäger et

TABLE 6. Adjustable coefficients for the C_p polynomial ($C_p = a + bT + cT^{-2} + dT^{-0.5}$, Eq. 9) for skutterudite and heazlewoodite

Phase	a	b	c	d
Skutterudite	0.1096	0.8507	−535.1	−0.2695
Heazlewoodite	0.1361	2.300	−872.4	−0.2490

Notes: The numerical values are scaled as required by SUPCRTBL. See text for details.

al. (2005). Our value is essentially identical to that of Weller and Kelley (1964) and only slightly higher than that of Stølen et al. (1991) (Table 5).

The perfect agreement for heazlewoodite confirms the accuracy of the data for the reference compounds and the applicability of high-temperature oxide-melt solution calorimetry. It lends support for the data for skutterudite where earlier data are missing.

Equilibria between nickel sulfides

The accuracy of the data for the nickel sulfides can be, to some extent, tested by comparison to known phase diagrams, as already presented in Gamsjäger et al. (2005). Sulfur pressure over nickel sulfide and the T - P (S_2 ,g) data were collected by Rosenqvist (1954) and Leegaard and Rosenqvist (1964). The pair heazlewoodite-millerite (β -NiS) is related by a simple reaction:



The data for millerite were taken from Gamsjäger et al. (2005). The $\log K_{10}$ values calculated with SUPCRTBL and the resulting sulfur gas fugacities are compared with the measured data in Figure 2. The temperature ranges of the calculations and measurements do not overlap, but linear extrapolation is possible. The difference between the $\log f_{S_2}$ values predicted with our data and those from Rosenqvist (1954) (Fig. 2) at $T = 900$ K is ≈ 1.5 , corresponding to $RT\Delta \ln f_{S_2}$ of ≈ 26 kJ·mol⁻¹. Optimization of the data to fit the high-temperature measurements of Rosenqvist (1954) would be misleading because the nickel sulfides tend to be non-stoichiometry at high temperatures (as $\text{Ni}_3\text{S}_{2\pm x}$, $\text{NiS}_{1\pm x}$, see Leegaard and Rosenqvist 1964). The deviation from stoichiometry is perhaps responsible for the mismatch seen in Figure 2. Additionally, these phases have high-temperature

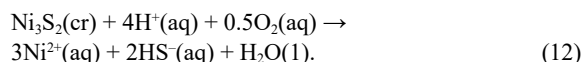
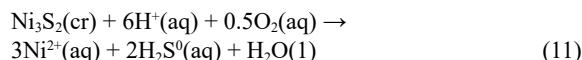
polymorphs with slightly different thermodynamic properties (see Gamsjäger et al. 2005). All in all, the result of this test is encouraging for the accuracy of the data for heazlewoodite and millerite. A more detailed calculation of the sulfur pressures in nickel-sulfide equilibria is provided by Gamsjäger et al. (2005) (their Fig. 5-32) at high temperatures.

No attempt was made to incorporate the thermodynamic data for vaesite (NiS_2) into these calculations, even though Chase (1998) and Gamsjäger et al. (2005) list data for this phase. These data, however, are associated with unusually large uncertainties. They indicate another underlying problem with these data. As a side note, we attempted to synthesize vaesite also for this study. The sample turned out to be a mixture of NiS_2 and Ni_3S_4 . These two phases should have pyrite-like and spinel-like structures, respectively. Powder XRD data for our sample shows only a pyrite-like structure. This puzzling structural relationship will be more closely investigated but could be potentially a reason (or one of the reasons) for the problems related to the measurements on vaesite. Finally, the database Thermoddem (Blanc et al. 2012) contains temperature-dependent $\log K$ values for a dissolution reaction involving vaesite. Yet, a closer look at the values in this database (<https://thermoddem.brgm.fr/species/nis2>, accessed on September 9, 2021) shows that C_p of vaesite was taken as a constant over 0–300 °C. Such treatment of thermodynamic data is highly misleading and should be avoided.

Equilibrium constants for dissolution reactions

Geochemical software used for modeling aqueous solutions, either around room temperature or at elevated temperatures, commonly requires tabulation of equilibrium constants for selected dissolution reactions involving the phase of interest. For this purpose, all data presented above were inserted into SUPCRTBL (Zimmer et al. 2016), and the equilibrium constants were calculated.

The calculations are slightly complicated by the fact that the nominal valences, calculated from the formulas, differ from the valences usually assigned to the participating elements (such as Ni^{2+} , S^{2-} , and so on). For heazlewoodite, the reactions to consider are:



Under most hydrothermal conditions, the aqueous species H_2S^0 will predominate over HS^- . The aggregate state of O_2 and H_2O is important inasmuch the software packages usually do not explicitly specify it for the master O_2 and H_2O species. The values of $\log K_{11}$ and $\log K_{12}$ in the temperature range 0–350 °C are listed in Online Materials¹ Table S1.

For skutterudite, the oxidation reactions are:

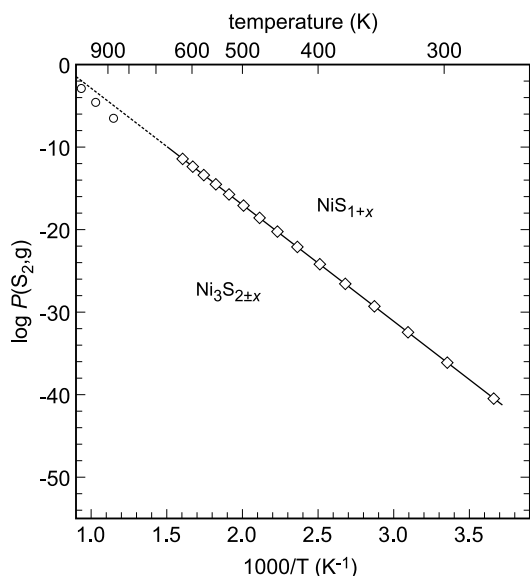
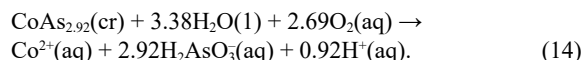
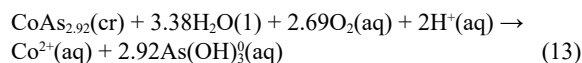


FIGURE 2. Equilibrium sulfur pressure for the pair heazlewoodite-millerite (reaction 10) calculated from the data presented and discussed in this work (diamonds) and experimentally measured by Rosenqvist (1954, circles). The linear fit is extrapolated to higher temperatures to allow for a visual judgment of the agreement between the two data sets.

For the arsenical species, $\text{As}(\text{OH})_3^0$ is prevalent in hydrothermal fluids, and $\text{AsO}(\text{OH})_2^-$ (this species is listed as H_2AsO_3^- in GWB or AsO_2^- in SUPCRTBL) is subordinate, predominant only at $\text{pH} > 8$ at $T = 300^\circ\text{C}$ (Testemale et al. 2011). The values of $\log K_{13}$ and $\log K_{14}$ in the temperature range $0\text{--}350^\circ\text{C}$ are listed in Online Materials¹ Table S1.

Some geochemical software accepts a function that expresses $\log K$ in terms of absolute temperature T in Kelvin instead of $\log K$ values at a pre-selected temperature grid. PHREEQC, for example, uses the function in its “-analytic” option:

$$\log K = A_1 + A_2T + A_3/T + A_4\log T + A_5/T^2. \quad (15)$$

GWB expresses the temperature dependence of $\log K$ as:

$$\log K = a + b(T - T_r) + c(T^2 - T_r^2) + d(1/T - 1/T_r) + e(1/T^2 - 1/T_r^2) + f \ln(T/T_r) \quad (16)$$

where T is absolute temperature in Kelvin and $T_r = 298.15\text{ K}$.

The fit parameters $A_1\text{--}A_5$ for Equation 15 and the reactions 11 through 14 are listed in Online Materials¹ Table S2. The fit parameters $a\text{--}f$ for Equation 16 and the reactions 11 through 14 are listed in Online Materials¹ Table S3.

RELATIONSHIP OF SKUTTERUDITE TO OTHER COBALT ARSENIDES

The $\Delta_r H^\circ$ value for skutterudite (Table 5) can be only compared to an estimate, which is significantly different. We are not aware of thermodynamic measurements on skutterudite.

The GWB and LLNL databases contain $\log K$ values for reactions involving safflorite (CoAs_2) and modderite (CoAs), even though no references are given. The $\log K_{T=298.15}$ values match those given in Charykova et al. (2011), who also gave no references. Wagman et al. (1982) listed only $\Delta_r H^\circ$ for these phases, also without references. For example, they gave $-61.5\text{ kJ}\cdot\text{mol}^{-1}$ for CoAs_2 , but Naumov et al. (1974) selected $-83\text{ kJ}\cdot\text{mol}^{-1}$. These data, even though of uncertain origin, allow the calculation of phase diagrams whose informative value should not be overrated. Scharrer et al. (2019) constructed elaborate models with these phases and generated estimates for the missing data. Ironically, they themselves do not recommend the use of some of the data they published (see their Table 3). We refrain from such practice and hold the opinion that geochemical modeling should be based on sound data. As pointed out by Henke (2009; appendix C) with respect to thermodynamics of arsenical phases, “once high-quality laboratory data are available, they may be used in geochemical computer models...”.

IMPLICATIONS

This work enhances the capabilities of geochemical modeling of hydrothermal ores, especially those of the so-called “five-element association” (e.g., Kreissl et al. 2018; Scharrer et al. 2019; Horn et al. 2021; Tourneur et al. 2021). Skutterudite is one of the major sources of cobalt in these ores, being used for the construction of lithium-ion batteries (Li et al. 2018). Therefore, understanding these ores, the ore-forming processes, and the identification of new resources is an important future task. This work also documented the capability of calorimetric techniques

to obtain highly accurate data for chalcogenides. Combination of the experimental data with the Kieffer model generated an accurate representation of high-temperature heat capacities and can be used to circumvent experimental difficulties associated with the measurements at high temperatures. This approach can be used to resolve some long-standing controversies in the thermodynamic data sets for common and less common chalcogenide minerals.

ACKNOWLEDGMENTS

We are thankful to Valentina L. Stolyarova and Gleb Pokrovski for their constructive criticism and comments. The work presented here was financially supported by a Deutsche Forschungsgemeinschaft grant MA 3927/32-1. Oxide melt solution calorimetry was supported by the U.S. Department of Energy Office of Basic Energy Sciences, under grant DE-FG02-97ER14749. The work of DACH is supported by RFBR, No. 20-35-70049.

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MANUSCRIPT RECEIVED OCTOBER 8, 2021

MANUSCRIPT ACCEPTED DECEMBER 7, 2021

MANUSCRIPT HANDLED BY DANIEL R NEUVILLE

Endnote:

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