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SUPERAMBIENT HEAT CAPACITIES OF SYNTHETIC STIBNITE, BERTHIERITE, AND CHALCOSTIBITE: REVISED THERMODYNAMIC PROPERTIES AND IMPLICATIONS FOR PHASE EQUILIBRIA

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Introduction

Stibnite (Sb_2S_3), berthierite (FeSb_2S_4), and chalcostibite (CuSbS_2) are important antimony-bearing minerals. Stibnite is the main ore mineral of antimony and occurs as an important accessory in many epigenetic ore deposits, especially in later stages of deposition or in peripheral facies of mineralization. Berthierite is a common accessory mineral in antimony deposits. Its occurrence, particularly in gold-antimony deposits, has received considerable scientific attention. Furthermore, stibnite, berthierite, and chalcostibite represent important reference phases for understanding phase equilibria in more complex systems, such as those containing tetrahedrite-tennantite solid solutions.

Barton (1971) emphasized the uncertainties in the low-temperature (<573 K) phase equilibria in the system Fe-Sb-S, particularly for reactions involving berthierite and gudmundite (FeSbS), which he attributed to the difficulty in extrapolating high-temperature phase equilibria data to lower temperatures. Thus, the application of high-temperature (>573 K) phase equilibrium studies to the study of ore deposits has been hampered by the difficulty in accurately extrapolating the high-temperature data to lower, more geologically relevant temperatures. Likewise, the extrapolation of low-temperature (≤ 298 K) enthalpy and heat capacity data to higher, more geologically pertinent temperatures has been hindered by an incomplete understanding of the thermodynamic properties of these minerals. Heat capacities measured by differential scanning calorimetry provide a means of bridging the gap between the low-temperature calorimetric studies and the high-temperature phase equilibrium studies. This study presents new heat capacity data for synthetic stibnite, berthierite, and chalcostibite from 340 to 760 K, which are used to revise the thermodynamic properties of these minerals. The new thermodynamic values for these minerals are used to improve our understanding of phase relations in the system Fe-Sb-S.

Materials and Experimental Methods

Stibnite, berthierite, and chalcostibite were synthesized from antimony metal (ASARCO, 99.999+ %, lot ZH-2262), iron wire (Materials Research Corp.,

VP grade, lot 2612201), copper wire (Baker and Adamson, 99.90%, lot J337), and native sulfur (ASARCO, 99.999+ %, lot 102). The iron wire was reduced in a stream of hydrogen gas at 873 K for 1 h. The copper wire was cleaned in acetone prior to use. For each phase, reagents were weighed in stoichiometric proportions with total masses between 1 and 3 g and sealed in evacuated silica tubes. The tubes were placed in a furnace at 1,023 K and reacted for 1 h and then quenched. The tubes were opened; the contents were ground under acetone, air-dried, and then resealed in evacuated silica tubes. The samples were annealed for two weeks at 748 ± 10 K and then quenched in ice water. The berthierite sample underwent two additional grinding and annealing cycles.

The samples were characterized by reflected light microscopy, powder X-ray diffraction, and electron microprobe analysis and were found to be stoichiometric and homogeneous within the analytic precision and >99 percent pure inasmuch as no impurity phases were detected. Cell parameters were determined using powder X-ray diffraction data from the synthetic material. Barium fluoride was used as an internal standard with stibnite; silicon (NBS-640) was used with berthierite and chalcostibite. The results of the electron microprobe and X-ray diffraction studies are presented in Table 1.

Heat capacities were measured from 340 to 760 K with a Perkin-Elmer DSC-2 differential scanning calorimeter following the procedures described by Hemingway et al. (1981). The calorimetric sample weights were 65.88, 58.72, and 58.76 mg for stibnite, chalcostibite, and berthierite, respectively. Samples were sealed in aluminum pans. Reweighing of the samples after the heat capacity measurements were completed indicated that desulfidation and/or oxidation were not a problem. Reaction between the samples and their aluminum pans also was not a problem; the examination of the pans after all measurements were made revealed clean, untarnished inner surfaces.

Results

The heat capacities (C_p°) measured by the present study from 340 to 760 K for stibnite, berthierite,

TABLE 1. Electron Microprobe and X-Ray Diffraction Data for Synthetic Stibnite, Berthierite, and Chalcostibite

	Stibnite	Berthierite	Chalcostibite
Wt percent			
Sb	72.29 ± 0.41	57.50 ± 0.61	49.24 ± 0.35
Fe	0.01 ± 0.02	13.07 ± 0.23	0.01 ± 0.01
Cu	0.02 ± 0.03	0.03 ± 0.03	25.57 ± 0.21
S	28.62 ± 0.33	30.33 ± 0.39	26.36 ± 0.15
Total	100.94 ± 0.68	100.93 ± 1.13	101.18 ± 0.40
n	18	15	24
Formula normalized to sulfur atoms			
Sb	2.00 ± 0.02	2.00 ± 0.02	0.98 ± 0.01
Fe		0.99 ± 0.01	
Cu			0.98 ± 0.01
S	3.00	4.00	2.00
Cell parameters (Å)			
a	11.228	11.461	6.015
b	11.309	14.173	14.540
c	3.834	3.771	3.802

All uncertainties are expressed as 2σ ; uncertainty in cell parameters is estimated at ± 0.001 Å; published cell parameters: stibnite (Pbnm), $a = 11.229$, $b = 11.311$, $c = 3.836$ Å (Bayliss and Nowacki, 1972); berthierite (Pnam), $a = 11.44$, $b = 14.12$, $c = 3.76$ Å (Buerger and Hahn, 1955); chalcostibite (Pnam), $a = 6.00$, $b = 14.45$, $c = 3.78$ Å (Hofman, 1933)

and chalcostibite are presented in Table 2 and Figure 1. None of the phases displayed any anomalous behavior. The measured heat capacities were fit by least squares to an equation of the form suggested by Haas and Fisher (1976). Terms that did not improve the precision of the regressions were discarded. The equation for stibnite was constrained to join smoothly the low-temperature C_p° data of Romanovskii and Tarasov (1960) and King and Weller (1962). The equation for berthierite was constrained to join smoothly the low-temperature C_p° data presented by Dzhabbarov (1985). The heat capacity data for chalcostibite were graphically extrapolated down to 298.15 K. For stibnite, berthierite, and chalcostibite, the heat capacity data were graphically extrapolated up to the decomposition temperatures of the phases (829, 836, and 826 K, respectively).

For stibnite, berthierite, and chalcostibite, the resulting equations ($J \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$; T in K; and the ranges for which they are valid) are C_p° (stibnite) = $166.1 - 0.0031 T + 654,000 T^{-2} - 911 T^{-0.5}$ (298–829 K); C_p° (berthierite) = $10.0 + 0.0793 T - 6,416,000 T^{-2} + 3,691 T^{-0.5}$ (298–836 K); and C_p° (chalcostibite) = $88.1 + 0.0404 T$ (298–826 K), which describe the data with an average absolute deviation of 0.3, 0.5, and 0.3 percent, respectively.

The heat content ($H_T^\circ - H_{298}^\circ$) data for stibnite from Johnson et al. (1981) are within the analytic

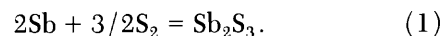
uncertainty of the integrated values from the present study below 700 K. However, the heat content data of Johnson et al. (1981) are greater than those of the present study by up to $1.45 \text{ kJ} \cdot \text{mole}^{-1}$ (2.2%) at 823 K, the melting point of stibnite. For the drop calorimetry data, eutectic melting of a slightly nonstoichiometric sample along the Sb_2S_3 -S join (769 K) or the Sb_2S_3 -Sb join (791 K) may be responsible for some of this deviation but probably cannot account for all of this behavior. Unfortunately, the synthesis and characterization of the sample of Johnson et al. (1981) is insufficiently documented to assess this possibility. Thus, the differential scanning calorimetry data of the present study is preferred for subsequent calculations.

Revised Thermodynamic Properties

Stibnite

Numerous workers have investigated the phase equilibria and thermodynamic properties of stibnite. Barton (1971) conducted a phase equilibrium study of the system Fe-Sb-S, made estimates of $\Delta_f G^\circ$ values, and summarized experimental work prior to that time. Mills (1974) compiled and evaluated the thermodynamic data for Sb_2S_3 . More recently, Johnson et al. (1981) determined a $\Delta_f H_{298}^\circ$ value by fluorine combustion calorimetry. They also measured superambient heat capacities by drop calorimetry. Bryndzia and Kleppa (1988a) determined a $\Delta_f H_{298}^\circ$ for stibnite by high-temperature reaction calorimetry. Despite the abundance of data, considerable uncertainty remains regarding the enthalpy of formation of stibnite (Table 3).

The C_p° expression from the present study was combined with the S_{298}° value for stibnite (Mills, 1974), which is the mean of the values of Romanovskii and Tarasov (1960) and King and Weller (1962), and high-temperature experimental data for the sulfidation of native antimony (Schenck and von der Forst, 1939) to calculate $\Delta_f G_{298}^\circ$, $\Delta_f H_{298}^\circ$, and an expression for $\Delta_f G^\circ$ as a function of temperature for stibnite. Following Barton (1971), the present study accepted the 673 K $\log f_{\text{S}_2}$ value of -9.24 (Schenck and von der Forst, 1939) for the reaction:



The comparison of the calculated curve for this reaction with the independent experimental determination of the sulfur fugacity associated with reaction 1 of Barton (1971) by the pyrrhotite indicator method confirms the validity of the resulting $\Delta_f G^\circ$ values (Fig. 2). The expression for $\Delta_f G^\circ$ as a function of temperature from the present study is identical to the expression of Barton (1971) within the experimental uncertainty. The thermodynamic properties of stibnite are summarized in Table 4.

TABLE 2. Experimental Molar Heat Capacities of Stibnite, Berthierite, and Chalcostibite

T (K)	Heat capacity (J · mole ⁻¹ · K ⁻¹)	T (K)	Heat capacity (J · mole ⁻¹ · K ⁻¹)	T (K)	Heat capacity (J · mole ⁻¹ · K ⁻¹)
Stibnite					
Series 1		468.8	126.2	560.4	128.2
338.9	120.4			570.4	128.3
349.0	121.1			579.5	128.2
359.1	122.1				
369.1	122.0	449.6	125.0		
379.2	122.4	459.7	125.3		
389.3	122.6	469.8	125.4	570.4	128.5
399.3	123.6	479.8	125.7	580.5	128.4
409.4	123.8	489.9	126.1	590.6	128.2
419.5	124.0	500.0	126.3	600.6	128.5
429.5	124.6	510.0	126.5	610.7	129.8
439.6	125.4	520.1	126.8	620.8	128.9
449.6	125.4	530.2	126.9	630.8	129.6
459.7	126.0	540.2	127.5	640.9	129.8
		550.3	126.5	649.9	130.5
Berthierite					
Series 1		469.8	188.1	620.8	189.8
338.9	180.5	479.8	189.0	630.8	190.5
349.0	181.8	489.9	190.2	640.9	192.0
359.1	182.7	500.0	189.7	649.9	193.6
369.1	183.9	510.0	190.1		
379.2	185.1	520.1	190.1		
389.3	186.1	530.2	190.5		
399.3	187.0	540.2	190.3	620.8	188.3
409.4	187.4	550.3	190.6	630.8	188.6
419.5	187.9	560.4	190.7	640.9	188.8
429.5	188.7	570.4	191.3	651.0	189.6
439.6	188.7	579.5	190.2	661.0	190.8
449.6	188.5			671.1	192.8
459.7	187.7			681.1	194.5
468.8	187.3			691.2	193.5
Series 2				701.3	193.4
449.6	186.7	560.4	189.2	711.3	191.7
459.7	187.3	570.4	188.8	721.4	192.4
		580.5	189.2	731.5	192.8
		590.6	189.2	741.5	193.7
		600.6	189.1	750.6	194.3
		610.7	189.5		
Chalcostibite					
Series 1		489.9	107.4		
338.9	101.5	500.0	107.3		
349.0	102.4	510.0	108.2	630.9	114.0
359.1	102.8	520.1	108.5	640.9	114.6
369.1	103.4	530.2	108.5	651.0	114.7
379.2	103.8	540.2	109.2	661.0	115.3
389.3	104.3	550.3	108.5	671.1	115.6
399.3	104.4	560.4	110.5	681.1	116.0
409.4	105.0	570.4	111.1	691.2	116.6
419.5	105.6	579.5	111.4	701.3	117.4
429.5	106.1			711.3	116.7
439.6	106.8			720.3	116.4
449.6	106.7				
459.7	107.0	570.4	111.6		
468.8	107.3	580.5	111.6		
		590.6	111.5	701.3	117.2
		600.6	112.0	711.3	117.2
Series 2		610.7	113.4	721.4	117.7
449.6	105.1	620.8	112.2	731.5	118.6
459.7	105.4	630.8	113.3	741.5	117.9
469.8	105.7	640.9	113.7	751.6	118.7
479.8	106.6	649.9	114.3	760.7	118.1

Molar masses: stibnite, 339.68 g; berthierite, 427.587 g; chalcostibite, 249.416 g

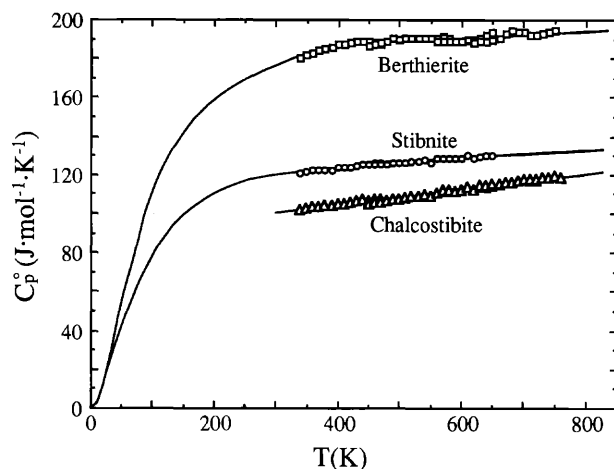


FIG. 1. Experimental superambient heat capacities for stibnite, berthierite, and chalcostibite. Solid curves represent smoothed values for heat capacities. Curves above 300 K are from the present study. The curve for stibnite below 300 K is from Romanovskii and Tarasov (1960) and King and Weller (1962). The curve for berthierite below 300 K is from Dzhabbarov (1985).

Berthierite

Phase equilibria involving berthierite have been studied by Barton (1971), Bortnikov et al. (1978), and Nekrasov and Konyushok (1982). All three studies used the pyrrhotite indicator technique (Toulmin and Barton, 1964) to measure sulfur fugacities in equilibrium with univariant assemblages. The first two studies were conducted under anhydrous conditions, whereas the third was under hydrothermal conditions. In addition, Dzhabbarov (1985) measured low-temperature (6–300 K) heat capacities for berthierite and presented an S_{298}° value for this mineral.

The present study combined the high-temperature phase equilibrium studies of Barton (1971), Bortnikov et al. (1978), and Nekrasov and Konyushok (1982), the S_{298}° of berthierite (Dzhabbarov, 1985),

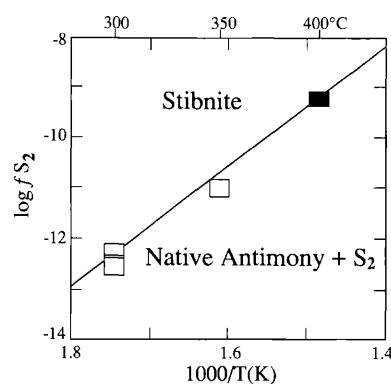
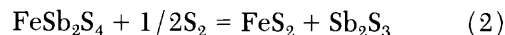
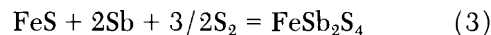


FIG. 2. Temperature- f_{S_2} diagram for reaction 1. The line represents the calculated curve from the present study. The filled square is the value from Schenck and von der Forst (1939), which was used to generate the thermodynamic parameters used in the present study. Open squares are from Barton (1971). The uncertainty in the temperature and $\log f_{S_2}$ values of Barton (1971) is $\pm 5^{\circ}\text{C}$ and $\pm 0.35 \log f_{S_2}$ units, respectively.

and the C_p° expression from the present study to calculate $\Delta_f G_{298}^{\circ}$, $\Delta_f H_{298}^{\circ}$, and an expression for $\Delta_f G^{\circ}$ as a function of temperature for berthierite. Specifically, the two berthierite-bearing reactions considered were:



where it intersects the pyrite-pyrrhotite buffer (Barton, 1971) and



within the pyrrhotite field (Barton, 1971; Bortnikov et al., 1978; Nekrasov and Konyushok, 1982). Barton (1971) reported an equilibrium temperature of $805 \pm 5 \text{ K}$ (532°C) for the five-phase invariant assemblage berthierite + pyrite + stibnite + pyrrhotite + vapor. At this temperature, the pyrite-pyrrhotite buffer defines a $\log f_{S_2}$ of -3.58 (Toulmin and Barton, 1964) for reaction 2 (Fig. 4). Using the free energy data for pyrite from Barton and Skinner (1979), a

TABLE 3. Comparison of $\Delta_f H_{298}^{\circ}$ Values for Stibnite Relative to Sb Metal and Crystalline S

Source	$\Delta_f H_{298}^{\circ}$ (kJ · mole ⁻¹)	Method
Pelabon (1902)	-152.72 ¹	H ₂ S/H ₂ mixing experiments
Jellinek and Zakowski (1925)	-154.81 ¹	H ₂ S/H ₂ mixing experiments
Britzke and Kapustinskii (1930)	-150.02 ¹	H ₂ S/H ₂ mixing experiments
Kelley (1937)	-162.34	Recalculated from published data
Sudo (1952)	-205.02 ¹	H ₂ S/H ₂ mixing experiments
Barton (1971)	-151.04	Calculated ²
Johnson et al. (1981)	-141.80	Fluorine combustion calorimetry
Bryndzia and Kleppa (1988a)	-129.72	Reaction drop calorimetry
This study	-151.35	Calculated ²

¹ Third law evaluation by Mills (1974) of published gas-mixing experimental data

² Calculated by the present study based on $\Delta_f G_{298}^{\circ}$ value

$\Delta_f G_{805}^\circ$ for stibnite calculated from the present study, and the $\log f_{S_2}$ value for reaction 2, a $\Delta_f G_{805}^\circ$ of $-259.19 \text{ kJ} \cdot \text{mole}^{-1}$ can be calculated for berthierite. Tight constraints on the equilibrium sulfur fugacity ($\log f_{S_2} = -12.46$) associated with reaction (3) at 573 K (300°C) can be obtained from the work of Nekrasov and Konyushok (1982) (Fig. 3). This value can be used to calculate a $\Delta_f G_{573}^\circ$ for berthierite ($-327.21 \text{ kJ} \cdot \text{mole}^{-1}$) using the free energy and activity-composition data for pyrrhotite of Toulmin and Barton (1964). A $\Delta_f G_{298}^\circ$ value that produced the best fit to the $\Delta_f G_{573}^\circ$ and $\Delta_f G_{805}^\circ$ values was calculated using the C_p° expression and S_{298}° value from Table 4. The resulting $\Delta_f G^\circ$ values were used to calculate the position of reaction 3 in terms of temperature and sulfur fugacity. A comparison of the calculated curve with the experimental data (Fig. 3) verifies the validity of the calculated $\Delta_f G^\circ$ values. The thermodynamic properties of berthierite are summarized in Table 4.

Chalcostibite

The present study combined the $\Delta_f G_{673}^\circ$ value from Craig and Lees (1972), based on the gas-mixing experiments of Schenck et al. (1939), the C_p° expression for chalcostibite from this study, and an estimate for the S_{298}° of chalcostibite to calculate $\Delta_f G_{298}^\circ = -132.86 \text{ kJ} \cdot \text{mole}^{-1}$, and $\Delta_f H_{298}^\circ = -130.79 \text{ kJ} \cdot \text{mole}^{-1}$ for chalcostibite. The estimate for the S_{298}° of chalcostibite ($149.2 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$) is based on the sum of the S_{298}° values for the component sulfides ($S_{298}^\circ(\text{CuSbS}_2) = 1/2 S_{298}^\circ(\text{Cu}_2\text{S}; \text{Grønvold and Westrum, 1987}) + 1/2 S_{298}^\circ(\text{Sb}_2\text{S}_3; \text{Mills, 1974})$). Seal et al. (1990) noted that the sum of the component S_{298}° values for smithite (AgAsS_2), proustite (Ag_3AsS_3), and chalcopyrite (CuFeS_2) are within 2.5 percent of the S_{298}° values of the compounds (Robie et al., 1985; Gurevich et al., 1989). Likewise, the sum of the S_{298}° values for the sulfide components of berthierite ($S_{298}^\circ(\text{FeS}; \text{Robie et al., 1979}) + S_{298}^\circ(\text{Sb}_2\text{S}_3; \text{Mills, 1974}) = 242.3 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$) is within 1.1 percent of the S_{298}° value for berthierite ($245.0 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$; Dzhahbarov, 1985). The paucity of entropy data for sulfosalts precludes the development of a more rigorous estimation method. Skinner et al. (1972) determined an upper stability for chalcostibite of 826 K. The recommended thermodynamic properties for chalcostibite are presented in Table 4. The calculated $\Delta_f G_{298}^\circ$ for chalcostibite based on the expression of Craig and Barton (1973) is approximately $8 \text{ kJ} \cdot \text{mole}^{-1}$ less negative than the value from the present study.

Bryndzia and Kleppa (1988b) measured the enthalpy change associated with the reaction $1/2\text{Cu}_2\text{S} + 1/2\text{Sb}_2\text{S}_3 = \text{CuSbS}_2$, which can also be used to calculate the thermodynamic properties of chalcostibite. Their data can be combined with the $\Delta_f H_{298}^\circ$ for

TABLE 4. Recommended Thermodynamic Properties for Stibnite, Berthierite, and Chalcostibite

Mineral	$\Delta_f G_{298}^\circ$ $\text{kJ} \cdot \text{mole}^{-1}$	$\Delta_f H_{298}^\circ$ $\text{kJ} \cdot \text{mole}^{-1}$	S_{298}° $\text{J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$	C_p° constants			$\Delta_f G_T^\circ$ $\text{kJ} \cdot \text{mole}^{-1}$	T range (K)
				a	b	c		
Stibnite	-149.98 (2.10)	-151.35 (2.30)	182.0 ¹ (3.4)	166.1	-0.0031	645,000	-911	$-360.91 + 0.1981 T + 1.892 T^{0.5}$ 298-829
Berthierite	-255.96 (6.50)	-256.19 (6.50)	245.0 ² (0.1)	10.0	0.0793	-6,416,000	3,691	$-540.82 + 0.2393 T + 3.163 T^{0.5}$ 298-836
Chalcostibite	-132.86 (4.20)	-130.79 (4.40)	149.2 (3.8)	88.1	0.0404			$-277.07 + 0.1033 T + 1.966 T^{0.5}$ 298-826

$\Delta_f G_{298}^\circ$ and $\Delta_f H_{298}^\circ$ relative to the elements and orthorhombic sulfur at 1 bar; $\Delta_f G_T^\circ$ relative to the elements and ideal S_2 gas at 1 bar; temperature (T) in K; $C_p^\circ = a + bT + cT^{-2} + dT^{-0.5}$ ($\text{J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$); $\Delta_f G_T^\circ$ ($\text{kJ} \cdot \text{mole}^{-1}$) expressions are polynomial regressions of calculated values and are valid for the temperature range; all values are from the present study except: ¹ Mills (1974); ² Dzhahbarov (1985); estimated uncertainties (2 σ) are presented in parentheses; thermodynamic data used in calculations for copper, antimony, orthorhombic sulfur, and ideal S_2 gas are from Robie et al. (1979); thermodynamic data for iron are from Haas and Chase (1989)

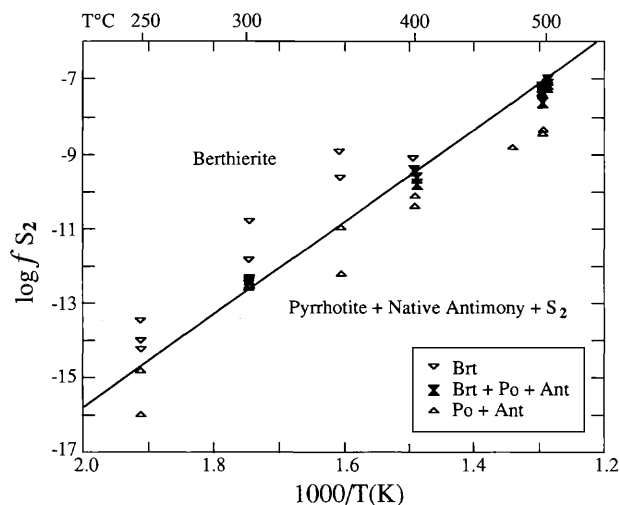


FIG. 3. Temperature- f_{S_2} diagram for reaction (3). The line represents the calculated curve from the present study. The activity of FeS in pyrrhotite used in the calculations was based on Toulmin and Barton (1964). Experimental data are from Barton (1971), Bortnikov et al. (1978), and Nekrasov and Konyushok (1982). The uncertainty in the experimental data is approximately $\pm 5^\circ\text{C}$ and $\pm 0.35 \log f_{S_2}$ units.

chalcocite ($-84.21 \text{ kJ} \cdot \text{mole}^{-1}$), based on a "third-law" evaluation (Robie, 1965) of the gas-mixing data of Brooks (1953), and the $\Delta_f H_{298}^\circ$ for stibnite from the present study to calculate a $\Delta_f H_{298}^\circ$ ($-137.98 \text{ kJ} \cdot \text{mole}^{-1}$) and S_{298}° ($138.5 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$) for chalcocite. The calculated S_{298}° value represents a 7.2 percent deviation from the estimated value. The rea-

son for this difference is not clear at present. Compared to values for other sulfides and sulfosalts discussed above, this amount of deviation from the sum of the component sulfides appears to be unprecedented. Therefore, the thermodynamic properties based on the estimated S_{298}° are preferred.

Phase Equilibria

The revised thermodynamic properties may be used to unravel some of the uncertainties in the low-temperature phase equilibria in the system Fe-Sb-S, as noted by Barton (1971). Thermodynamic data for stibnite and berthierite are from the present study; data for gudmundite (FeSbS) and seinäjokite (FeSb_2) are from Barton (1970); and all other data are from Barton and Skinner (1979). Unit activities are assumed for all components corresponding to solid phases except for FeS in pyrrhotite, which was modeled using the expressions of Toulmin and Barton (1964). Due to the colinearity of FeS, FeSbS, and Sb, the formula Fe_{1-x}S for pyrrhotite is necessary to describe accurately the stoichiometry of the products and reactants in reaction 7. For all other reactions, the simpler formula FeS is sufficient. Reactions that limit the stability of berthierite are presented in Figures 4 and 5. Below its melting point at 836 K (563°C), the stability of berthierite is dominantly limited by reactions 2 and 3. Its lower temperature stability occurs at the intersection of reaction 1 and the reaction

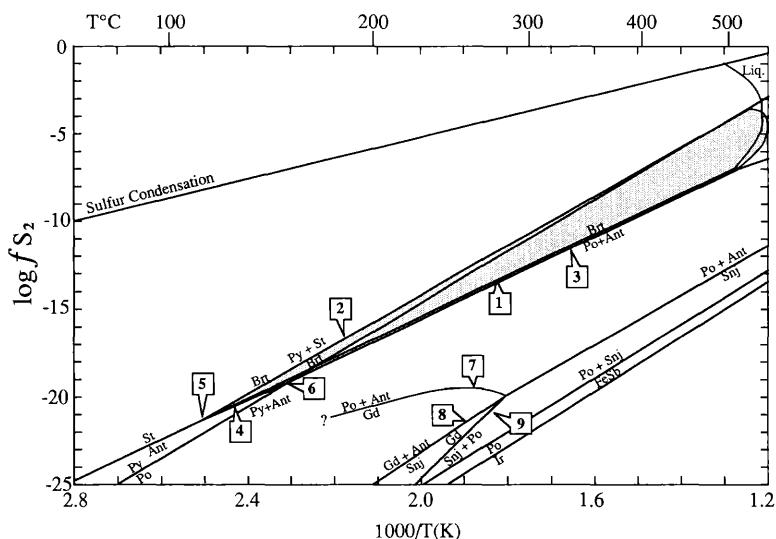
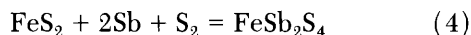


FIG. 4. Calculated phase equilibria in the system Fe-Sb-S. Shaded field represents the stability of berthierite. The numbers correspond to the reactions discussed in the text. Reactions 1 to 6 were calculated from the present study. All others are based on Barton (1971) and Barton and Skinner (1979). Abbreviations: berthierite (Brt); gudmundite (Gd); native antimony (Ant); native iron (Ir); pyrite (Py); pyrrhotite (Po); stibnite (St); seinäjokite (Snj).

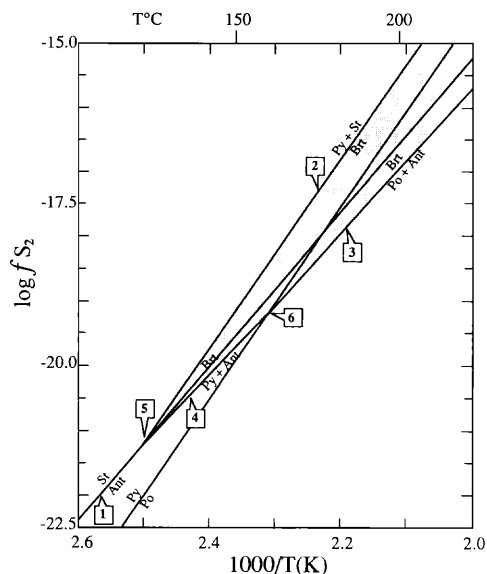
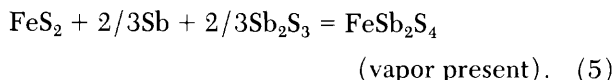
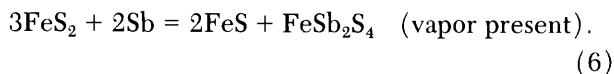


FIG. 5. Calculated phase equilibria in the system Fe-Sb-S for the low-temperature portion of Figure 4. The numbers correspond to the reactions discussed in the text. Reactions 1 to 6 were calculated from the present study. All others are based on Barton (1971) and Barton and Skinner (1979). Abbreviations: berthierite (Brt); native antimony (Ant); pyrite (Py); pyrrhotite (Po); stibnite (St).

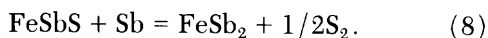
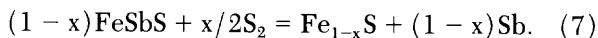
along the stibnite-native antimony curve at 398 ± 30 K (125°C) at the invariant point corresponding to the reaction



Reaction 4 has a restricted stability that is limited between 398 and 433 ± 30 K (160°C), the invariant point corresponding to the reaction



Reactions that restrict the stability of gudmundite and seinäjokite have also been calculated and include:



and



These reactions merge at 553 K (280°C), the thermal maximum for gudmundite (Clark, 1966). The position of reaction 7 at lower temperatures is difficult to assess because of the large uncertainty in the thermal dependence of the Gibbs free energy of gudmundite.

The present study has provided insight into many of the uncertainties in the low-temperature (<673 K) phase equilibria in the system Fe-Sb-S as noted by Barton (1971). However, numerous questions still remain. The large uncertainties in temperatures calculated for the invariant points that limit the stability of berthierite can be decreased by improvements in the thermodynamic data for associated phases or by direct, experimental determination of the invariant points. Unfortunately, such experimental efforts must contend with the formidable kinetic barriers imposed by these low temperatures. Uncertainties in the low-temperature phase relations involving gudmundite can most easily be diminished by obtaining heat capacity data for this mineral.

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