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Standard molar enthalpies of formation of sulfosalts in the Ag-As-S system and thermochemistry of the sulfosalts of Ag with As, Sb, and Bi

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ABSTRACT

High-temperature direct-synthesis calorimetry of the silver thioarsenite minerals smithite ($AgAsS_2$), trechmannite ($AgAsS_2$), and proustite (Ag_3AsS_3) at 793 K yielded mean values for the standard enthalpy of formation from the elements of -59.1 ± 2.3, -74.77 ± 2.9, and -111.3 ± 3.4 $kJ \cdot mol^{-1}$, respectively.

The enthalpy of transformation of the low-temperature polymorph of $AgAsS_2$ (trechmannite) to the high-temperature polymorph (smithite) was determined to be 15.65 ± 1.7 $kJ \cdot mol^{-1}$. At the equilibrium temperature of this transformation, 593 K, this yields an entropy of transformation of 26.4 ± 3.0 $J \cdot K^{-1} \cdot mol^{-1}$.

A systematic study of the thermochemistry of the sulfosalts of Ag with the Group V elements As, Sb, and Bi shows that the enthalpies of formation for the low-temperature polymorphs become progressively more exothermic in the order Bi → Sb → As. The enthalpies of transformation from the low- to high-temperature polymorphs of $AgBiS_2$ ($\beta \rightarrow \alpha$ matildite), $AgSbS_2$ ($\alpha \rightarrow \beta$ miargyrite), and $AgAsS_2$ (trechmannite → smithite) become more endothermic in the order Bi ≈ Sb → As, whereas the corresponding entropies of transformation of these minerals (i.e., ΔS_{trans}) increases in the order Sb → Bi → As. For the transformation of α- to β-miargyrite, $\Delta S_{trans} \approx 2R \ln 2$ and may be attributed to the complete disordering of Ag and Sb atoms in the miargyrite structure. This approximate equality is in marked contrast to both $AgAsS_2$ and $AgBiS_2$ for which $\Delta S_{trans} \gg 2R \ln 2$.

The molar volume differences (i.e., ΔV_{trans}) for these polymorphic transformations are negative and decrease in magnitude in the order $AgAsS_2 \rightarrow AgSbS_2 \rightarrow AgBiS_2$. Each of the polymorphic transformations therefore involves (at 298 K) a decrease in molar volume and a positive entropy change with no apparent correlation between ΔV_{trans} and ΔS_{trans}.

INTRODUCTION

In this paper we present new enthalpy of formation data for the sulfosalt minerals that lie on the join Ag_2S-As_2S_3, obtained by high-temperature direct-synthesis calorimetry. The present study is an extension of the previous calorimetric investigations into the thermochemistry of sulfosalt minerals in the systems Ag-Bi-S, Ag-Sb-S, and Cu-Sb-S (Bryndzia and Kleppa, 1988a, 1988b, and 1988c, respectively).

The sulfosalts on the joins Ag_2S-As_2S_3 (i.e., smithite, trechmannite, and proustite) and Ag_2S-Sb_2S_3 (i.e., miargyrite and pyrargyrite) are collectively referred to as the ruby-silver minerals. They are widespread in their distribution and occur in a diverse range of ore deposit types; although minor constituents in most polymetallic sulfide ore deposits, the ruby-silver minerals proustite and pyrargyrite may in some cases constitute the bulk of mineable silver mineralization.

There are inherent limitations associated with experimental studies of pure synthetic phases, since sulfosalt minerals in nature are often compositionally much more complex than their synthetic analogues. However, in view of the fact that for most sulfosalt minerals there is a dearth of reliable thermochemical data, working with the pure end-member synthetic minerals is a logical first step.

Previous work on the system Ag-As-S

The phases and phase relations in the system Ag-As-S have been studied by Jaeger and van Klooster (1912), Gaudin and McGlashan (1938), Béland (1948), Toulmin (1963), Hall and Yund (1964), Hall (1966), Roland (1968, 1970), Wehmeier et al. (1968), and Bardsley and Jones (1968). Jaeger and van Klooster (1912) presented a phase diagram for the join Ag_2S-As_2S_3 determined from melting relations along the join, showing that four solid phases (Ag_2S, Ag_3AsS_3, $AgAsS_2$, and As_2S_3) and three eutectics are present in the system. The three eutectics occur at 16.9, 39.8, and ~96 mol% As_2S_3. Subsequent work by Gaudin and McGlashan (1938), Hall (1966), and Roland (1970) has confirmed their findings (see Fig. 1, taken from Roland, 1970; after Jaeger and van Klooster, 1912). The sulfosalts on the join Ag_2S-As_2S_3 are smithite and trech-

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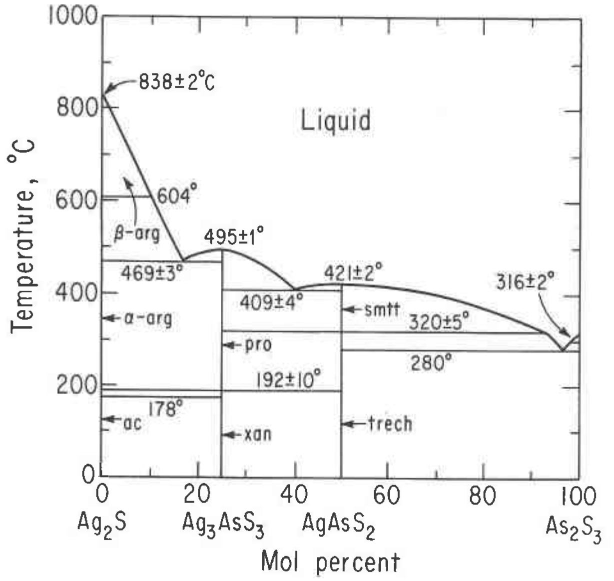

Fig. 1. Phase relations along the join Ag_2S-As_2S_3, in the presence of vapor (modified from Roland, 1970; after Jaeger and von Klooster, 1912). Abbreviations are as follows: ac, acanthite; arg, argentite; xan, xanthoconite; pro, proustite; trech, trechmannite; smtt, smithite. The restricted stability field of cubic smithite reported by Hall (1966) (415 to 421 °C), has been omitted for reasons discussed in the text.

mannite ($AgAsS_2$) and proustite and xanthoconite (Ag_3AsS_3); both compositions melt congruently.

Wehmeier et al. (1968) published a very different diagram for the join Ag_2S-As_2S_3, but, according to Roland (1970), the appearance of the S-rich phase Ag_7AsS_6 in many of their experiments showed that either equilibrium was not maintained or that their compositions were not strictly binary. The synthetic phase Ag_5AsS_4 has been omitted from Figure 1 since it could not be synthesized by Roland (1970), even though Hall (1966) reported it.

$AgAsS_2$ exists as two modifications in nature. These are the relatively rare minerals smithite and trechmannite, which are monoclinic and hexagonal, respectively. Hall (1966) reported a third structural form of $AgAsS_2$; this form—the highest-temperature one, α-smithite—is cubic and is apparently isostructural with β-miargyrite (β-$AgSbS_2$) and α-matildite (α-$AgBiS_2$). According to Hall (1966), the cubic modification has a very restricted temperature stability range from 415 °C to 421 °C. The cubic phase was not observed by Roland (1970) or by us. X-ray powder data for synthetic smithite formed in our experiments and previously reported by Roland (1970) are in perfect agreement with natural monoclinic smithite reported by Berry and Thompson (1962) and with the synthetic material of Béland (1948). Roland (1970) reported the melting temperature of smithite to be 421 ± 2 °C, the same temperature at which Hall (1966) reported the cubic modification of smithite to melt. Synthetic trechmannite was first made by Roland (1968) by annealing smithite at 290 °C for 10 d; it was shown to be hexagonal, having the same cell dimensions as natural trechmannite reported by Nowacki and Kunz (1961). The equilibrium temperature of the smithite-trechmannite inversion has been determined to be 320 ± 5 °C (Hall, 1966; Roland, 1970).

Ag_3AsS_3 also exists in two modifications in nature. The low-temperature modification, which is monoclinic, is the rare mineral xanthoconite. The high-temperature modification, which is hexagonal, is the mineral proustite, an important and relatively abundant silver ore mineral. Xanthoconite, as with its analogue in the system Ag-Sb-S, pyrostilpnite (Ag_3SbS_3), is always reported to occur with its high-temperature dimorph, proustite. It was first synthesized in aqueous media by Béland (1948), who found that in all runs in which xanthoconite formed, the major phase was proustite. Toulmin (1963) found that proustite showed no sign of inversion to xanthoconite when annealed at 135 °C for 17 months. Hall (1966) was able to establish the conversion temperature of xanthoconite to proustite to be 192 ± 10 °C. This was later confirmed by Roland (1970). Proustite was grown as large single crystals of optical quality by Bardsley and Jones (1968) and by Wehmeier et al. (1968). X-ray powder data for synthetic proustite formed in our experiments are in nearly perfect agreement with those documented for synthetic proustite by Wernick et al. (1958). Using various X-ray techniques, Roland (1970) showed that proustite remains stoichiometric up to its melting point of 495 °C.

In this communication we present new high-temperature, direct-synthesis calorimetric data on the enthalpies of formation of trechmannite, smithite, and proustite. Because it is not possible to synthesize pure xanthoconite, its enthalpy of formation could not be measured. The standard enthalpies of formation of the end-member simple sulfides Ag_2S and As_2S_3 have been reported previously by Bryndzia and Kleppa (1988a and 1988d). The new enthalpy data for the silver-arsenic sulfosalts are compared below with enthalpy data previously reported for the sulfosalts of Ag with Bi and Sb (Bryndzia and Kleppa, 1988a and 1988b, respectively). We also report molar-volume data for the sulfosalts of Ag with the Group V elements As, Sb, and Bi.

EXPERIMENTAL METHODS

Calorimetry

The caloarimetric experiments reported in the present communication were carried out at 793 K in a Calvet-type twin microcalorimeter. The principal features of this type of apparatus have been described in detail previously by Kleppa (1972) and by Bryndzia and Kleppa (1988a, 1988b).

Enthalpies of formation of the sulfosalts on the join Ag_2S-As_2S_3 were obtained by measuring the heat effects associated with the reaction of elemental Ag and As with S at 793 K. All samples were dropped from room temperature into the calorimeter. Two series of experiments were performed for each sulfosalt. In the first series, the elements react to form the sulfosalts; in the second series, the heat contents of the sulfosalts formed in the previous experiments are determined. The difference in the two measured enthalpies gives the standard molar heat of formation of the sulfosalt. Calibrations were based on the heat content of pure Au at 793 K (66.542 J·g^{-1}) taken from Kelley (1960).

Starting materials

The starting materials used in the experiments were as follows: S—sublimed USP powder, Lot 344371, J. T. Baker Chemical Co.; Ag—AESAR Johnson-Matthey Inc., silver powder, 5–9 µm, Catalog no. 11402; and As—AESAR Johnson-Matthey Inc., 2–6 mm, Catalog no. 11170. Electron-microprobe analyses of our starting materials indicated that the elements were free of metallic impurities. The As was separated from any oxide by gently distilling off any volatile As_2O_3 under vacuum and was always stored in evacuated quartz tubes to prevent oxidation.

Components were weighed out in stoichiometric proportions to form the compounds $AgAsS_2$ and Ag_3AsS_3. In all cases the powders were thoroughly mixed by dry grinding in an agate mortar and then pelletized. Approximately 1 g of material was used in each experiment. To minimize the possibility of any prereaction occurring in our experiments, the elapsed time between preparation of pelletized charges and their subsequent reaction in the calorimeter was in every case less than 1 h. This approach is the same as was adopted previously in our calorimetric determination of the enthalpy of formation of Ag_2S from the elements (Bryndzia and Kleppa, 1988a). The container used in the drop experiments was silica-glass tubing, 6-mm outside diameter, with 1-mm wall thickness, sealed under vacuum. Reaction products were routinely examined by X-ray and electron-microprobe analysis.

RESULTS

Standard enthalpy of formation of smithite, $AgAsS_2$, from the elements

The standard enthalpy of formation of smithite was obtained by determining the heat effects associated with consecutive drops of the same sample (i.e., sample + silica container) from room temperature into the calorimeter. In the first drop, 100% reaction occurs between the elements which, at 793 K, react to form a liquid having the stoichiometry of the smithite being synthesized. In subsequent drops the heat content of the same silica container + the reaction product is measured. The silica container is chemically inert and therefore does not take part in the reaction. The difference between the measured heat effect in the first drop and the average of subsequent drops of the same sample is directly related to the enthalpy of formation of the sample in the silicia container. The calculation of the standard molar enthalpy of formation of smithite may be summarized by the following: (1) $\Delta H_{\text{reaction}}$ for

$$n_{\text{SiO}_2(\text{container}),298} + n_{\text{Ag}(s),298} + n_{\text{As}(s),298} + 2n_{\text{S}(s),298} = n_{\text{SiO}_2,793} + n_{\text{AgAsS}_2(l),793}, \quad (1a)$$

and (2), the heat content $[H_{793} - H_{298}]$ for

$$n_{\text{SiO}_2,298} + n_{\text{AgAsS}_2(s),298} = n_{\text{SiO}_2,793} + n_{\text{AgAsS}_2(l),793}. \quad (1b)$$

Subtracting 1b from 1a yields

$$\Delta H^0_{\text{f,AgAsS}_2,298} = \Delta H_{\text{reaction}} - (H_{793} - H_{298})/n_{\text{AgAsS}_2}. \quad (1c)$$

TABLE 1. Standard molar enthalpy of formation of smithite ($AgAsS_2$)

Expt.	n_{SiO_2} (mmol)	n_{AgAsS_2} (mmol)	$\Delta H_{\text{reaction}}$ (J)	$H_{793} - H_{298}$ (J) (±1 s.d.)	$\Delta H^0_{\text{f,AgAsS}_2,298}$ (kJ·mol^{-1})
1(a)	23.573	3.930	802.2		
1(b)				1032.7 1053.8 1021.8 1041.2 1037.4 ± 11.7	−59.85
2(a)	20.772	3.906	700.4		
2(b)				948.6 932.3 940.5 ± 8.2	−61.47
3(a)	22.962	3.889	784.3		
3(b)				992.5 1011.8 1002.2 ± 9.7	−56.03

$\Delta H^0_{\text{f,AgAsS}_2,298} = \{\Delta H_{(a)} - [H_{793} - H_{298}]_{(b)}\}/n_{\text{AgAsS}_2}$
$\Delta H^0_{\text{f,(mean)}} = -59.12 \pm 2.3$ kJ·mol^{-1} (±1 s.d., $N = 3$)

The liquid of $AgAsS_2$ stoichiometry formed in Reaction 1a crystallizes as the high-temperature modification of $AgAsS_2$, smithite, which persists metastably on cooling to room temperature. In 1b the heat content of smithite is measured. Table 1 summarizes the results on the synthesis of smithite. From three series of experiments, we obtain a mean value of −59.12 ± 2.3 kJ·mol^{-1} (±1 s.d.) for the standard enthalpy of formation of smithite from the elements at 298 K.

Enthalpy of transformation of trechmannite to smithite and standard enthalpy of formation of trechmannite, $AgAsS_2$, from the elements

In order to obtain the enthalpy of formation of the low-temperature modification of $AgAsS_2$, trechmannite, it is necessary to obtain a value for the enthalpy of transformation of techmannite to smithite. Figure 1 shows that the inversion temperature for trechmannite to smithite is 320 ± 5 °C. The synthesis of trechmannite and its characteristic X-ray powder pattern were reported by Roland (1968), who showed that annealing a solid of $AgAsS_2$ composition at 290 °C for 315 h, was sufficient to achieve the inversion of smithite to trechmannite. Approximately 3 g of smithite were ground in an agate mortar, packed into silica-glass tubes, sealed under vacuum and annealed at 285 ± 4 °C for about 290 h. The X-ray powder pattern of the annealed material shows that it was identical to that obtained by Roland (1968, Fig. 1). Based on the ratio of peak heights of the dominant X-ray peak in pure smithite and in the annealed material, the yield of trechmannite was estimated to be >98%.

The enthalpy of transformation of trechmannite to smithite was obtained by measuring the enthalpy changes associated with the following reactions, which involved consecutive drops of the trechmannite sample contained in an evacuated silica-glass tube:

TABLE 2. The enthalpy of transformation of trechmannite to smithite

Expt.	n_{SiO_2} (mmol)	n_{AgAsS_2} (mmol)	ΔH_1* (J)	ΔH_2† (J) (±1 s.d.)	$\Delta H^{tr\text{-}sm}_{trans}$‡ (kJ·mol⁻¹)
1(a)	29.966	4.065	1325		
1(b)				1241 1264 1266 1243 1254 ± 12	17.47
2(a)	31.926	4.061	1425		
2(b)				1354 1350 1387 1392 1371 ± 19	13.30
3(a)	30.708	5.131	1469		
3((b)				1396 1355 1397 1395 1386 ± 18	16.18

* ΔH_1: trechmannite(*s*), 298 K = $AgAsS_2(l)$, 793 K.

† ΔH_2: smithite(*s*), 298 K = $AgAsS_2(l)$, 793 K.

‡ $\Delta H^{tr\text{-}sm}_{trans}$: trechmannite(*s*), 298 K − smithite(*s*), 298 K = $\{[\Delta H(1) - \Delta H(2)]/n_{AgAsS_2}\}$ = 15.65 ± 1.7 kJ·mol⁻¹ (±1 s.d., N = 3). $\Delta H^0_{f,trechmannite(s),298} = \Delta H^0_{f,smithite(s),298} - \Delta H^{tr\text{-}sm}_{trans} = -74.77 \pm 2.9$ kJ·mol⁻¹.

$$\Delta H(1) = \text{trechmannite}(s),\ 298\text{ K} \rightarrow AgAsS_2(l),\ 793\text{ K}$$

$$\Delta H(2) = \text{smithite}(s),\ 298\text{ K} \rightarrow AgAsS_2(l),\ 793\text{ K}$$

Hence,

$$\Delta H^{tr\text{-}sm}_{trans} = \Delta H(1) - \Delta H(2). \tag{2a}$$

Based on three separate series of experiments summarized in Table 2, we obtain a mean value of 15.65 ± 1.7 kJ·mol⁻¹ (±1 s.d.) for the enthalpy of transformation of trechmannite to smithite at 298 K. If this value is assumed to be independent of temperature and if the equilibrium temperature of the trechmannite to smithite transformation is 593 K, this yields an entropy of transformation of about 26.4 J·K⁻¹·mol⁻¹.

An estimate of the enthalpy of formation of trechmannite may now be obtained from the data in Tables 1 and 2, and the following relationship:

$$\Delta H^0_{f,trech.,298} = \Delta H^0_{f,smith.,298} - \Delta H^{tr\text{-}sm}_{trans}, \tag{2b}$$

which yields a mean value of −74.8 ± 2.9 kJ·mol⁻¹ for the standard enthalpy of formation of trechmannite from the elements at 298 K.

Standard enthalpy of formation of proustite, Ag_3AsS_3, from the elements

Table 3 summarizes the results of our three series of synthesis experiments on the enthalpy of formation of Ag_3AsS_3, based on the enthalpy changes associated with reactions analogous to those implied by 1a and 1b, already given in detail for smithite. We obtained a mean value of −111.27 ± 3.4 kJ·mol⁻¹ (±1 s.d.) for the enthalpy of formation of proustite from the elements at 298 K.

TABLE 3. Standard molar enthalpy of formation of proustite (Ag_3AsS_3)

Expt.	n_{SiO_2} (mmol)	$n_{Ag_3AsS_3}$ (mmol)	$\Delta H_{reaction}$ (J)	$H_{793} - H_{298}$ (J) (±1 s.d.)	$\Delta H^0_{f,AgAsS_3}$ (kJ·mol⁻¹)
1(a)	23.355	2.467	826.2		
1(b)				1092.2 1116.5 1101.7 1103.5 ± 10.0	−112.4
2(a)	22.516	2.466	826.8		
2(b)				1105.5 1113.9 1109.7 ± 10.0*	−114.7
3(a)	23.783	2.474	820.6		
3(b)				1085.7 1083.4 1084.6 ± 10.0*	−106.7

$\Delta H^0_{f,Ag_3AsS_3,298\text{ K}} = \{\Delta H(a) - [H_{793} - H_{298}](b)\}/n_{Ag_3AsS_3}$

$\Delta H^0_{f,(mean)} = -111.27 \pm 3.4$ kJ·mol⁻¹ (±1 s.d., N = 3)

* ±1 s.d. assumed to be the same as for experiment 1.

DISCUSSION

With the enthalpies of formation of the silver thioarsenite sulfosalts, we are able to summarize all of our experimental calorimetric data for the sulfosalts of Ag with the Group V elements As, Sb, and Bi. All of the silver sulfosalts in Table 4 are simple stoichiometric combinations of the Group V sulfides orpiment, As_2S_3, stibnite, Sb_2S_3, and bismuthinite, Bi_2S_3 with acanthite, Ag_2S. Most of the data in column 1 of Table 4 has been obtained by high-temperature direct-synthesis calorimetry from the elements, with the exception of the silver thioantimonite sulfosalts for which the enthalpies of formation were obtained by direct combination of the simple end-member sulfides, i.e., $Ag_2S + Sb_2S_3$ (column 2). For these minerals we have calculated the enthalpies of formation from the elements. In column 3, the sums of the enthalpies of formation of the end-member simple sulfides are given.

All of the silver sulfosalts in Table 4 with a metal : sulfur ratio of 1 : 1 have two polymorphs; column 4 presents the experimentally measured enthalpy of transformation of the low- to high-temperature polymorph. Column 5 gives the temperature of the respective polymorphic transformations. Column 6 gives the entropy of the polymorphic transformations calculated from the data in columns 4 and 5. Column 7 gives the estimted entropy for the polymorphic transformations based on the assumption of complete disordering of a two-metal-atom system, i.e., $\Delta S_{trans} = 2R \ln 2$ (where R is the gas constant).

In a previous study of sulfosalts in the system Ag_2S-Bi_2S_3, Bryndzia and Kleppa (1988a) noted that for the sulfosalts β-matildite (the low-temperature polymorph) and pavonite, the enthalpy of mixing of the simple end-member sulfides to form the sulfosalts was, within the limits of experimental error, equal to zero, i.e., $\Delta H^0_{mix} \approx$

Table 4. Summary of thermochemical data for the sulfosalts of Ag with As, Sb, and Bi

Mineral	Formula	(1) Elements	(2) Sulfides	(3) Σsulfides	(4) ΔH_{trans} (kJ·mol^{-1})	(5) T_{trans} (K)	(6) ΔS_{trans}	(7) $2R \ln 2$
		$\Delta H^0_{f,298}$ (kJ·mol^{-1})					(J·K^{-1}·mol^{-1})	
acanthite	Ag_2S	−31.2 ± 0.8						
orpiment	As_2S_3	−83.0 ± 3.8						
stibnite	Sb_2S_3	−129.7 ± 3.8						
bismuthinite	Bi_2S_3	−135.2 ± 2.5						
trechmannite	$AgAsS_2$	−74.77 ± 2.9		−57.1 ± 2.3	tr → sm	593 ± 5	26.4 ± 3.0	11.5
smithite	$AgAsS_2$	−59.1 ± 2.3			15.65 ± 1.7			
xanthoconite*	Ag_3AsS_3							
proustite	Ag_3AsS_3	−111.3 ± 3.4		−88.3 ± 3.1				
α-miargyrite	α-$AgSbS_2$	(−84.6 ± 4.6)†	−4.1 ± 2.3	−80.5 ± 2.3	α → β	653 ± 5‡	13.3 ± 2.1	11.5
β-miargyrite	β-$AgSbS_2$	(−75.9 ± 3.2)†	+4.6 ± 0.9		8.7 ± 1.4			
pyrostilpnite*	Ag_3SbS_3							
pyrargyrite	Ag_3SbS_3	(−119.5 ± 3.9)†	−7.8 ± 0.8	−111.7 ± 3.1				
β-matildite	β-$AgBiS_2$	−81.7 ± 6.7		−83.2 ± 1.7	β → α	468 ± 5	22.5 ± 9.8	11.5
α-matildite	α-$AgBiS_2$	−71.2 ± 2.1			10.5 ± 4.6			
pavonite	$AgBi_3S_5$	−219.5 ± 3.7		−218.4 ± 4.2				

* Not studied.
† Calculated.
‡ Estimated.

0. It should be noted that the estimated error in column 1 represents experimental error (±1 s.d.), whereas the error in column 3 represents the sum of errors involved in the calculation of ΔH_f from the sulfides. The high-temperature polymorph α-matildite has a significant positive enthalpy of mixing, $\Delta H^0_{\text{mix}} \approx 12$ kJ·mol^{-1}, indicating that it is entropy stabilized (Bryndzia and Kleppa, 1988a).

Similar conclusions may be drawn for the silver thioantimonite sulfosalts in Table 4. For the low-temperature polymorph α-miargyrite, direct-synthesis calorimetry from the end-member sulfides (column 2) shows that the ΔH^0_{mix} is slightly exothermic (column 2). In the case of the high-temperature polymorph β-miargyrite, the heat of mixing is positive and, as in the case of α-matildite, indicates that this mineral must also be entropy stabilized. There is no analogous sulfosalt to pyrargyrite in the Ag_2S-Bi_2S_3 system. However, our data for pyrargyrite indicate that it has a modest exothermic enthalpy of formation relative to the sum of the enthalpies of formation of its end-member sulfides.

The silver-arsenic sulfosalts have significantly more exothermic enthalpies of formation compared to the sum of the end-member sulfide enthalpies of formation. From the preceding discussion, it can be seen that in going from β-matildite through to α-miargyrite and trechmannite, the enthalpies of formation of the sulfosalts of Ag with the Group V elements become progressively more exothermic in the order Bi → Sb → As. The same conclusions may be drawn from the enthalpy data for pyrargyrite and proustite. Consistent with this trend of increasing exothermic enthalpies of formation of the silver sulfosalts is the observation that the enthalpies of transformation from the low- to high-temperature polymorphs of matildite (β → α), miargyrite (α → β), and $AgAsS_2$ (trechmannite → smithite) also increase in the order Bi ≈ Sb → As (column 4, Table 4). However, there is no comparable trend in the entropy of the transformations for these minerals calculated from the data in columns 4 and 5 and given in column 6.

A comparison of the results in column 6 with those in column 7 shows that the transformation entropies of β → α matildite and trechmannite → smithite are considerably greater than would be estimated from $2R \ln 2$ on the basis of assumed complete disorder of two metal atoms in the respective sulfosalts. Bryndzia and Kleppa (1988b) concluded that in the case of miargyrite, the entropy of transformation may in large measure be attributed to the disordering of Ag and Sb atoms. This implies therefore that the difference (i.e., excess) between the observed transformation entropies and $2R \ln 2$, for both matildite and smithite-trechmannite, may be due to some other nonconfigurational-entropy contribution inherent in the structures of these minerals.

The calorimetric technique used to measure the enthalpies of transformation given in Table 4 permits calculation of the entropy of transformation at 298 K, assuming that the transformation enthalpy is independent of temperature. However, this need not always be true. In the case of the transformation of β- to α-matildite, for example, the transformation enthalpy and hence entropy, could not be determined with meaningful precision using the present calorimetric technique. This may be because the transformation is convergent in nature, i.e., a function of temperature. Another shortcoming of the present technique is that it does not reveal anything about the nature of the transformation, i.e., whether it is displacive or reconstructive. The magnitude of the transformation enthalpy may also be quite different at the temperature of the transformation relative to 298 K. We hope to resolve many of these uncertainities by applying differential scan-

Table 5. Molar-volume data for the sulfosalts of Ag with As, Sb, and Bi

Mineral	Formula	(1) GFW	(2) D_x (g·cm^{-3})	(3) Molar V (cm^3)	(4) ΔV_{trans} (cm^3)	(5) ΣV (cm^3)
acanthite	Ag_2S	247.80	7.24	34.23		
orpiment	As_2S_3	246.02	3.49	70.49		
stibnite	Sb_2S_3	339.68	4.63	73.37		
bismuthinite	Bi_2S_3	514.14	6.81	75.50		
trechmannite	$AgAsS_2$	246.91	4.78	51.62	tr → sm	52.36
smithite	$AgAsS_2$	246.91	5.18	47.63	−3.99	52.36
xanthoconite*	Ag_3AsS_3	494.71	5.53	89.46	xa → pro	86.59
proustite	Ag_3AsS_3	494.71	5.68	87.17	−2.29	86.59
α-miargyrite	$AgSbS_2$	293.74	5.25	55.93	$\alpha \rightarrow \beta$	53.80
β-miargyrite	$AgSbS_2$	293.74	5.40*	54.40	−1.53	53.80
pyrostilpnite*	Ag_3SbS_3	541.54	5.98	90.63	ps → pa	88.03
pyrargyrite	Ag_3SbS_3	541.54	5.86	92.49	+1.86	88.03
β-matildite	$AgBiS_2$	380.97	6.99	54.50	$\beta \rightarrow \alpha$	54.87
α-matildite	$AgBiS_2$	380.97	7.03*	54.19	−0.31	54.87
pavonite	$AgBi_3S_5$	895.11	6.78	132.02		

* Calculated from unit-cell volume.

ning calorimetry to the transformations of the sulfosalts of Ag with As, Sb, and Bi, and we feel that any further discussion on the entropies of transformation of these minerals is not warranted at this time.

Molar volumes for all the sulfides and sulfosalts in Table 4 were calculated from the densities and molecular weights of the respective minerals and are summarized in Table 5. The densities used in our calculations were all obtained from the *Mineral Powder Diffraction File* (JCPDS, 1986). We have only used the theoretical densities (D_x, column 2) predicted from the best available crystal-structure determinations. Measured densities are less reliable and in many instances are significantly different from the predicted densities, possibly owing to impure material being used in the density determination. In any case, the structural refinements for all of the minerals involved are of sufficient quality so that it may be assumed that the theoretically predicted densities are on the whole reliable. In all cases, however, molar volumes calculated from the measured densities, where available, are consistent with those calculated using theoretical densities. In Table 5, column 3 gives the calculated molar volume of the sulfosalts of Ag with the Group V elements As, Sb, and Bi. Column 4 gives the volume changes for the polymorphic transformations discussed previously, and column 5 gives the molar volume of the sulfosalts estimated from a sum of the molar volumes of the respective end-member simple sulfides.

It can be seen from column 3 in Table 5 that both miargyrite and matildite have very similar molar volumes, whereas trechmannite and smithite have considerably smaller molar volumes. Smithite in particular appears to be anomalous in this regard. It should be noted that the molar volumes of both matildite and trechmannite-smithite are less than those obtained from the volume sum of the end-member sulfides (column 5), whereas for miargyrite the calculated molar volume is larger than the volume sum of the end-member sulfides. Both the predicted (column 3) and calculated (column 5) molar volumes of the sulfosalts increase in the order As → Sb → Bi, consistent with an increase in the estimated size of the basic structural units in these sulfosalts, i.e., the Group V element polyhedra (Takéuchi and Sadanaga, 1969, their Table 4).

Another interesting feature of the molar-volume data in Table 5 is the observation that the magnitude of the molar-volume difference (i.e., $|\Delta V_{trans}|$) for the low- to high-temperature polymorphic transformations decreases in the order $AgAsS_2 \rightarrow AgSbS_2 \rightarrow AgBiS_2$ and that ΔV_{trans} is negative in every case. Each of the polymorphic transitions therefore involves a decrease in molar volume and a positive entropy change with no apparent correlation between ΔV_{trans} and ΔS_{trans}. A departure from the above trend is observed for the transformation of pyrostilpnite to pyrargyrite that has a positive volume change, but for which the entropy of transformation is unknown.

Hoffmann (1935a, 1935b, 1938) and Hellner (1958) showed that the structures of many sulfides and sulfosalts may be derived from the PbS (galena) NaCl-structure type, principally by substitution and distortion of the cubic cell (Wuensch, 1974). Matildite, $AgBiS_2$ (Geller and Wernick, 1959), and miargyrite, $AgSbS_2$ (Knowles, 1964), are typical of sulfosalts which at high temperature transform to the disordered cubic, PbS-type structure (Graham, 1951; Wernick, 1960). There is some uncertainty as to whether there exists a cubic, high-temperature polymorph of smithite. Both trechmannite and smithite have distorted galena-type structures (Matsumoto and Nowacki, 1969; Hellner and Burzlaff, 1964), with trechmannite being unique in that it is a defect structure in which certain metal and S sites are unoccupied. This structure may explain the anomalously low density of trechmannite (column 2, Table 5), and the relatively large volume change for the transformation of trechmannite to smithite.

Approximate temperature-dependent free-energy expressions for a large number of sulfosalts were derived by Craig and Barton (1973). Their model was based on the assumption of near-ideal mixing of simple sulfide end-members to produce sulfosalts of intermediate composition. Their estimates of the free energy of reaction from the end-member sulfides (Eq. 3) assumed the heats of mixing to be zero (i.e., $\Delta H^0_{\text{mix}} = 0$):

$$\Delta G_{\text{m}}/T = (1.2 \pm 0.8)(R \sum_i N_i \ln N_i). \tag{3}$$

In this calculation, ΔG_{m} is equal to $-T\Delta S_{\text{m}}$, where ΔS_{m} is the entropy of mixing and N_i is the mole fraction of the ith simple sulfide component. In the absence of enthalpy data for sulfosalts, their ideal-mixing model did not include a heat-of-mixing term.

In the case of the sulfosalts pavonite and β-matildite, Bryndzia and Kleppa (1988a) concluded that the assumption of zero heat of mixing made by Craig and Barton (1973) was reasonable. This may also be true for α-miargyrite and pyrargyrite. However, this clearly is not a valid assumption for the silver thioarsenite sulfosalts, or the high-temperature disordered phases α-miargyrite and β-matildite. Craig and Barton (1973) suggested that it would be desirable to divide the $\Delta G_{\text{m}}/T$ term into two parts, one estimated from the crystal structure as an entropy change, and the remainder as a nonideal enthalpy term. Nonideal mixing may well be important in minerals such as the silver thioarsenites and the disordered high-temperature polymorph of matildite, which appear to possess a significant nonconfigurational entropy contribution.

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REFERENCES CITED

Bardsley, W., and Jones, O. (1968) On the crystal growth of optical quality proustite and pyrargyrite. Journal of Crystal Growth, 3/4, 268–271.

Béland, R. (1948) Synthesis of some sulfarsenites of silver in alkali sulfide solutions. Economic Geology, 43, 119–132.

Berry, L.G., and Thompson, R.M. (1962) X-ray data for ore minerals. Geological Society of America Memoir 85, 281 p.

Bryndzia, L.T., and Kleppa, O.J. (1988a) Standard enthalpies of formation of sulfides and sulfosalts in the Ag-Bi-S system by high temperature, direct synthesis calorimetry. Economic Geology, 83, 174–181.

——— (1988b) High-temperature reaction calorimetry of solid and liquid phases in the quasi-binary system Ag_2S-Sb_2S_3. Geochimica et Cosmochimica Acta, 52, 167–176.

——— (1988c) High-temperature reaction calorimetry of solid and liquid phases in part of the quasi-binary system Cu_2S-Sb_2S_3. American Mineralogist, 73, 707–713.

——— (1988d) Standard molar enthalpies of formation of realgar (α-AsS) and orpiment (As_2S_3) by high-temperature, direct-synthesis calorimetry. Journal of Chemical Thermodynamics, 20, 755–764.

Craig, J.R., and Barton, P.B. (1973) Thermochemical approximations for sulfosalts. Economic Geology, 68, 493–506.

Gaudin, A.M., and McGlashan, D.W. (1938) Sulfide silver minerals—A contribution to their pyrosynthesis and to their identification by selective irridescent filming. Economic Geology, 33, 143–193.

Geller, S., and Wernick, J.H. (1959) Ternary semiconducting compounds with sodium chloride–like structure; $AgSbS_2$, AgSbTe, $AgBiS_2$, $AgBiSe_2$. Acta Crystallographica, 12, 46–54.

Graham, A.R. (1951) Matildite, aramayoite, miargyrite. American Mineralogist, 36, 436–449.

Hall, H.T. (1966) The systems Ag-Sb-S, Ag-As-S, and Ag-Bi-S: Phase relations and mineralogical significance, 172 p. Ph.D. thesis, Brown University.

Hall, H.T., and Yund, R.A. (1964) Equilibrium relations among some silver sulfosalts and arsenic sulfides (abs.). Transactions of the American Geophysical Union, 45, 122.

Hellner, E. (1958) A structural scheme for sulfide minerals. Journal of Geology, 66, 503–525.

Hellner, E., and Burzlaff, H. (1964) Die struktur des smithits $AgAs_2$. Naturwissenschaften, 51, 35–36.

Hoffmann, W. (1935a) Ergebnisse der strukturbestimmung komplexer sulfide. I. Die struktur von zinnsulfür, SnS, und teallit, $PbSnS_2$. Zeitschrift für Kristallographie, 92, 161–173.

——— (1935b) II. Beitrag zur kristallchemie der sulfosalze des arsens, antimons und wismuts. Zeitschrift für Kristallographie, 92, 174–185.

——— (1938) Die struktur des miargyrits. Preussiche Akademie der Wissenschaften, Physikalisch-mathematische Klasse, Sitzungsberichte, 111–119.

Jaeger, F.M., and van Klooster, H.S. (1912) Studien über natürliche und künstliche sulfantimonite und sulfarsenite. Zeitschrift für Anorganische und Allegmeine Chemie, 78, 245–269.

JCPDS. (1986) Mineral powder diffraction file: Minerals data book. Compiled by the JCPDS International Centre for Diffraction Data, Swarthmore, Pennsylvania.

Kelley, K.K. (1960) Contributions to the data on theoretical metallurgy. XIII. High temperature heat-capacity, and entropy data for the elements and inorganic compounds. U.S. Bureau of Mines Bulletin 584, 232 p.

Kleppa, O.J. (1972) Oxide melt solution calorimetry. Institute du Centre National de la Recherche Scientifique, Colloque 201. Thermochimie, Paris CNRS, 119–127.

Knowles, C.R. (1964) A redetermination of the structure of miargyrite, $AgSbS_2$. Acta Crystallographica, 17, 297–317.

Matsumoto, T., and Nowacki, W. (1969). The crystal structure of trechmannite, $AgAsS_2$. Zeitschrift für Kristallographie, 129, 163–177.

Nowacki, W., and Kunz, V. (1961) Strukturelle untersuchungen an sulfosalzen von Lengenbach, Binnatal (Kt. Wallis), Teil 3, Gitterkonstanten und Raumgruppe von hatchit und trechmannite. Neues Jahrbuch für Mineralogie Monatshefte, 94–95.

Roland, G.W. (1968) Synthetic trechmannite. American Mineralogist, 53, 1208–1214.

——— (1970) Phase relations below 575 °C in the system Ag-As-S. Economic Geology, 65, 241–252.

Takéuchi, Y., and Sadanaga, R. (1969) Structural principles and classification of sulfosalts. Zeitschrift für Kristallographie, 130, 346–368.

Toulmin, P., III. (1963) Proustite-pyrargyrite solid solutions. American Mineralogist, 48, 725–736.

Wehmeier, F.H., Laudise, R.A., and Shiever, J.W. (1968) The system Ag_2S-As_2S_3 and the growth of crystals of proustite, smithite, and pyrargyrite. Materials Research Bulletin, 3, 767–778.

Wernick, J.H. (1960) Constitution of the $AgSbS_2$-PbS, $AgBiS_2$-PbS, $AgBiS_2$-$AgBiSe_2$ systems. American Mineralogist, 45, 591–611.

Wernick, J.H., Geller, S., and Benson, K.E. (1958) Synthetic proustite, Ag_3AsS_3. Analytical Chemistry, 30, 303.

Wuensch, B.J. (1974) Sulfide crystal chemistry. Mineralogical Society of America Short Course Notes, 1, W21–W43.

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