

High-temperature reaction calorimetry of solid and liquid phases in part of the quasi-binary system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$

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ABSTRACT

High-temperature reaction calorimetry has been applied in a thermochemical study of solid and liquid phases in part of the quasi-binary system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$. The enthalpies of formation at 298 K of the sulfosalts chalcostibite (CuSbS_2) and monoclinic skinnerite (Cu_3SbS_3) from their end-member component sulfides (Cu_2S and Sb_2S_3) were determined to be $-20.2 \pm 2.1 \text{ kJ}\cdot\text{mol}^{-1}$ and $-24.8 \pm 2.7 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

Mixtures of solid Cu_2S and liquid Sb_2S_3 at 895 K were studied by solid-liquid reaction calorimetry, and by dilution calorimetry, with pure liquid Sb_2S_3 . Measurements of the solid-liquid enthalpies of mixing (in $\text{kJ}\cdot\text{mol}^{-1}$) yielded the linear expression

$$\Delta H_{\text{mix}}^{\text{S-L}}/X_{\text{Cu}_2\text{S}} = -9.25 + 18.75X_{\text{Cu}_2\text{S}}$$

based on experiments with values of $X_{\text{Cu}_2\text{S}}$ ranging from 0.1 to 0.4. This equation is consistent with a symmetrical, regular-solution model and implies that the heat of fusion of Cu_2S at 895 K (for $X_{\text{Cu}_2\text{S}} = 1.00$) is $9.5 \text{ kJ}\cdot\text{mol}^{-1}$. Our data yield an average value for $\Delta C_{P,\text{S-L,Cu}_2\text{S}}$ of $6.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

INTRODUCTION

In this paper we present new calorimetric data for solid and liquid phases in the system Cu-Sb-S, obtained by high-temperature reaction calorimetry. The present study is an extension of our previous calorimetric investigations into the thermochemistry of sulfosalt minerals in the systems Ag-Bi-S and Ag-Sb-S (Bryndzia and Kleppa, 1988a, 1988b, respectively).

Sulfosalt minerals are commonly widespread in their distribution and occur in a diverse range of ore-deposit types, yet the lack of reliable thermochemical data for these minerals makes them attractive targets for experimental study. Most naturally occurring sulfosalt minerals are compositionally more complex than their synthetic analogues, which means that interpreting laboratory studies is often difficult. This is especially true for tetrahedrite, which occurs in the ternary system Cu-Sb-S and is probably the most common sulfosalt in the Earth's crust (Skinner et al., 1972). It is nonetheless highly desirable to obtain reliable thermochemical data for the synthetic analogues of naturally occurring sulfosalt minerals as a first step toward better understanding the processes and mechanisms by which these minerals form in nature.

Sulfosalts are sulfide minerals that contain one of the Group V elements (As, Sb, or Bi) as an essential component (Berry, 1965; Staples, 1972). It has been suggested that the principal feature distinguishing a sulfosalt from a sulfide is the presence of TS_3 ($\text{T} = \text{As, Sb, or Bi}$) pyramids in the structure of the sulfosalt (Hellner, 1958; Nowacki, 1969; Takéuchi and Sadanaga, 1969). However,

neither of the above criteria is free of ambiguity (Wuensch, 1974; Craig, 1974). Most sulfosalts may be regarded as intermediate phases on joins between simple sulfides, as in the $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ system that is the focus of the present investigation.

Previous work in the system Cu-Sb-S

The phases and phase relations in the system Cu-Sb-S have been studied by Cambi and Elli (1965), Skinner et al. (1972), Tatsuka and Morimoto (1973, 1977), Karup-Møller and Makovicky (1974), Makovicky and Skinner (1978, 1979), and Lind and Makovicky (1982).

Cambi and Elli (1965) determined the liquidus surface along the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$. Their proposed phase diagram contains three eutectics: at 583.2°C and 83.28 mol% Cu_2S , at 541.8°C and 58.73 mol% Cu_2S , and at 496.0°C and 20.12 mol% Cu_2S . The solid phases reported by Cambi and Elli (1965) as belonging to this join include chalcocite, tetrahedrite solid solution, chalcostibite, and stibnite.

The results of a comprehensive study of phase relations in the system Cu-Sb-S by Skinner et al. (1972) contradicted the findings of Cambi and Elli (1965), particularly with respect to the composition-stability relationships of tetrahedrite. Cambi and Elli (1965) reported an extreme composition range for tetrahedrite of $4\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ to $3\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ (i.e., $\text{Cu}_8\text{Sb}_2\text{S}_7$ to Cu_3SbS_3). These compositions lie along the quasi-binary join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ in the ternary system Cu-Sb-S. According to Skinner et al. (1972), tetrahedrite is a ternary compound whose com-

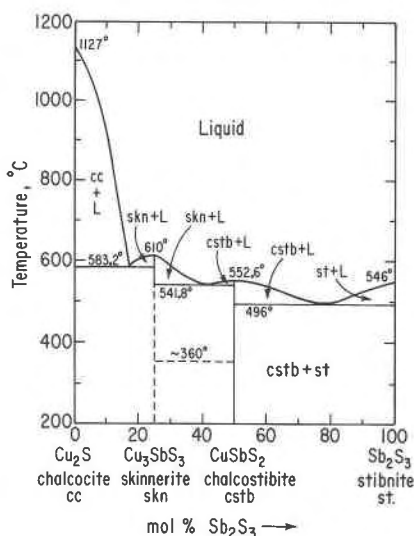


Fig. 1. Phase relations on the Cu_2S - Sb_2S_3 quasi-binary join modified from Cambi and Elli (1965), as discussed in the text. The low-temperature Cu_2S -rich region of the diagram is poorly understood and has been simplified for clarity. At 622°C , the system is binary only for compositions with $X_{\text{Cu}_2\text{S}} \leq 0.40$, as discussed in the text.

position does not lie on the join Cu_2S - Sb_2S_3 , although the extreme Cu-rich end of the tetrahedrite composition field observed by Skinner et al. (1972) almost reaches the join Cu_2S - Sb_2S_3 . Subsequent studies of tetrahedrite phase relations by Tatsuka and Morimoto (1973, 1977), Makovicky and Skinner (1978, 1979), and Lind and Makovicky (1982) have confirmed the ternary nature of tetrahedrite solid solutions in the system Cu-Sb-S. These references should be consulted for a detailed explanation of tetrahedrite phase relations. Figure 1 shows the liquidus surface along the join Cu_2S - Sb_2S_3 , modified after Cambi and Elli (1965). Figure 1 has been simplified to include only the eutectics observed by Cambi and Elli (1965) and the solid phases of interest to the present study. The principal sulfosalts on the join Cu_2S - Sb_2S_3 are the minerals chalcostibite and skinnerite, both of which melt congruently.

Chalcostibite (CuSbS_2). Hoffman (1932) showed that chalcostibite is orthorhombic. According to Skinner et al. (1972), the synthetic product appears in all respects identical to the natural compound. It does not depart from its stoichiometric formula and contains no reported inversions. X-ray diffraction analysis of our synthetic CuSbS_2 gave a powder pattern the same as that obtained by Hoffman (1932) for a natural chalcostibite sample and almost identical to the powder pattern of Lind and Makovicky (1982) for a synthetic chalcostibite sample. The melting temperature for chalcostibite obtained by Cambi and Elli (1965) is 552.6°C , which is essentially identical to the $553 \pm 2^\circ\text{C}$ reported by Skinner et al. (1972).

Skinnerite (Cu_3SbS_3). The existence of this phase was first reported by Gaudin and Dicke (1939). Godovikov et al. (1971) prepared it by sintering Cu_2S and Sb_2S_3 at

480 and 530°C . Verduch and Wagner (1957) determined the free energy of formation of Cu_3SbS_3 at 400°C , showing it to be more stable than its component simple sulfides, Cu_2S and Sb_2S_3 . Skinner et al. (1972) determined its phase relations in the system Cu-Sb-S. The existence of skinnerite as a mineral was confirmed by Karup-Møller and Makovicky (1974).

Skinner et al. (1972) reported that Cu_3SbS_3 disappears at high temperature by melting congruently at $607.5 \pm 3^\circ\text{C}$. This temperature is almost the same as the tetrahedrite melting temperature, 610°C , reported by Cambi and Elli (1965). Our work confirms that the melting temperature of Cu_3SbS_3 is $\sim 610^\circ\text{C}$.

According to Skinner et al. (1972), Cu_3SbS_3 is only stable above $359 \pm 2^\circ\text{C}$, below which the compositionally equivalent assemblage chalcostibite + tetrahedrite + antimony is stable. Tatsuka and Morimoto (1973), however, observed that Cu_3SbS_3 breaks down below $361 \pm 2^\circ\text{C}$ to tetrahedrite + antimony only. Tatsuka and Morimoto (1977) conducted annealing and cooling experiments on melts of Cu_3SbS_3 composition (called pseudotetrahedrite by them). In agreement with the findings of Skinner et al. (1972), they were able to produce a single homogeneous phase with Cu_3SbS_3 composition at room temperature, by rapidly cooling a melt of the same composition. In contrast though, slow cooling of this same phase annealed at 250°C resulted in the breakdown of Cu_3SbS_3 to an assemblage of digenite, famatinite, antimony, and tetrahedrite. On the basis of these results, Tatsuka and Morimoto (1977) concluded that their pseudotetrahedrite of Cu_3SbS_3 composition obtained by rapid cooling from 300°C must be metastable at room temperature. In view of these findings, Karup-Møller and Makovicky (1974) explained preservation of natural skinnerite as due either to favorable cooling conditions or to stabilization by a very small amount of Ag.

Although Cu_3SbS_3 can be readily quenched to room temperature, this is complicated by a metastable, reversible polymorphic inversion to a low-temperature form at $122 \pm 3^\circ\text{C}$. The inversion is rapid and the high-temperature form cannot be quenched. DTA analysis reported by Skinner et al. (1972) shows that no other inversions occur in Cu_3SbS_3 up to its melting temperature. They also reported that the stable low-temperature form of skinnerite is monoclinic, whereas the high-temperature form is orthorhombic. Karup-Møller and Makovicky (1974) found that the naturally occurring skinnerite was identical to the low-temperature monoclinic polymorph synthesized by Skinner et al. (1972).

Our synthetic Cu_3SbS_3 material was X-rayed, and the patterns obtained were compared with the published powder patterns for both synthetic and natural skinnerite (Karup-Møller and Makovicky, 1974) and for synthetic pseudotetrahedrite of Cu_3SbS_3 composition (Tatsuka and Morimoto, 1977). Agreement with the pattern for pseudotetrahedrite is near perfect, whereas agreement with the X-ray powder pattern for natural and synthetic skinnerite is not as good. In the pseudotetrahedrite sample

prepared by Tatsuka and Morimoto (1977), which was cooled rapidly from 300 °C, superstructure reflections were present. In our quenched samples of Cu_3SbS_3 , superstructure reflections were absent. Similar observations were reported by Chen and Chang (1974). In slowly cooled melts of the same composition, which still yielded a single phase pseudotetrahedrite (Cu_3SbS_3), superstructure reflections similar to those reported by Tatsuka and Morimoto (1977) were observed. We used the quenched product in our calorimetric experiments.

Scope of the present calorimetric study

From the $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ phase diagram in Figure 1, it can be seen that an extensive liquid range exists in this quasi-binary system. At 622 °C (895 K), the operating temperature of our calorimeter, this liquid encompasses a range in composition from the pure $\text{Sb}_2\text{S}_{3(l)}$ end member ($X_{\text{Cu}_2\text{S}} = 0$) to $X_{\text{Cu}_2\text{S}} \cong 0.83$. In this region, the calculated $\log f_{\text{S}_2}$ ranges from -4.8 in equilibrium with pure $\text{Sb}_2\text{S}_{3(l)}$ to -6.0 in equilibrium with $\text{Cu}_2\text{S}_{(s)}$. This is approximately the same range encountered in our previous calorimetric experiments in the system Ag-Sb-S (Bryndzia and Kleppa, 1988b), where we found that loss of S from the calorimeter during experiments was not a problem. Since sulfide liquids in the system Cu-Sb-S may find future use as calorimetric solvents suitable for high-temperature solution calorimetry for sulfide and sulfosalts minerals, we have studied the thermochemistry of the $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ system in some detail. In this communication we present new high-temperature direct-synthesis calorimetric data on the enthalpies of formation of the sulfosalts chalcostibite (CuSbS_2) and skinnerite (Cu_3SbS_3), as well as results on the integral enthalpies of mixing of solid Cu_2S with liquid Sb_2S_3 at 895 K.

EXPERIMENTAL METHODS

Calorimetry

The calorimetric experiments reported in the present communication were carried out at 895 K in a Calvet-type twin microcalorimeter. The principal features of this type of apparatus have been described in detail previously by Kleppa (1972), Watanabe and Kleppa (1983), Topor and Kleppa (1986), and Bryndzia and Kleppa (1988b). Calibrations were based on the heat content of pure Au at 895 K (81.057 J/g, taken from Kelley, 1960).

Starting materials

The starting materials were Sb_2S_3 (antimony sulfide, black powder, Lot no. 31548, J. T. Baker Chemical Co.) and Cu_2S (copper(II) sulfide, Catalog no. 12342, Aesar, Johnson-Matthey, Inc.). Electron-microprobe analyses of our starting materials indicated that the only detectable impurity was ~ 0.4 wt% Fe in Sb_2S_3 and ~ 0.6 wt% Fe in Cu_2S .

Experimental techniques

In all experiments that involved Sb_2S_3 as a component, the Sb_2S_3 powder was cast into rods by melting it at 680 °C in evacuated silica tubes of 6-mm outside diameter with 1-mm walls.

Cast stibnite rods were dropped into the calorimeter from room temperature.

Enthalpies of formation of sulfosalts. The enthalpies of formation of chalcostibite (CuSbS_2) and skinnerite (Cu_3SbS_3) were determined by reaction of stoichiometric proportions of $\text{Cu}_2\text{S}:\text{Sb}_2\text{S}_3$, which were pelletized and dropped into the calorimeter from room temperature. Two series of experiments were performed for each sulfosalt. In the first series, Cu_2S and Sb_2S_3 reacted to form a melt; in the second series the heat content of the solid sulfosalt was measured by dropping pellets of a previously synthesized crystalline phase from room temperature into the calorimeter where a melt of the same composition formed. The difference in the measured enthalpies for the two sets of experiments is the heat of formation of the sulfosalt at room temperature from its component simple sulfides.

Solid-liquid and liquid-liquid mixing experiments. Two types of mixing experiments were carried out in the course of the present study. In the first type of experiment, cast rods of Sb_2S_3 were dropped from room temperature into a fused silica crucible yielding a pool of pure liquid Sb_2S_3 at 895 K. To this liquid were added pellets of Cu_2S from room temperature, forming a liquid mixture with the desired mole fraction of Cu_2S ($X_{\text{Cu}_2\text{S}}$). In order to obtain the enthalpy of solid-liquid mixing at 895 K, i.e., $\Delta H_{\text{mix}}^{\text{sl}}$, it was necessary to correct the observed enthalpy of reaction for the heat content of Cu_2S at 895 K. From three separate determinations, obtained by dropping pellets of Cu_2S into the calorimeter from room temperature and measuring the associated heat effects, we obtained a mean value for $[H_{895} - H_{298}]_{\text{Cu}_2\text{S}}$ of 58.03 ± 0.08 kJ·mol⁻¹; we used this value to correct the observed enthalpies in all experiments in which Cu_2S was dropped from room temperature. Our heat content value for Cu_2S at 895 K is in excellent agreement with the values of 58.07 and 57.78 kJ·mol⁻¹ given by Robie et al. (1979) and King et al. (1973), respectively.

In the second type of experiment, liquid $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ of known composition was mixed with pure liquid Sb_2S_3 at calorimeter temperature. The advantages of this type of experiment are that heat-content corrections are not required and that heats of mixing or dilution are measured directly. For these experiments, we utilized the same calorimetric cell arrangement used in similar experiments in the system Ag-Sb-S, described in detail by Bryndzia and Kleppa (1988b). In all experiments at 895 K, the calorimeter was continually flushed with a steady stream of purified Ar to prevent oxidation of the sulfide melt.

As reported by Bryndzia and Kleppa (1988b), in experiments involving Sb_2S_3 it was observed that during the long durations of some experiments (~ 6 h), very small amounts of Sb_2S_3 were lost from the calorimetric cell. These losses were found to be of the order of ~ 2 wt% of the total mass of material in the calorimeter and were of no consequence compared to other errors. Loss of S also was negligible.

RESULTS

Enthalpies of formation of chalcostibite (CuSbS_2) and skinnerite (Cu_3SbS_3), from Cu_2S and Sb_2S_3 at 298 K

$\Delta H_{\text{f,CuSbS}_2,298}$ Tables 1a and 1b summarize the results of experiments on the enthalpy of formation of CuSbS_2 based on the enthalpy changes associated with the following two reactions: (1) $\Delta H_{\text{reaction}}$



TABLE 1A. The enthalpy of reaction for $\frac{1}{2}\text{Cu}_2\text{S}_{(s),298} + \frac{1}{2}\text{Sb}_2\text{S}_{3(s),298} = \text{CuSbS}_{2(l),895}$

Expt. no.	n_{CuSbS_2} (mmol)	ΔH_{obs} (J)	$\Delta H_{\text{reaction}}$ (kJ·mol ⁻¹)
1	3.837	344.1	89.7
2	4.028	371.9	92.3
3	4.742	440.9	93.0
4	4.910	463.5	94.4
Average $\Delta H_{\text{reaction}} = 92.4 \pm 1.7 \text{ kJ} \cdot \text{mol}^{-1} (\pm 1s, n = 4)$			

TABLE 1B. The heat content of chalcostibite based on the reaction $\text{CuSbS}_{2(s),298} = \text{CuSbS}_{2(l),895}$

Expt. no.	n_{CuSbS_2} (mmol)	ΔH_{obs} (J)	$(H_{895} - H_{298})$ (kJ·mol ⁻¹)
1	3.227	361.8	112.1
2	4.678	528.2	112.9
3	4.099	462.8	112.9
Average $[H_T - H_{298}] = 112.6 \pm 0.4 \text{ kJ} \cdot \text{mol}^{-1} (\pm 1s, n = 3)$			
$\Delta H_{f,\text{CuSbS}_2} = \Delta H_f - (H_{895} - H_{298}) = -20.2 \pm 2.1 \text{ kJ} \cdot \text{mol}^{-1}$			

and (2) the heat content $[H_{895} - H_{298}]$



Subtracting Equation 1b from 1a yields

$$\Delta H_{f,\text{CuSbS}_{2,298}} = \Delta H_{\text{reaction}} - (H_{895} - H_{298}) \quad (1c)$$

From four separate determinations of the enthalpy of reaction and three determinations of the heat content, we obtain a mean value of $-20.2 \pm 2.1 \text{ kJ} \cdot \text{mol}^{-1}$ for the enthalpy of formation of chalcostibite from Cu_2S and Sb_2S_3 at 298 K.

$\Delta H_{f,\text{Cu}_3\text{SbS}_3,298}$. Tables 2a and 2b summarize the results of experiments on the enthalpy of formation of Cu_3SbS_3 based on the enthalpy changes associated with the following two reactions: (1) $\Delta H_{\text{reaction}}$



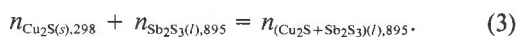
and (2) the heat content $[H_{895} - H_{298}]$



From three determinations of the enthalpy of reaction and three determinations of the heat content, we obtain a mean value of $-24.8 \pm 2.7 \text{ kJ} \cdot \text{mol}^{-1}$ for the enthalpy of formation of the low-temperature, monoclinic form of skinnerite from Cu_2S and Sb_2S_3 at 298 K.

Integral enthalpies of mixing of Cu_2S and Sb_2S_3 at 895 K

Solid-liquid mixing experiments. In these experiments pellets of Cu_2S were dropped from room temperature into a pool of liquid Sb_2S_3 to produce a melt of known composition, i.e., $X_{\text{Cu}_2\text{S}}$. The reaction that occurs in the calorimeter can be described by the following equation:



The heat effects, ΔH_{obs} , associated with these reactions

TABLE 2A. The enthalpy of reaction for $\frac{3}{2}\text{Cu}_2\text{S}_{(s),298} + \frac{1}{2}\text{Sb}_2\text{S}_{3(s),298} = \text{Cu}_3\text{SbS}_{3(l),895}$

Expt. no.	$n_{\text{Cu}_3\text{SbS}_3}$ (mmol)	ΔH_{obs} (J)	$\Delta H_{\text{reaction}}$ (kJ·mol ⁻¹)
1	3.637	494.0	135.0
2	3.143	430.6	137.0
3	3.097	434.3	140.2
Average $\Delta H_{\text{reaction}} = 137.7 \pm 1.9 \text{ kJ} \cdot \text{mol}^{-1} (\pm 1s, n = 3)$			

TABLE 2B. The heat content of Cu_3SbS_3 based on the reaction $\text{Cu}_3\text{SbS}_{3(s),298} = \text{Cu}_3\text{SbS}_{3(l),895}$

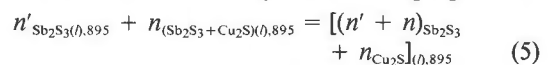
Expt. no.	$n_{\text{Cu}_3\text{SbS}_3}$ (mmol)	ΔH_{obs} (J)	$(H_{895} - H_{298})$ (kJ·mol ⁻¹)
1	3.430	558.1	162.7
2	2.133	344.8	161.6
3	2.238	364.9	163.1
Average $(H_T - H_{298})_{\text{Cu}_3\text{SbS}_3} = 162.5 \pm 0.8 \text{ kJ} \cdot \text{mol}^{-1} (\pm 1s, n = 3)$			
$\Delta H_{f,\text{Cu}_3\text{SbS}_3} = \Delta H_f - (H_{895} - H_{298}) = -24.8 \pm 2.7 \text{ kJ} \cdot \text{mol}^{-1}$			

were measured and are given in column 5 of Table 3. The enthalpy of mixing between solid and liquid may be calculated according to Equation 4:

$$\Sigma \Delta H_{\text{mix}}^{\text{S-L}} = \frac{\Sigma (\Delta H_{\text{obs}} - [H_{895} - H_{298}]_{\text{Cu}_2\text{S}})}{\Sigma n(\text{Cu}_2\text{S} + \text{Sb}_2\text{S}_3)} \quad (4)$$

i.e., the observed heat effect corrected for the heat content of solid Cu_2S at 895 K. The integral heat of mixing of solid Cu_2S with the melt includes a contribution from the heat of fusion of solid Cu_2S (at 895 K) plus the liquid-liquid heat of mixing. For reasons that will be discussed later, a relatively limited liquid range along the join Cu_2S - Sb_2S_3 was amenable to calorimetric study, i.e., $X_{\text{Cu}_2\text{S}} \leq 0.40$. From the data in Table 3, it can be seen that in this range, $\Delta H_{\text{mix}}^{\text{S-L}}$ is exothermic. The results of the experiments in Table 3 (column 8) have been plotted in Figure 2 against composition. It should be noted that in Table 3, no. 7(b) represents an experiment in which solid Cu_2S was added from room temperature to a melt of $(\text{Cu}_2\text{S} + \text{Sb}_2\text{S}_3)$ of known initial composition ($X_{\text{Cu}_2\text{S}} = 0.10$).

Dilution experiments. The results of all dilution experiments are summarized in Table 4. This table reports the results of two series of measurements in which a melt of known initial composition ($X_{\text{Cu}_2\text{S}}$) is made more Sb_2S_3 rich by the addition of liquid Sb_2S_3 . In each case, the initial melt composition was the final melt produced in the previous solid + liquid experiments (Table 3). ΔH_{obs} is the observed integral heat of mixing of liquid Sb_2S_3 with this melt at 895 K. The reaction that occurs in the calorimeter can be described by the following equation:



$$\Sigma \Delta H_{\text{mix}}^{\text{S-L}} = \Sigma \Delta H_{\text{obs}} / \Sigma n_{(\text{Cu}_2\text{S} + \text{Sb}_2\text{S}_3)} \quad (6)$$

The results of the three dilution experiments in Table 4 have also been included in Figure 2. As can be seen from

Figure 2, the results of the dilution experiments are very consistent with those of the solid-liquid mixing experiments, and there is considerable overlap in composition between the two types of mixing experiments.

All the data in Figure 2 may be described by a simple function obtained by a least-squares linear-regression procedure. The equation for the line of best fit is

$$\Sigma \Delta H_{\text{mix}}^{\text{S-L}} / X_{\text{Cu}_2\text{S}} = -9.25 + 18.75 X_{\text{Cu}_2\text{S}} \quad (7)$$

for which the units are $\text{kJ} \cdot \text{mol}^{-1}$ and the correlation coefficient (r^2) = 0.94. This r^2 value indicates that Equation 7 is an excellent fit to the data in Tables 3 and 4.

The solid-liquid heat of mixing is the sum of two parts, viz,

$$\Delta H_{\text{mix}}^{\text{S-L}} = X_{\text{Cu}_2\text{S}} \Delta H_{\text{fusion, Cu}_2\text{S}} + \Delta H^{\text{L-L}} \quad (8)$$

where $X_{\text{Cu}_2\text{S}}$ is the mole fraction of Cu_2S in the melt, $\Delta H_{\text{fusion, Cu}_2\text{S}}$ is the heat of fusion of solid Cu_2S at 895 K, and $\Delta H^{\text{L-L}}$ is the heat of mixing of undercooled liquid Cu_2S and liquid Sb_2S_3 (at 895 K).

Dividing through Equation 8 by $X_{\text{Cu}_2\text{S}}$ results in

$$\Delta H_{\text{mix}}^{\text{S-L}} / X_{\text{Cu}_2\text{S}} = (\Delta H^{\text{L-L}} / X_{\text{Cu}_2\text{S}}) + \Delta H_{\text{fusion, Cu}_2\text{S}} \quad (9)$$

If we assume that

$$\Delta H^{\text{L-L}} = X_{\text{Cu}_2\text{S}} X_{\text{Sb}_2\text{S}_3} \lambda, \quad (10)$$

where λ is the interaction parameter, Equation 9 may be rewritten as

$$\Delta H_{\text{mix}}^{\text{S-L}} / X_{\text{Cu}_2\text{S}} = X_{\text{Sb}_2\text{S}_3} \lambda + \Delta H_{\text{fusion, Cu}_2\text{S}} \quad (11)$$

Equation 11 is similar in form to Equation 7. A plot of $\Delta H_{\text{mix}}^{\text{S-L}}$ against $X_{\text{Cu}_2\text{S}}$ results in a straight line, with a slope equal to the interaction parameter, λ . The intercept of the line at $X_{\text{Cu}_2\text{S}} = 1.00$ gives the heat of fusion of solid Cu_2S at 895 K.

The fact that the observed solid-liquid integral enthalpies of mixing in Figure 2 define a linear function indicates that mixing of undercooled liquid Cu_2S and liquid Sb_2S_3 in the high Sb_2S_3 range may be approximated by a symmetrical, regular-solution model such as is implied by Equation 10. The intercept in Figure 2 for a melt with $X_{\text{Cu}_2\text{S}} = 1.00$ gives an approximate value of the heat of fusion of Cu_2S at 895 K, $\Delta H_{\text{fusion, Cu}_2\text{S}, 895} \approx 9.5 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$. Even though this value is obtained by extrapolation significantly beyond the range of our experiments, it is believed that our estimated heat of fusion for Cu_2S at

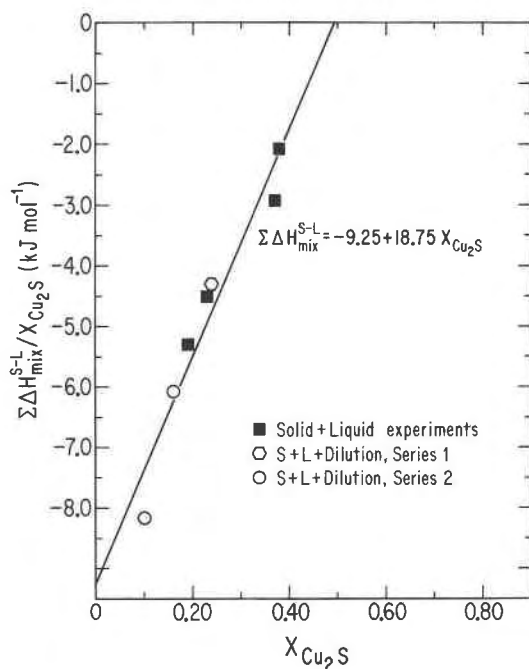


Fig. 2. Integral enthalpies of mixing between Cu_2S and Sb_2S_3 based on solid-liquid mixing experiments (filled symbols, from column 8 in Table 3) and solid-liquid dilution experiments (open symbols, from column 7 in Table 4). The straight line is the line of best fit to all the data, as explained in the text.

895 K is a very reasonable one in view of the excellent fit of Equation 7 to the experimental data.

Our result is in excellent agreement with the value of $9.6 \text{ kJ} \cdot \text{mol}^{-1}$ reported by Richardson and Antill (1955), obtained from equilibrium measurements on solid and liquid $\text{Na}_2\text{S} + \text{Cu}_2\text{S}$ mixtures, in the temperature range 836–1242 K. The heat of fusion of Cu_2S at its melting point (1400 K) is given as $12.84 \text{ kJ} \cdot \text{mol}^{-1}$ by King et al. (1973). A comparison of this result with our own value implies an average difference between the heat capacity of liquid and solid Cu_2S , i.e., $\Delta C_{P,S-L}$, of about $6.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. This value may be compared with the corresponding value of $4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $\Delta C_{P,S-L}$ calculated by Bryndzia and Kleppa (1988b) for Ag_2S at 880 K and the literature value at the melting point (1103 K). Mills (1974) reported the heat of fusion of Cu_2S at 1402 K to be 9.6

TABLE 3. Summary of results for solid-liquid mixing experiments

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Expt. no.	$n_{\text{Sb}_2\text{S}_3}$ (mmol)	$n_{\text{Cu}_2\text{S}}$ (mmol)	$X_{\text{Cu}_2\text{S}}$	ΔH_{obs} (J)	$(H_T - H_{298})$ (J)	$\Sigma \Delta H_{\text{mix}}^{\text{S-L}} =$ $\Sigma[(5) - (6)]/\Sigma n$ ($\text{J} \cdot \text{mol}^{-1}$)	$\Sigma \Delta H_{\text{mix}}^{\text{S-L}} / X_{\text{Cu}_2\text{S}}$ ($\text{kJ} \cdot \text{mol}^{-1}$)
1	8.230	2.509	0.23	134.6	145.8	-1042	-4.53
2	6.698	4.063	0.38	227.3	235.8	-790	-2.08
3	6.570	3.908	0.37	215.7	227.1	-1088	-2.94
7a	10.800	1.200	0.10	*	*	-817*	-8.17*
7b	10.800	1.373	0.19	18.13	19.02	-1011	-5.32

Note: Based on addition of solid Cu_2S from room temperature to liquid Sb_2S_3 at 880 K.

* Values calculated based on the $\Sigma \Delta H_{\text{mix}}^{\text{S-L}}$ from experiment 5b (Table 4).

TABLE 4. Summary of results for dilution experiments

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Expt. no.	$\Delta n_{\text{Sb}_2\text{S}_3}$ (mmol)	$n_{\text{Cu}_2\text{S}}$ (mmol)	$X_{\text{Cu}_2\text{S}}$	ΔH_{obs} (J)	$\Sigma \Delta H_{\text{M}}^{\text{S-L}} =$ $\Sigma(5)/\Sigma n$ (J·mol ⁻¹)	$\Sigma \Delta H_{\text{M}}^{\text{S-L}}/X_{\text{Cu}_2\text{S}}$ (kJ·mol ⁻¹)
4a	8.230	2.509	0.23	-11.2*	-1042*	-4.53*
4b	4.821	2.509	0.16	-4.0	-973	-6.08
5a	5.600	1.080	0.16	-6.5**	-973**	-6.08**
5b	4.210	1.080	0.10	-2.4	-817	-8.17
6a	6.570	3.908	0.37	-11.4†	-1088†	-2.94†
6b	5.671	3.908	0.24	-5.3	-1034	-4.31

Note: Based on addition of liquid Sb_2S_3 to solid Cu_2S , or to a Cu_2S -rich melt at calorimeter temperature (895 K).

* Experiment 4a is the same as experiment 1, Table 3.

** Values calculated on the basis of the value of $\Sigma \Delta H_{\text{M}}^{\text{S-L}}$ from experiment 4b.

† Values calculated on the basis of the value of $\Sigma \Delta H_{\text{M}}^{\text{S-L}}$ from experiment 3, Table 3.

$\text{kJ}\cdot\text{mol}^{-1}$, based on the data of Richardson and Antill (1955) and assuming that $\Delta C_{P,S-L} = 0$. We suggest that the preferred value of the heat of fusion of Cu_2S at its melting point is that reported by King et al. (1973).

DISCUSSION

Even though Figure 1 shows that an extensive liquid range exists along the join Cu_2S - Sb_2S_3 at 895 K (622 °C), ranging from $X_{\text{Cu}_2\text{S}} = 0$ to $X_{\text{Cu}_2\text{S}} \approx 0.83$, we were able to perform satisfactory experiments over only about one-half of this liquid range, i.e., up to $X_{\text{Cu}_2\text{S}} \approx 0.40$. We observed depressed (too exothermic) enthalpies of mixing compared to Equation 7 for melts with $X_{\text{Cu}_2\text{S}} \geq 0.40$. Examination of the solidified melts by SEM revealed the presence of a multiphase assemblage in Sb_2S_3 - Cu_2S melts with $X_{\text{Cu}_2\text{S}} \geq 0.40$. On textural grounds, the most likely cause for the depressed enthalpies of mixing at 895 K was the precipitation of a solid Sb-Cu alloy ($\sim\text{Sb}_{0.90}\text{Cu}_{0.10}$). These results are consistent with ternary, not binary solution behavior along this portion of the Cu_2S - Sb_2S_3 join. For melts with $X_{\text{Cu}_2\text{S}} \leq 0.40$, however, only a single homogeneous phase was observed by SEM, indicating that mixing of the components to form melts in this range was

truly binary. For this reason, the data in Figure 2 are restricted to this limited range of compositions.

The enthalpies of formation of CuSbS_2 and Cu_3SbS_3 were obtained via the thermodynamic cycle summarized by Equations 1a and 1b (for CuSbS_2), both of which involve a melt at 895 K. The fact that the melt formed is ternary rather than binary is of no consequence since the melt was of the same composition in both cases.

Summary of thermochemical data for the sulfosalts chalcostibite (CuSbS_2) and skinnerite (Cu_3SbS_3)

Verdusch and Wagner (1957) determined the Gibbs free energies of formation of CuSbS_2 and Cu_3SbS_3 at 400 °C from Cu_2S and Sb_2S_3 , using the reduction equilibrium data of Schenck et al. (1939) and their own electrochemical results. The Gibbs free-energy values they reported for CuSbS_2 and Cu_3SbS_3 at 400 °C are -3293.0 and -3033.4 J/equivalent (where an equivalent is defined as containing one-half of a S atom), or -13.17 and -18.20 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. These values were recalculated by Craig and Lees (1972, Table 1) as -11.93 and -18.25 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. These free energies are summarized together with our own new enthalpy data for these minerals in Table 5. In the present discussion, we assume that the enthalpies of formation of CuSbS_2 and Cu_3SbS_3 from their component sulfides will not be significantly different at 673 K from the values at 298 K. Under this assumption, we calculate, from the Gibbs free energies and our own enthalpies, the approximate entropies of formation given in Table 5 for CuSbS_2 and Cu_3SbS_3 from their component sulfides.

We note that the entropies of formation given in Table 5 are small negative values, consistent with the significant negative enthalpies of formation of these minerals. For the analogous Ag-bearing sulfosalts in the system Ag_2S - Sb_2S_3 , miargyrite (AgSbS_2), and pyrargyrite (Ag_3SbS_3), we found small negative enthalpies of formation and small positive entropies of formation from their component sulfides Ag_2S and Sb_2S_3 (Bryndzia and Kleppa, 1988b).

We feel that it would be instructive to comment briefly on the apparent metastability of Cu_3SbS_3 (Tatsuka and Morimoto, 1977) as opposed to naturally occurring skin-

TABLE 5. Summary of thermochemical data for CuSbS_2 and Cu_3SbS_3 from their component sulfides (Cu_2S and Sb_2S_3)

T (K)	ΔG_f^* (kJ·mol ⁻¹)	ΔH_f^{**} (kJ·mol ⁻¹)	ΔS_f^\dagger (J·K ⁻¹ ·mol ⁻¹)
CuSbS ₂ , chalcostibite			
298‡	-17.10†	-20.2 ± 2.1	-10.4 ± 3.1†
673‡	-13.17	-20.2 ± 2.1	-10.4 ± 3.1
	-11.93††	-20.2 ± 2.1	-12.3 ± 3.1
Cu ₃ SbS ₃ , skinnerite			
298§	-21.88†	-24.8 ± 2.7	-9.8 ± 4.0†
673‡	-18.20	-24.8 ± 2.7	-9.8 ± 4.0
	-18.25††	-24.8 ± 2.7	-9.7 ± 4.0

* From Verdusch and Wagner (1957) and Craig and Lees (1972).

** Experimental, this study, as discussed in the text.

† Calculated, this study, as discussed in the text.

†† Recalculated values from Craig and Lees (1972, Table 1).

‡ Orthorhombic.

§ Monoclinic.

nerite (Karup-Møller and Makovicky, 1974). Assuming that the high-temperature entropies of formation in Table 5 will not be significantly different at 298 K, together with our experimentally measured enthalpies, it is possible to provide an estimate of the free energies of formation for both chalcostibite and skinnerite at 298 K. These data yield values of -17.10 and -21.88 kJ·mol⁻¹ for the free energies of formation of chalcostibite and skinnerite, respectively; this result shows that there is little difference in the free energies of formation between the two minerals relative to their end-member sulfides. In fact, these data suggest that both synthetic Cu₃SbS₃ and naturally occurring skinnerite are stable minerals at 298 K and that the small amount of Ag reported to occur in natural skinnerite (<2 mol% Ag, Table 1 in Karup-Møller and Makovicky, 1974) is unlikely to be an important factor in the stabilization of this mineral. The reason that skinnerite is a rare mineral in nature therefore remains enigmatic.

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