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HEAT CAPACITY AND ENTROPY OF BORNITE (Cu_5FeS_4) BETWEEN 6 AND 760 K AND THE THERMODYNAMIC PROPERTIES OF PHASES IN THE SYSTEM Cu–Fe–S

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ABSTRACT

Heat capacities of synthetic bornite (Cu_5FeS_4) have been measured by quasi-adiabatic calorimetry between 5 and 351 K and between 338 and 761 K by differential scanning calorimetry. The heat capacity of bornite exhibits a λ-type anomaly at 65 ± 1 K associated with the antiferromagnetic ordering of the spins of the Fe^{3+} ions. Between 140 and 255 K, there is a broad hump in C_p° which, in our opinion, may be caused by charge transfer involving $Fe^{2+} - Fe^{3+}$ and $Cu^+ - Cu^{2+}$. At 470 ± 2 and 535 ± 2 K there are sharp peaks in the heat capacity caused by ordering of the copper, iron and vacancies and the consequent crystallographic changes. At 298.15 K, the heat capacity and entropy of bornite are 242.9 ± 0.6 and 398.5 ± 1.0 $J{\cdot}mol^{-1}{\cdot}K^{-1}$, respectively. Enthalpies and Gibbs free energies of formation of chalcopyrite and bornite are evaluated based on heat capacities (5 to 760 K) and the entropy for bornite, published calorimetric ($\Delta_f H^\circ$ and C_p°) data for chalcopyrite, thermodynamic data for pyrite, and sulfur fugacity data for the reaction: $5CuFeS_2 + S_2 = Cu_5FeS_4 + 4FeS_2$. Previous studies show that all phases in this reaction are stoichiometric within analytical uncertainty from 673 to 773 K. Therefore, no adjustments for solid-solution effects are needed. Revised expressions for the Gibbs free energy of formation for selected phases in the system Cu–Fe–S are presented below, relative to the elements and ideal S_2 gas.

Phase	$\Delta_f G^\circ_{T(K)}$ $kJ{\cdot}mol^{-1}$	T range
Covellite (CuS)	$-125.13 + 0.05670\,T + 0.8422\,T^{0.5}$	298 – 780 K
Anilite ($Cu_{1.75}S$)	$-137.64 + 0.06459\,T$	298 – 312 K
Chalcocite (Cu_2S)	$-161.45 + 0.00078\,T + 1.8850\,T^{0.5}$	298 – 1400 K
Chalcopyrite ($CuFeS_2$)	$-369.64 + 0.05154\,T + 4.5690\,T^{0.5}$	298 – 820 K
Bornite (Cu_5FeS_4)	$-715.99 + 0.00339\,T + 9.2550\,T^{0.5}$	298 – 1200 K
Nukundamite ($Cu_{5.5}FeS_{6.5}$)	$-766.15 + 0.37540\,T + 5.1938\,T^{0.5}$	298 – 774 K

Keywords: thermodynamic properties, entropy, Gibbs free energy, heat capacity, bornite, chalcopyrite, chalcocite, nukundamite, anilite, covellite.

SOMMAIRE

Nous avons mesuré la capacité calorifique de la bornite synthétique, Cu_5FeS_4, par calorimétrie quasi-adiabatique entre 5 et 351 K, et par calorimétrie différentielle à balayage entre 338 et 761 K. La capacité calorifique de la bornite démontre une anomalie de type λ à 65 ± 1 K associée à la mise en ordre antiferromagnétique des spins des ions Fe^{3+}. Entre 140 et 255 K, nous notons la présence d'un bombement flou dans la fonction C_p°, qui résulterait d'un transfert de charges impliquant les couples Fe^{2+}–Fe^{3+} et Cu^+–Cu^{2+}. La mise en ordre du cuivre, du fer et des lacunes, et les ajustements cristallographiques conséquents, sont à l'origine de pics très prononcés dans la capacité calorifique à 470 ± 2 et à 535 ± 2 K. A 298.15 K,

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la capacité calorifique et l'entropie de la bornite seraient 242.9 ± 0.6 et 398.5 ± 1.0 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, respectivement. Les enthalpies et les énergies libres de formation de Gibbs de la chalcopyrite et de la bornite peuvent être évaluées à partir de la capacité calorifique (de 5 à 760 K) et l'entropie de la bornite, les données calorimétriques publiées ($\Delta_f H^\circ$ et C°_p) sur la chalcopyrite, les données thermodynamiques sur la pyrite, et les données sur la fugacité du soufre pour la réaction $5CuFeS_2 + S_2 = Cu_5FeS_4 + 4\ FeS_2$. Les études antérieures montrent que toutes les phases participant à cette réaction sont stoechiométriques, compte tenu des erreurs analytiques, entre 673 et 773 K. C'est donc dire qu'aucun ajustement n'est nécessaire pour les effets dus aux solutions solides. Nous présentons ici les expressions révisées pour l'énergie libre de formation de Gibbs de certaines phases dans le système Cu–Fe–S, par rapport aux éléments et à un gaz S_2 idéal.

Phase	$\Delta_f G^\circ_{T(K)}$ $\mathrm{kJ \cdot mol^{-1}}$	Intervalle de T
Covellite (CuS)	$-125.13 + 0.05670\ T + 0.8422\ T^{0.5}$	298 – 780 K
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Bornite (Cu_5FeS_4)	$-715.99 + 0.00339\ T + 9.2550\ T^{0.5}$	298 – 1200 K
Nukundamite ($Cu_{5.5}FeS_{6.5}$)	$-766.15 + 0.37540\ T + 5.1938\ T^{0.5}$	298 – 774 K

Mots-clés: propriétés thermodynamiques, entropie, énergie libre de Gibbs, capacité calorifique, bornite, chalcopyrite, chalcocite, nukundamite, anilite, covellite.

INTRODUCTION

Bornite is an important ore mineral of copper. It commonly occurs in a variety of ore deposits formed under a wide range of geological conditions, from low-temperature sediment-hosted stratiform copper deposits to high-temperature porphyry copper deposits. Equally important, it occupies a central portion of the system Cu–Fe–S and is stable from ambient temperatures to in excess of 1373 K. Accordingly, an accurate understanding of its thermodynamic properties is essential to understanding the thermodynamics and phase equilibria of the system Cu–Fe–S. This study presents new data on the heat capacity of synthetic bornite from 6 to 760 K, which are used in conjunction with published results of phase-equilibrium studies and thermodynamic data to revise the thermodynamic values for this mineral. A critical evaluation of the thermodynamic properties of other selected phases in the system Cu–Fe–S also is presented.

SYNTHESIS AND CHARACTERIZATION OF BORNITE

Bornite was prepared in five batches of approximately 5 g each from copper wire (Baker & Adamson, 99.90%, Lot J337), iron wire (Materials Research Corporation, VP grade, Lot 26/2201), and sulfur (ASARCO, 99.999+%, Lot 102). The copper was cleaned in acetone prior to weighing. The iron wire was reduced in a stream of hydrogen gas at 873 K for 1 h and immediately stored under vacuum until needed. Stoichiometric proportions of reagents for Cu_5FeS_4 were weighed and loaded into silica-glass tubes. The tubes were evacuated, sealed using an oxy–hydrogen torch, placed in a furnace at 1023 ± 10 K and reacted for 48 h. The tubes were opened, the contents ground in a ceramic mortar under acetone, air-dried, and resealed in evacuated silica-glass tubes. The tubes were returned to the furnace and annealed at 1023 ± 10 K. After two weeks, the samples were removed from the furnace and allowed to cool to room temperature. The tubes were opened, and the contents were disaggregated by light grinding in a ceramic mortar. A small portion of each batch was removed for characterization. Compositionally heterogeneous batches, as indicated by electron-microprobe analysis, were reground under acetone, resealed in evacuated silica tubes and annealed for an additional two weeks. After final disaggregation, the samples were immediately resealed in evacuated silica tubes for storage until the calorimetric analysis was conducted. Following three cycles of annealing, batch BN3 remained heterogeneous for unexplained reasons and was excluded from further study. The grain size of the sample used for our calorimetric measurements was –5 +40 mesh.

The samples were characterized by reflected-light microscopy, scanning electron microscopy, powder X-ray diffraction and electron-microprobe analysis. They were found to be stoichiometric and homogeneous within analytical precision, and >99% pure inasmuch as no impurity phases were detected. Bornite samples were analyzed for Cu, Fe and S using the Cu*K*α, Fe*K*α and S*K*α lines at an accelerating voltage of 25 kV and a beam current of 160 nA. Peak, and high and low background counts were measured for 20 seconds each on both the standard and unknowns. A synthetic bornite (R-bornite) was used as a standard for Cu, Fe and S. The results of the electron-microprobe analyses are presented in Table 1. Powder X-ray diffraction yielded reflections that are consistent with the orthorhombic (*Pbca*) modification of bornite (Koto & Morimoto 1975). Cell parameters

TABLE 1. ELECTRON-MICROPROBE DATA FOR SAMPLES OF SYNTHETIC BORNITE

Sample	BN1	BN2	BN3	BN4	BN5	Total (BN1, 2,4 &5)
Cu Wt.%	62.98	62.73	63.06	63.44	63.27	63.06
(± 1σ)	(0.41)	(0.21)	(0.20)	(0.16)	(0.20)	(0.39)
Fe Wt.%	11.00	11.20	10.57	10.94	10.98	11.04
(± 1σ)	(0.09)	(0.13)	(0.21)	(0.07)	(0.10)	(0.15)
S Wt.%	25.43	25.21	24.67	25.40	25.41	25.35
(± 1σ)	(0.19)	(0.13)	(0.19)	(0.08)	(0.10)	(0.17)
Total Wt.%	99.41	99.14	98.30	99.78	99.66	99.45
(± 1σ)	(0.56)	(0.22)	(0.22)	(0.12)	(0.18)	(0.42)
			Normalized to 4 Sulfur Atoms			
Cu	5.00	5.02	5.16	5.04	5.03	5.02
(± 1σ)	(0.03)	(0.04)	(0.39)	(0.03)	(0.03)	(0.03)
Fe	0.99	1.02	0.98	0.99	0.99	1.00
(± 1σ)	(0.01)	(0.01)	(0.01)	(0.01)	(0.01)	(0.01)
ΣMetal	5.99	6.04	6.14	6.02	6.02	6.02
(± 1σ)	(0.03)	(0.03)	(0.05)	(0.03)	(0.03)	(0.03)
n	9	6	12	6	6	27

TABLE 2. EXPERIMENTAL HEAT CAPACITIES OF BORNITE BETWEEN 5 AND 351 K MEASURED BY ADIABATIC CALORIMETRY

T K	Heat Capacity J·mol⁻¹·K⁻¹	T K	Heat Capacity J·mol⁻¹·K⁻¹	T K	Heat Capacity J·mol⁻¹·K⁻¹	T K	Heat Capacity J·mol⁻¹·K⁻¹
		150.91	208.6			7.57	1.426
Series 1		155.16	209.8	Series 8		8.35	2.437
						9.26	3.766
311.47	244.4	Series 5		208.08	226.9	10.47	5.447
316.40	246.0			210.89	228.1	11.88	7.490
321.36	248.3	160.80	211.5	213.67	228.0	13.88	10.43
326.31	248.0	167.24	214.4	216.50	228.8	16.24	15.61
		173.43	216.4	219.13	229.5	18.69	21.83
Series 2		179.69	218.5	221.78	230.0	21.77	30.39
		185.49	220.2	224.47	230.7	25.38	40.77
331.45	249.1	191.29	222.1	227.18	231.4	29.12	51.59
336.64	249.1	197.12	223.9	229.93	232.9	33.05	62.92
341.52	249.7	203.00	225.4	232.72	233.2	36.97	76.47
346.41	251.4	208.93	227.2	235.53	233.5	40.86	84.55
351.38	252.1	214.93	228.6	238.37	234.2	45.20	93.81
		221.02	229.4			49.79	103.5
Series 3		227.24	230.6	Series 9			
		233.63	232.9			Series 11	
66.16	146.8	240.16	233.8	255.74	235.4		
70.45	145.4			261.49	236.9	54.05	109.9
74.03	149.3	Series 6		267.08	237.2	58.36	119.1
77.74	153.4			272.71	238.8	62.63	136.7
81.25	157.9	246.77	235.0	278.39	239.9		
		253.46	235.7	284.06	240.5	Series 12	
Series 4		260.20	236.9	289.72	241.1		
				295.37	241.7	61.81	133.3
88.63	165.3	Series 7		301.01	243.7	62.79	138.8
93.58	169.7			306.65	243.7	63.71	143.4
98.26	173.7	53.34	110.6	312.27	245.1	64.64	145.7
103.02	177.3	55.70	113.6			65.60	146.2
107.57	180.7	57.60	118.4	Series 10		66.56	145.2
112.05	184.6	59.54	124.9			67.51	144.4
116.49	187.4	61.54	134.0	5.72	0.6371		
120.88	190.0	63.49	143.6	6.08	0.7091	Series 13	
125.23	192.9	65.43	147.3	5.95	0.5648		
129.55	196.2	67.36	145.1	5.95	0.5843	199.49	223.9
133.85	199.1	69.25	144.8	6.25	0.7057	205.03	225.6
138.14	200.9	71.10	145.7	6.32	0.7943	210.26	226.6
142.41	203.5	72.92	147.4	6.57	1.092		
146.66	205.9	74.72	149.8	7.01	1.301		

of the synthetic bornite were determined using powder X-ray-diffraction data with Cu*K*α_1 radiation and silicon (NBS–640) as an internal standard. The cell parameters for the synthetic bornite from the present study, *a* 10.969(7), *b* 21.90(1), *c* 10.952(7) Å, are in reasonable agreement with the parameters reported by Kanazawa *et al.* (1978) for a natural bornite of unreported composition.

HEAT CAPACITY AND ENTROPY OF BORNITE

Low-temperature measurements

The heat capacity at low temperature was measured by means of the intermittent heating technique using the adiabatically shielded calorimeter described by Robie (1987). The mass of the sample used for our measurements was 14.6062 g. The formula weight used in our calculations was 501.841 g·mol^{-1}. The sample was loaded into the calorimeter, and a vacuum was pumped; after 1 hour at approximately 7 Pa, the calorimeter was backfilled and sealed with dry helium at a pressure of 6 kPa. The precision of our measurements is 10% at temperatures less than 15 K, 0.5% between 15 and 50 K, and 0.2% above 50 K. Our measurements of heat capacity are listed in chronological order of measurement in Table 2 and are shown in Figure 1.

At 65 ± 1 K, there is a λ-type peak in the heat capacity of bornite that arises from antiferromagnetic ordering of the magnetic moments of the Fe^{3+} (Fig. 2). The temperature of the maximum in the heat capacity is in good agreement with the Néel temperature (T_N) reported by Jagadeesh *et al.* (1981), 67.5 ± 0.5 K, and by Allais & Curien (1970), 65 K, both from magnetic susceptibility measurements. It is, however, 13 K lower than the value given by Townsend *et al.* (1977), 76 ± 2 K, also from susceptibility studies. The measurements of Townsend *et al.* (1977) were taken approximately 13 K apart near the Néel temperature and thus do not constrain T_N tightly. Townsend *et al.* (1977) also suggested that a second transition might

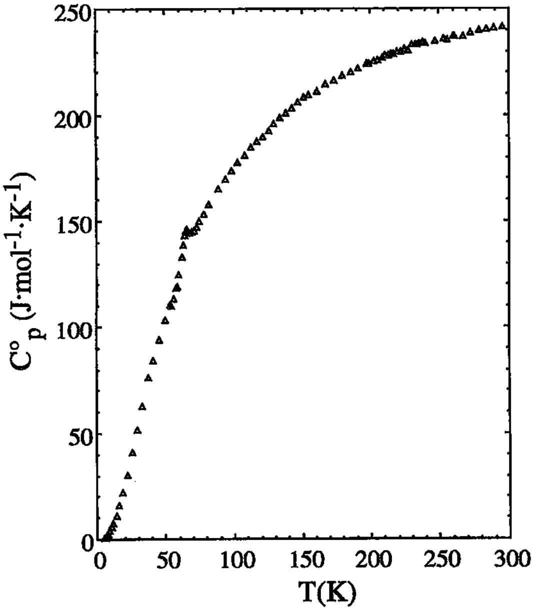

FIG. 1. Low-temperature heat capacity data for bornite.

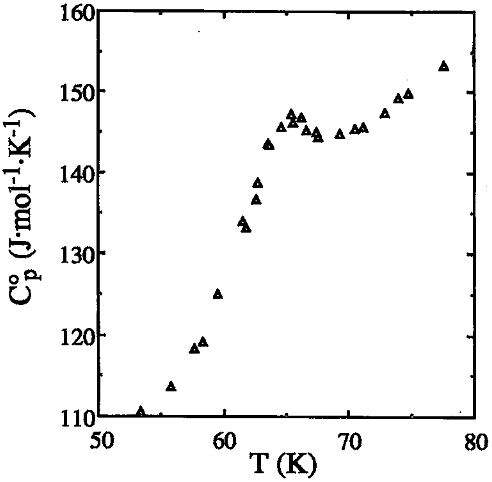

FIG. 2. Heat capacity data for bornite near λ-transition at 65 K.

exist near 8 K. Within the scatter of the data on heat capacity, no evidence was found to support the existence of an 8 K transition. Over the temperature range of 140 to 255 K, the heat capacity of bornite exceeds that which one would estimate by smoothly connecting values below 140 with those in the range 260 to 350 K. Thus there appears to be an excess or hump in the heat capacity function, somewhat similar to that found by Robie *et al.* (1988) for ilvaite. At 200 K, this "excess" C°_p is approximately 3.3 J•mol^{-1}•K^{-1}. We suspect that this excess heat capacity is associated with the charge-transfer equilibrium $Fe^{3+} + Cu^+ = Fe^{2+} + Cu^{2+}$, as discussed by Jagadeesh *et al.* (1981) and also by Shemilt *et al.* (1981). Unfortunately, there are no electrical conductivity data in this temperature range on pure Cu_5FeS_4 to test this hypothesis.

High-temperature measurements

Superambient heat capacities were measured from 340 to 760 K with a Perkin–Elmer DSC–2 differential scanning calorimeter (DSC) using the procedures described by Hemingway *et al.* (1981). Our measurements were made on a sample weighing 46.32 mg, with scanning rates of 5 and 10 K•min^{-1} and a sensitivity of 0.0084 W. The heat capacities are listed in their chronological order of measurement in Table 3 and are shown in Figure 3. At 300 K, the stable form of bornite is orthorhombic (Morimoto & Kullerud 1961, Koto & Morimoto 1975). Upon heating, bornite first transforms to an intermediate cubic modification, and then to a different cubic form having the anti-fluorite structure (Kanazawa *et al.* 1978). Both changes produce sharp maxima in the heat capacity, the first at 470 ± 2 K, and the second at 535 ± 2 K (Fig. 3).

TABLE 3. EXPERIMENTAL HEAT CAPACITIES OF BORNITE BETWEEN 338 AND 761 K MEASURED BY DIFFERENTIAL SCANNING CALORIMETRY

T K	Heat Capacity J·mol^{-1}·K^{-1}	T K	Heat Capacity J·mol^{-1}·K^{-1}	T K	Heat Capacity J·mol^{-1}·K^{-1}	T K	Heat Capacity J·mol^{-1}·K^{-1}
		452.7	279.3	516.1	390.1	555.3	334.2
Series 1		453.7	280.9	517.1	391.4	556.3	334.6
		454.7	281.8	518.1	393.1	565.4	332.4
338.9	249.3	455.7	284.9	519.1	394.0	566.4	332.3
349.0	251.2	456.7	288.1	520.1	395.8	567.4	331.9
359.1	252.7	457.7	290.9	521.1	397.1	568.4	332.1
369.1	255.0	458.7	296.6	522.1	399.8	569.4	331.7
379.2	257.2	459.7	304.3	523.1	401.9	569.9	331.5
389.3	260.0	460.7	314.4	524.1	404.5		
399.3	262.2	461.7	331.9	525.1	406.9	Series 4	
409.4	261.7	462.7	355.4	526.1	411.1		
419.5	263.7	463.7	379.3	527.1	413.9	560.4	334.0
428.5	266.5	464.7	401.2	528.2	418.2	570.4	331.7
		465.8	439.8	529.2	424.9	580.5	329.5
Series 2		466.8	496.7	530.2	435.9	590.6	329.0
		467.8	583.4	531.2	451.9	600.6	328.3
429.5	265.9	468.8	711.5	532.2	467.1	610.7	327.6
430.5	264.8	469.8	910.4	533.2	483.0	620.8	327.6
431.5	263.9	470.8	1160.8	534.2	501.0	630.8	327.7
432.5	265.5	471.8	1216.2	535.2	524.2	640.9	328.0
433.5	265.5	472.8	824.5	536.2	514.7	651.0	327.7
434.5	266.0	473.8	423.0	537.2	429.7	660.0	327.7
435.6	266.3	482.9	349.7	538.2	361.4		
436.6	267.1	483.9	351.2	539.2	345.3	Series 5	
437.6	267.1	484.9	351.7	540.2	341.3		
438.6	271.4	485.9	354.0	541.2	339.9	651.0	324.5
439.6	266.1	486.9	355.8	542.2	341.2	661.0	322.3
440.6	268.8	487.9	356.5	543.3	338.6	671.1	323.0
441.6	269.7	488.9	357.3	544.3	338.1	681.1	323.2
442.6	269.6	489.4	358.4	545.3	337.9	691.2	324.6
443.6	270.0			546.3	337.2	701.3	322.1
444.6	268.9	Series 3		547.3	337.4	711.3	323.5
445.6	271.7			548.3	336.4	721.4	323.5
446.6	272.2	510.0	382.2	549.3	336.4	731.5	324.3
447.6	274.0	511.0	382.4	550.3	337.4	741.5	324.9
448.6	275.4	512.1	383.9	551.3	336.7	751.6	324.6
449.6	276.2	513.1	385.5	552.3	336.9	760.7	324.7
450.7	277.8	514.1	387.4	553.3	334.4		
451.7	277.3	515.1	386.8	554.3	334.2		

Previous measurements by drop calorimetry (H°_T–H°_{298}) up to 1105 K by Pankratz & King (1970) gave transition temperatures of 485 and 540 K. The sample of Pankratz & King (1970) also is synthetic and was prepared at 923 to 958 K. Kanazawa *et al.* (1978) presented DSC traces showing these transitions occurring at 460 and 530 K, respectively, on heating

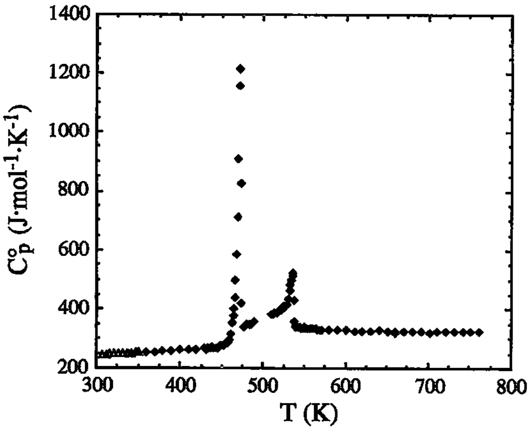

FIG. 3. High-temperature heat capacity data for bornite. Adiabatic calorimeter measurements are depicted as triangles; differential scanning calorimeter measurements are depicted as diamonds.

of synthetic Cu_5FeS_4. The variations of the transition temperature among the several investigations probably arise from small compositional differences in the samples, differences in the practical scales of temperature used and, in the case of the drop calorimetry, the difficulty in determining the exact temperature of transition.

Entropy

Our measurements of heat capacity were extrapolated to 0 K by means of the usual C°_p/T *versus* T^2 plot. Between 5 and 100 K, the data were smoothed using a mechanical spline, and between 100 and 350 K, smoothing was done by computer. The derived values for the thermodynamic functions are listed in Table 4. The high-temperature heat capacity data, measured by differential scanning calorimetry, join smoothly (± 0.5 %) with the heat capacities obtained with the low-temperature adiabatic calorimeter.

TABLE 4. THERMODYNAMIC FUNCTIONS FOR BORNITE

Temperature	Heat Capacity	Entropy	Enthalpy Function	Gibbs Energy Function
T	C°_p	S_T-S_0	$(H_T$-$H_0)/T$	$-(G_T$-$H_0)/T$
K			$J{\cdot}mol^{-1}{\cdot}K^{-1}$	
5	0.360	0.086	0.068	0.018
10	4.720	1.227	0.973	0.245
15	12.90	4.600	3.508	1.092
20	26.07	10.01	7.420	2.590
25	39.83	17.22	12.44	4.780
30	54.08	25.77	18.22	7.550
35	67.68	35.12	24.31	10.81
40	81.50	45.07	30.60	14.47
45	93.40	55.38	36.94	18.44
50	103.9	65.76	43.11	22.65
55	112.8	76.12	49.08	27.04
60	126.4	86.43	54.88	31.55
65	146.4	97.39	61.20	36.19
70	145.0	108.2	67.19	40.96
80	156.3	128.2	77.58	50.62
90	166.6	147.2	86.92	60.30
100	175.0	165.2	95.32	69.90
110	182.6	182.3	102.9	79.35
120	189.5	198.4	109.8	88.60
130	196.5	213.9	116.2	97.65
140	202.5	228.7	122.2	106.5
150	207.2	242.8	127.7	115.2
160	211.4	256.4	132.8	123.6
170	215.2	269.3	137.5	131.8
180	218.7	281.7	141.9	139.7
190	221.8	293.6	146.1	147.5
200	224.7	305.0	149.9	155.1
210	227.3	316.1	153.6	162.5
220	229.6	326.7	157.0	169.7
230	231.8	337.0	160.2	176.8
240	233.7	346.9	163.2	183.7
250	235.4	356.4	166.0	190.4
260	237.0	365.7	168.7	197.0
270	238.5	374.7	171.3	203.4
280	240.0	383.4	173.7	209.7
290	241.6	391.8	176.0	215.8
300	243.2	400.0	178.2	221.8
310	244.9	408.0	180.4	227.7
320	246.6	415.8	182.4	233.4
330	248.4	423.5	184.4	239.1
340	250.2	430.9	186.3	244.6
350	252.0	438.2	188.1	250.0
273.15	239.0	377.4	172.1	205.4
298.15	242.9	398.5	177.8	220.7

At 298.15 K, the measured value for the entropy, 398.5 ± 1.0 $J{\cdot}mol^{-1}{\cdot}K^{-1}$, exceeds that *estimated* by King *et al.* (1973), 362.3 $J{\cdot}mol^{-1}{\cdot}K^{-1}$, by 36.2 $J{\cdot}mol^{-1}{\cdot}K^{-1}$. On the other hand, the value for the entropy change S°_{800}–S°_{298} *measured* by drop calorimetry by Pankratz & King (1970) and in the present investigation by differential scanning calorimetry agree to within 0.3%. Although our values for the temperatures for the transitions in bornite differ from those of Pankratz & King (1970), our heat capacities above 350 K agree with theirs to within 1 to 1.5% except in the immediate vicinity of the two transitions, 470 to 535 K.

THERMODYNAMIC PROPERTIES OF PHASES IN THE SYSTEM Cu–Fe–S

Chalcopyrite

The thermodynamic properties of chalcopyrite ($CuFeS_2$) were derived by combining the Δ_fH° values calculated from CuS and FeS and from Cu and FeS_2 given by Cemič & Kleppa (1988), the S°_{298} from Robie *et al.* (1985), the high-temperature heat capacity data from Pankratz & King (1970) for chalcopyrite, and the data for the elements and component sulfides from Table 5. The Δ_fG° values recommended in the present study are preferred over published values (Barton & Skinner 1979, Robie *et al.* 1985) because the previous studies derived their values from sulfur fugacity data for the reaction:

$$Cu_5FeS_4 + 4\ FeS_2 = 5\ CuFeS_2 + S_2 \qquad (1)$$

and published Δ_fG° values for bornite (Barton & Skinner 1979, Robie *et al.* 1985), which were based on the 748 K invariant point for the assemblage bornite + pyrrhotite + copper + iron + vapor of Yund & Kullerud (1966). Bornite in this assemblage displays considerable metal/sulfur nonstoichiometry and Cu-for-Fe substitution away from the ideal 5Cu: 1Fe: 4S stoichiometry (Fig. 4). Toulmin & Barton (1964) and Barton (1973) demonstrated considerable deviations from ideal behavior in the thermodynamic mixing properties of the $Fe_{1-x}S$, $Cu_{2-x}S$ and $CuFeS_{2-x}$ solid solutions due to metal-to-sulfur nonstoichiometry. Therefore, any Δ_fG° values for bornite based on this invariant point and any resulting Δ_fG° values for chalcopyrite based on these values for bornite are subject to significant uncertainties. The recommended thermodynamic values for chalcopyrite are presented in Table 5.

TABLE 5. RECOMMENDED THERMODYNAMIC VALUES FOR SELECTED PHASES IN THE SYSTEM Cu-Fe-S

Phase Formula	Formula Weight (g)	Molar Volume V_{298} (cm^3)	S°_{298} (J·mol^{-1}·K^{-1})	$\Delta_fH^\circ_{298}$* (kJ·mol^{-1})	$\Delta_fG^\circ_{T(K)}$** (kJ·mol^{-1})	References
Copper Cu	63.546	7.11 ±0.00	33.14 ±0.03	0.00	0.00	Robie *et al.* (1976), Martin (1987)
Iron Fe	55.847	7.09 ±0.00	27.28 ±0.13	0.00	0.00	Cox *et al.* (1989)
Sulfur S (orthorhombic)	32.066	15.51 ±0.01	32.05 ±0.05	0.00	0.00	Cox *et al.* (1989)
Sulfur S_2 (ideal gas)	64.132	24789.20 ±0.02	228.17 ±0.01	128.60 ±0.30	$163.98 - 0.05054\ T - 4.0093\ T^{0.5}$ [± 0.1 %; 298 to 882 K]	Cox *et al.* (1989)
Covellite CuS	95.612	20.44 ±0.01	67.25 ±0.14	-54.57 ±0.25	$-125.13 + 0.05670\ T + 0.8422\ T^{0.5}$ [± 0.2 %;298 to 780 K]	Westrum *et al.* (1987), Ferrante *et al.* (1981), Potter (1977), Stuve (1982), Cemic & Kleppa (1988)
Anilite $Cu_{1.75}S$	143.272	25.79 ±0.02	107.51 ±0.16	-73.33 ±0.30	$-137.64 + 0.06459\ T$ [± 0.1 %; 298 to 312 K]	Grønvold *et al.* (1987), Grønvold & Westrum (1980), Potter (1977)
Chalcocite Cu_2S	159.158	27.49 ±0.01	116.22 ±0.20	-83.86 ±1.12	$-161.45 + 0.00078\ T + 1.8850\ T^{0.5}$ [± 0.6 %; 298 to 1400 K]	Grønvold & Westrum (1987), Ferrante *et al.* (1981), Brooks (1952), Richardson & Antill (1955), Sudo (1950), Bielen (1965), Pankratz & King (1970), Cemic & Kleppa (1988)
Troilite FeS	87.913	18.20 ±0.03	60.33 ±0.17	-101.00 ±1.00	$-175.94 + 0.03176\ T + 1.3960\ T^{0.5}$ [± 0.7 %; 298 to 1300K]	Grønvold *et al.* (1959), Robie (1965), Coughlin (1950), Chase *et al.* (1985), Cemic & Kleppa (1988)
Pyrite FeS_2	119.979	23.94 ±0.01	52.93 ±0.13	-171.54 ±1.67	$-303.59 + 0.18839\ T + 0.4515\ T^{0.5}$ [± 0.1 %; 298 to 1015 K]	Grønvold & Westrum (1962), Toulmin & Barton (1964), Coughlin (1950)
Chalcopyrite $CuFeS_2$	183.525	43.92 ±0.01	124.90 ±0.20	-194.93 ±4.84	$-369.64 + 0.05154\ T + 4.5690\ T^{0.5}$ [± 0.7 %; 298 to 820 K]	Robie *et al.* (1985), Pankratz & King (1970), Cemic & Kleppa (1988)
Cubanite $CuFe_2S_3$	271.438	67.44 ±0.06	205.00 ±0.40			Sirota et al. (1985), Mizota et al. (1985)
Bornite Cu_5FeS_4	501.841	98.72 ±0.10	398.50 ±0.80	-371.60 ±2.10	$-715.99 + 0.00339\ T + 9.2550\ T^{0.5}$ [± 0.1 %; 298 to 1200 K]	This Investigation, Pankratz & King (1970), Schneeberg (1973), Barton & Toulmin (1964)
Nukundamite $Cu_{5.5}FeS_{6.5}$	613.779	278.00 ±0.50			$-766.15 + 0.37540\ T + 5.1938\ T^{0.5}$ [± 0.6 %; 298 to 774 K]	This Investigation, Schneeberg (1973)

* Relative to the elements and orthorhombic sulfur; ** Relative to the elements and ideal S_2 gas; the uncertainty and valid temperature range are listed below equations.

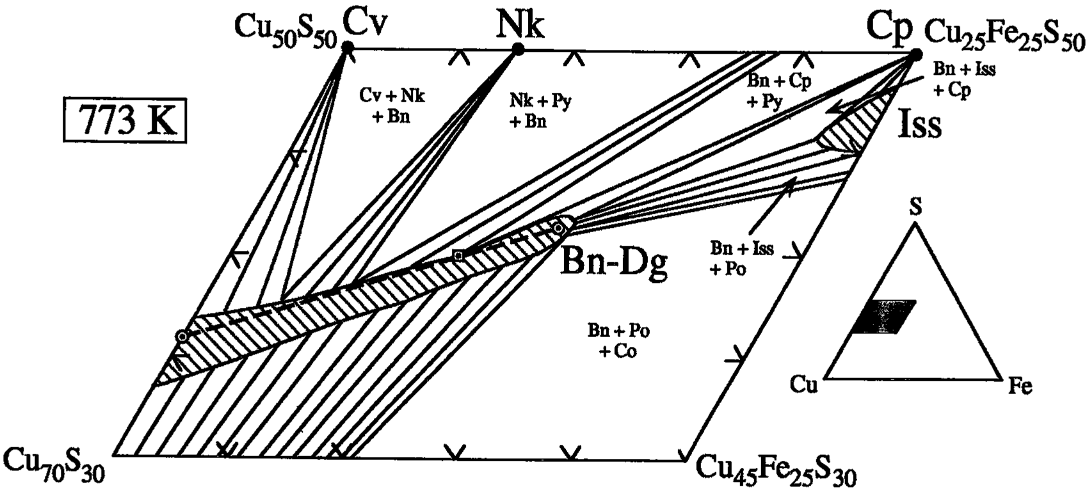

FIG. 4. Phase relations of a portion of the Cu–Fe–S ternary at 773 K around the bornite–digenite solid-solution field. The dashed line and symbols represent the pseudobinary discussed in the text. The circles represent the end-member compositions; the square represents stoichiometric bornite, Cu_5FeS_4 (= $Cu_{1.25}Fe_{0.25}S$). The diagonally stippled fields represent the compositional ranges for bornite–digenite and intermediate solid-solution. The diagram is constructed from data from Yund & Kullerud (1966), Barton (1973), Cabri (1973), Roseboom (1966) and Kojima & Sugaki (1985). Abbreviations: Co native copper, Dg digenite, Cv covellite, Nk nukundamite, Cp chalcopyrite, Po pyrrhotite, Iss intermediate solid-solution, Bn bornite.

Bornite

The thermodynamic values for bornite (Cu_5FeS_4) were derived by combining $S°_{298}$ and the heat capacity from the present study and the heat content data from Pankratz & King (1970) for bornite, the thermodynamic data for chalcopyrite, pyrite and the elements from Table 5, and the sulfur fugacity data for Reaction 1. Kojima & Sugaki (1985) demonstrated that the equilibrium compositions for all solid phases in Reaction 1 are stoichiometric within analytical uncertainty in their experimental run-products for 673 and 773 K (Fig. 4). Therefore, no adjustments to the thermodynamic values are necessary for nonstoichiometry of solid phases for temperatures less than 773 K. The equilibrium data for Reaction 1 were taken from a best-fit of the data from Schneeberg (1973) and Barton & Toulmin (1964). A "third-law" evaluation (Robie 1965) of the data of Schneeberg (1973) indicates that the data for his Run 1 are far superior than those for his Run 2 because of thermal drift in the data for Run 2. Consequently, the present study used the data from Run 1 only. At 748 K, the assemblage bornite + chalcopyrite + pyrite + vapor defines $\log f(S_2) = -2.4 \pm 0.2$ (Fig. 5). This $\log f(S_2)$ value results in a $\Delta_f G°_{748K}$ value for bornite (Cu_5FeS_4) of –460.31 kJ·mol^{-1}.

The validity of this value can be assessed by comparing it with the sum of the $\Delta_f G°_{748K}$ values for component sulfides that total 5Cu:1Fe:4S (Table 6).

TABLE 6. COMPARISON OF $\Delta_f G°_{748\ K}$ VALUES FOR COMPONENTS SUMMING TO THE COMPOSITION Cu_5FeS_4

Components	$\Delta_f G°_{748\ K}$* kJ·mol^{-1}
$2Cu_2S + CuS + FeS$	-392.28
$2.5Cu_2S + 0.5\ FeS + 0.5FeS_2$	-405.45
$4(0.231Cu_{1.800}S + 0.769Cu_{1.100}Fe_{0.325}S)$	-438.82
$4(\Sigma X_i \Delta_f G°_i + RT\Sigma X_i \ln X_i)$**	-452.27
Cu_5FeS_4	-460.31

* Relative to the elements and ideal S_2 gas.
** For the components $Cu_{1.800}S$ ($X = 0.231$) and $Cu_{1.100}Fe_{0.325}S$ ($X = 0.769$); $R = 8.3144$ J·mol^{-1}·K^{-1} (see text).

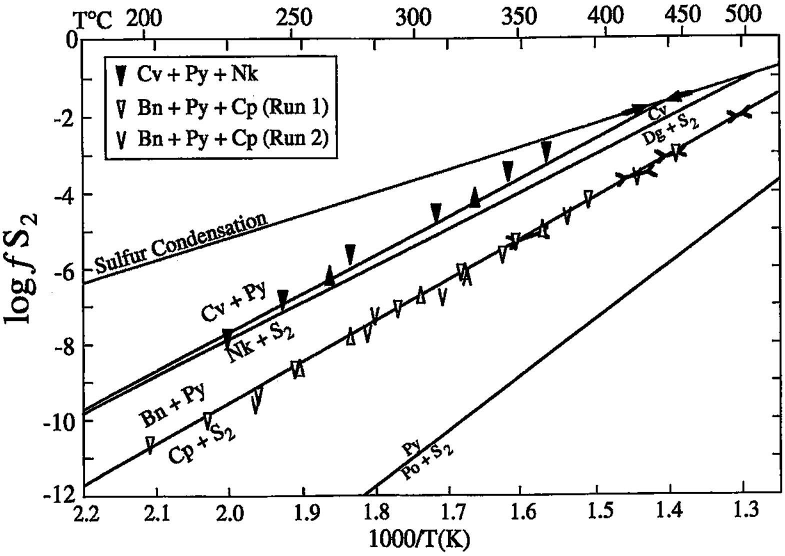

FIG. 5. T – $\log f(S_2)$ diagram for selected experimental data for reactions in the system Cu–Fe–S. The positions of the pyrite–pyrrhotite and covellite–digenite buffers are plotted for reference (Barton & Skinner 1979). Abbreviations: Cv covellite, Dg digenite, Py pyrite, Po pyrrhotite, Bn bornite, Cp chalcopyrite, Nk nukundamite. The symbols for the Cv + Py + Nk and Bn + Py + Cp assemblages represent reversal brackets from the data of Schneeberg (1973). The heavy-lined symbols along the Bn + Py + Cp curve are reversal brackets from Barton & Toulmin (1964). The heavy arrows along the sulfur condensation curve represent the uncertainty in the Cv + Py breakdown temperature determined by Roseboom & Kullerud (1958). The positions of the curves for bornite- and nukundamite-bearing reactions were calculated on the basis of the data presented in Table 5.

The $\Delta_fG°_{748K}$ value for bornite from the present study is significantly more negative than the sum of values for Cu_2S + CuS + FeS and Cu_2S + FeS + FeS_2. Furthermore, stoichiometric bornite (Cu_5FeS_4 = $Cu_{1.250}Fe_{0.250}S$) is colinear with the bornite composition ($Cu_{1.100}Fe_{0.325}S$) in equilibrium with the invariant assemblage (bornite + pyrrhotite + iron + copper + vapor) of Yund & Kullerud (1966) at 748 K and digenite of composition $Cu_{1.800}S$ (Fig. 4). For the join $Cu_{1.800}S$ – $Cu_{1.100}Fe_{0.325}S$, the mole fraction of $Cu_{1.100}Fe_{0.325}S$ in stoichiometric bornite (Cu_5FeS_4) is 0.769, and that for $Cu_{1.800}S$ is 0.231. The $\Delta_fG°_{748K}$ of $Cu_{1.100}Fe_{0.325}S$ can be evaluated from the invariant point of Yund & Kullerud (1966), and the data in Table 5. This approach results in a $\Delta_fG°_{748K}$ of –111.66 kJ·mol^{-1} for $Cu_{1.100}Fe_{0.325}S$. A Gibbs–Duhem integration of the data of Rau (1967, 1974) was used to evaluate the $\Delta_fG°_{748K}$ of $Cu_{1.800}S$ and resulted in a value of –103.21 kJ·mol^{-1}. The calculated $\Delta_fG°$ of bornite is significantly more negative than $4[0.231\ \Delta_fG°\ (Cu_{1.800}S) + 0.769\ \Delta_fG°\ (Cu_{1.100}Fe_{0.325}S)]$. For ideal mixing along the join $Cu_{1.800}S$ – $Cu_{1.100}Fe_{0.325}S$ (Fig. 4), $\Delta_fG°_{748K}$ (Cu_5FeS_4) is equal to $4(\Sigma X_i\Delta_fG°_i + RT\Sigma X_i \ln X_i)$, where X_i is the mole fraction of the end-member, $\Delta_fG°_i$ is the molar Gibbs free energy of formation for the end-member, and R = 8.3144 J·mol^{-1}·K^{-1}. This value is slightly less negative than the value for bornite from the present study (Table 6).

The $\Delta_fG°$ values of bornite recommended in the present study (Table 5) are preferred over published values (Robie *et al.* 1985, Barton & Skinner 1979, King *et al.* 1973) because the previous studies derived their values from estimated entropies and the invariant point for the assemblage bornite + iron + pyrrhotite + copper + vapor at 748 K from Yund & Kullerud (1966). As discussed in the context of the thermodynamic properties of chalcopyrite, the equilibrium composition of bornite in this assemblage deviates significantly from the stoichiometric composition of bornite in Reaction 1. Thus, any resulting values of Gibbs free energy are subject to the uncertainties associated with nonideality of the bornite solid-solution. The $\Delta_fG°$ values for bornite from the present study are more negative than the published values by a minimum of 2.5 kJ·mol^{-1} at 298 K and 15.7 kJ·mol^{-1} at 748 K (Table 7).

TABLE 7. COMPARISON OF $\Delta_fG°$ VALUES FOR BORNITE (Cu_5FeS_4)

Source	$\Delta_fG°_{298\ K}$* kJ·mol^{-1}	$\Delta_fG°_{748\ K}$* kJ·mol^{-1}
This Study	-554.02 ±2.1	-460.31 ±2.1
King et al. (1973)	-551.53	-440.25
Barton & Skinner (1979)	-542.34 ±8.4	-441.59 ±8.4
Robie et al. (1985)	-542.39 ±2.1	-444.90 ±2.1

* Relative to the elements and ideal S_2 gas.

Chalcocite

The thermodynamic values for chalcocite (Cu_2S) were derived by a "third-law" evaluation of the gas-mixing data of Brooks (1952) and Richardson & Antill (1955), combined with the entropy and heat capacity data for chalcocite from Ferrante *et al.* (1981) and Grønvold & Westrum (1987), and the thermodynamic data for the elements in Table 5. The gas-mixing data of Brooks (1952) and Richardson & Antill (1955) (Fig. 6) were weighted according to the number of measurements reported by each study and were selected because of their greater consistency over a larger range in temperature relative to the data of Bielen (1965), Sudo (1950), and Kordes & Rackow (1952). The $S°_{298}$ value (116.22 ± 0.20 J·mol^{-1}·K^{-1}) is the average of the values of Ferrante *et al.* (1981) and Grønvold & Westrum (1987). The "third-law" analysis of the present study yielded an enthalpy of reaction of 63.23 ± 1.00 kJ at 298.15 K for the reaction

$$Cu_2S + H_2 = 2\,Cu + H_2S \qquad (2).$$

A $\Delta_fH°_{298}$ value of –83.86 ± 1.12 kJ·mol^{-1} results by subtracting $\Delta_fH°_{298}$ for H_2S (Robie *et al.* 1979). Using the entropy values in Table 5, a $\Delta_fG°_{298}$ of –88.81 ± 1.17 kJ·mol^{-1} can be calculated relative to elemental copper and orthorhombic sulfur. The recommended thermodynamic values for chalcocite are presented in Table 5. The $\Delta_fH°_{298}$ value is more strongly negative than the values taken from Potter (1977), –80.71 kJ·mol^{-1}, Pankratz *et al.* (1987), 75.73 kJ·mol^{-1}, Mills (1974), –79.50 kJ·mol^{-1}, and Cemič & Kleppa (1988), –80.21 kJ·mol^{-1}. Note that the analysis of Mills (1974) used a much higher and incorrect value for $S°_{298}$ of Cu_2S (Anderson 1932).

Covellite and anilite

The thermodynamic values for covellite (CuS) were derived by combining the $\Delta_fG°_{298}$ given by Potter (1977) from galvanic cell measurements with published data on entropy and heat capacity from Ferrante *et al.* (1981) and Westrum *et al.* (1987) and the data for the elements in Table 5. The $S°_{298}$ value represents the average of the two published values. Covellite has an upper thermal stability of 780 ± 3 K, where it decomposes to digenite + liquid sulfur (Kullerud 1965).

The thermodynamic values for anilite ($Cu_{1.75}S$) were derived by combining the $\Delta_fG°_{298}$ given by Potter (1977) from galvanic cell measurements with published data on entropy and heat capacity from Grønvold *et al.* (1987) and the data for the elements in Table 5. Anilite has an upper thermal stability at 1 atm of 312 K, where it decomposes to low digenite + covellite (Grønvold *et al.* 1987).

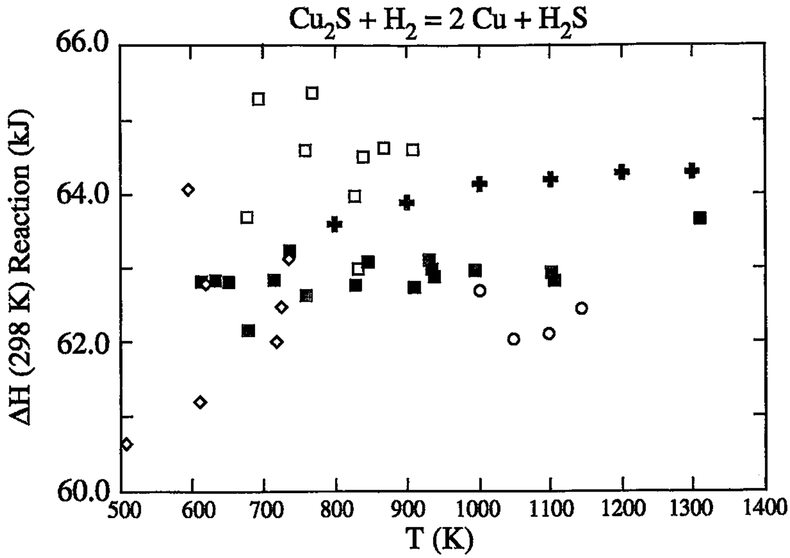

FIG. 6. Gas mixing data for the reaction $Cu_2S + H_2 = 2 Cu + H_2S$. The ΔH (298 K) values were calculated from the equilibrium data of Brooks (1952) (filled squares), Richardson & Antill (1955) (crosses), Bielen (1965) (open squares), Sudo (1950) (open circles), and Kordes & Rackow (1952) (open diamonds).

Nukundamite

Considerable confusion has surrounded the identities, characteristics and stabilities of the minerals nukundamite and idaite. We accept the distinction made by Sillitoe & Clark (1969), Clark (1970), Cabri (1973) and Rice *et al.* (1979), and define nukundamite as approximated by the formula $Cu_{5.5}FeS_{6.5}$, and idaite, by Cu_3FeS_4. In early experimental work in the system Cu–Fe–S, Merwin & Lombard (1937), Roseboom & Kullerud (1958), Yund & Kullerud (1966) and Sugaki *et al.* (1975) investigated the stability of $Cu_{5.5}FeS_{6.5}$, but referred to it as "idaite". In later experimental studies, Wang (1984) and Kojima & Sugaki (1985) conformed to the designation of $Cu_{5.5}FeS_{6.5}$ as nukundamite. Wang (1984) investigated the stability of idaite relative to nukundamite and concluded that idaite is a metastable phase that breaks down upon heating to nukundamite + chalcopyrite above 543 K. The study of Schneeberg (1973) is problematic because he investigated equilibria involving a phase that he called "idaite", but failed to report any information characterizing the phase in his experiments. In light of the results of Wang (1984) regarding the metastability of idaite, we tentatively assume here that the equilibria measured by Schneeberg (1973) actually involved the phase nukundamite rather than idaite.

Schneeberg (1973) determined the equilibrium sulfur fugacity corresponding to the reaction:

$$Cu_{5.5}FeS_{6.5} + 1/2\ S_2 = 11/2\ CuS + FeS_2 \quad (3)$$

from 491 to 667 K. Likewise, Roseboom & Kullerud (1958) determined the equilibrium temperature (707 K) for this reaction along the sulfur condensation curve (Fig. 5). The projection of the equilibrium $\log f(S_2)$ expression of Schneeberg (1973) to 707 K yields $\log f(S_2) = -1.1$, which is 0.6 greater than the value calculated for the sulfur condensation curve using the data in Table 5. In the present study, we selected the visual best-fit to the reversals of Schneeberg (1973) and the isobaric invariant point of Roseboom & Kullerud (1958). The thermodynamic values for nukundamite were calculated using the resulting curve for Reaction 3 and the thermodynamic data for covellite and pyrite listed in Table 5.

DISCUSSION

Considerable progress has been made in understanding the thermodynamics and phase equilibria of the system Cu–Fe–S, but much more work needs to be done. The limited equilibrium data-base available and the complication of superambient transitions for many of the phases in the system do not justify a multiple regression analysis of the thermodynamic data at this time. Despite the progress made in the present study, the analytical uncertainty associated with the enthalpies of formation and Gibbs free energies of chalcopyrite and bornite remains one of the greatest hindrances to an accurate evaluation of the thermodynamic properties of this system. Future work also should be directed toward an improvement in our understanding of the thermodynamics of the bornite solid-solution and the intermediate solid-solution. The copper sulfide solid-solutions digenite and djurleite have been the subject of numerous studies, but no comprehensive attempt has been made to reconcile the variety of data available. Considerable uncertainty still exists in the phase equilibria and thermodynamics for phases such as cubanite ($CuFe_2S_3$), talnakhite ($Cu_9Fe_8S_{16}$), mooihoekite ($Cu_9Fe_9S_{16}$), and haycockite ($Cu_4Fe_5S_8$). Likewise, owing to the central location of nukundamite in the ternary system, the previously discussed discrepancy in the phase-equilibrium studies must be addressed. The resolution of these problems will be essential to a full understanding of this system. The low-temperature thermodynamics and phase equilibria in the system will have growing significance in problems surrounding mine-site environmental issues.

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