

# The stabilities of antlerite and $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ : their formation and relationships to other copper(II) sulfate minerals

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## Abstract

The stabilities of antlerite,  $\text{Cu}_3\text{SO}_4(\text{OH})_4$ , and a synthetic compound whose stoichiometry is here established as  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ , have been determined at 5 °C intervals between 10 °C and 45 °C, using solution methods. The results of the experiments show that antlerite is stable with respect to the compound  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  only at temperatures above 30 °C. Below 30 °C a change in the relative stabilities of these two basic copper(II) sulfates occurs, and the compound  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ , although unknown at present as a mineral, instead, is stable. Under these conditions, it does not react to give antlerite if kept in contact with water. Once isolated from its mother liquor, however, the dihydrate undergoes rapid dehydration to yield antlerite. Thermodynamic quantities for the two phases have been derived from equilibrium measurements. At 298.2K, values of  $\Delta_f G^\circ$  for the compounds  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}(\text{s})$  and antlerite are  $-1919.6(14)$  and  $-1445.0(10)$  kJ mol<sup>-1</sup>, respectively. The results have been used to construct stability field diagrams for the system  $\text{CuO-H}_2\text{O-SO}_3$  at 25 °C and at 35 °C. These diagrams have been used to illustrate the chemical conditions under which the two compounds might be expected to form in the oxidised zones of cupriferous base metal orebodies.

KEYWORDS: antlerite, sulfates, dihydrate, stability field diagrams.

## Introduction

THE basic copper(II) sulfate antlerite,  $\text{Cu}_3\text{SO}_4(\text{OH})_4$ , has been the subject of a considerable body of mineralogical and laboratory-based investigation, both in terms of its abundance in the oxidised zones of cupriferous orebodies in arid regions (Palache *et al.*, 1951) and its relationships to brochantite,  $\text{Cu}_3\text{SO}_4(\text{OH})_6$ , chalcantite,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , and tenorite,  $\text{CuO}$ . Posnjak and Tunell (1929) first showed the mineral to possess a field of thermodynamic stability between those of chalcantite and brochantite in the temperature range 50–200 °C. Aided by this result, Brady (1938) and Jarrell (1944) were able to elucidate occurrences in the

most famous deposit of the mineral at Chuquimata in Chile, where the paragenetic sequence chalcantite → antlerite → brochantite → tenorite is observed, due to decreasing sulfate ion concentration with increasing distance from the primary sulfide source (in conjunction with increasing pH). The extent of the deposit at this locality, together with a laboratory study of the mineral brochantite, led Silman (1958) to an estimate of  $\Delta_f G^\circ$  at 298.2K for antlerite of  $-1445.6$  kJ mol<sup>-1</sup>, a value that has continued to be used in calculations involving the species.

Since values of the free energy of formation of related copper minerals and their component ions have been revised subsequently, it was felt that the estimate upon which value of the free energy of antlerite was based (Silman, 1958) may have required similar revision. Therefore an investigation of the relevant portion of the  $\text{CuO-H}_2\text{O-SO}_3$  system was begun to establish experimentally the phase relationships of the minerals brochantite, antlerite, and chalcantite in the tem-

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perature range appropriate to naturally occurring secondary copper(II) sulfate deposits. The results of this study are presented below, and they indicate that the previously estimated phase relationships of Silman (1958) do not represent the relative stabilities of the minerals at 25°C, but rather are close to those at temperatures approaching 35°C. Such average temperatures might be expected to exist only in the hot, arid regions where antlerite is relatively abundant. Below this temperature antlerite was not observed to crystallise from solution. This result, coupled with an experimentally determined value for the free energy of formation of  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}(\text{s})$  at 298.2K, has led to the establishment of an equilibrium model which has then been applied to several natural occurrences of the copper(II) sulfates and used in turn to comment on the probable mode of crystallisation of antlerite at somewhat elevated ambient temperatures. In addition, the possible formation of antlerite at lower temperatures *via* the desiccation of the dihydrate is discussed.

### Experimental

*Synthesis of the basic copper(II) sulfates.* To a series of stirred aqueous solutions (100 cm<sup>-3</sup>) containing  $\text{CuSO}_4$  (0.2, 0.4, 0.6, 1.0 mol dm<sup>-3</sup>) was added various quantities of  $\text{CO}_2$ -free aqueous NaOH solution (0.5 mol dm<sup>-3</sup>) such that the 4:3 (OH:Cu) end-point was not exceeded. After the additions, the reaction vessels were left stirring in a thermostatted water bath. Small amounts of the mixture were removed at various intervals. The solid phase formed was collected at the pump on a glass sinter and dried *in vacuo* over silica gel at room temperature. Washing of the precipitates of antlerite and  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  with distilled water prior to drying is liable to result in decomposition of the material to brochantite (Posnjak and Tunell, 1929; Balarew and Markov, 1986). Furthermore, prolonged desiccation *in vacuo* or lengthy exposure to the atmosphere results in dehydration of  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  to give antlerite.

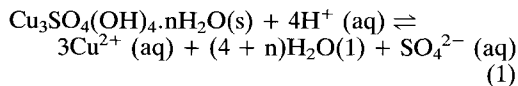
Identities of the compounds synthesised were established by X-ray powder diffraction methods using a 114.6 mm diameter Debye-Scherrer camera and Cu-K $\alpha$  radiation. The patterns obtained were compared with those in the JCPD powder diffraction file for antlerite, brochantite and posnjakite and the stoichiometry of  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  was established by analysis. Infrared spectra were recorded using a Perkin Elmer 783 spectrophotometer, with samples

prepared either in pressed KBr discs or in Nujol mulls, and compared with reference data (Ridkosal and Povondra, 1982; Balarew and Markov, 1986; Braithwaite, 1982). Care is required in the measurement of the infrared spectrum of  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ , since even the pressure of grinding the powder to prepare a suitable mull is liable to cause decomposition to antlerite.

*Equilibrium solubility measurements.* Five reaction solutions of greater than 0.5 mol dm<sup>-3</sup>  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were employed for each of the temperature steps to be studied. To these, aqueous 0.5 mol dm<sup>-3</sup> NaOH (10 cm<sup>3</sup>) was added in the manner described above. The reaction vessels were then sealed and placed in a Grant SB3/74GB water bath thermostatted at the desired temperature ( $\pm 0.1^\circ\text{C}$ ). The temperatures chosen for equilibration were at 5°C intervals between 10°C and 45°C. Preliminary experiments established that equilibrium was achieved in less than one week. The use of aqueous NaOH thus alleviated the difficulties concerning the time required for equilibration encountered by earlier workers (Young and Stearn, 1916; Bell and Murphy, 1926), as described by Posnjak and Tunell (1929). Prior to filtration, the pH of the solution was measured using a Radiometer PH85 pH meter fitted with a combination electrode. The solid was collected at the pump using a 0.45  $\mu$  millipore filter and identified using infrared and X-ray powder diffraction methods. Due to the high levels of  $\text{Cu}^{2+}$  remaining in the solution, total  $\text{Cu}^{2+}$  (aq) concentrations were measured using the iodometric method described by Vogel (1961). The total sulfate concentration was then calculated, based on a knowledge of the stoichiometry of the solid phase formed and the known starting concentrations. Analytical concentrations, pH measurements and calculated solution concentrations using the computational methods employed (*vide infra*) are given in the Appendix.

*Derivation of solubility and related thermodynamic properties.* Species distributions in aqueous solutions in equilibrium with the solid phases were calculated from equilibrium solubility and pH data using the computer program COMICS (Perrin and Sayce, 1967). Equilibrium constants for  $\text{CuSO}_4$  (aq) and  $\text{HSO}_4^-$  (aq) were taken from Smith and Martell (1976) and corrected for both temperature and ionic strength. Under the conditions of pH obtaining in these experiments, hydrolysis of the copper(II) ion can be ignored (Baes and Mesmer, 1976). This is fortunate because no reliable enthalpy data appear to be available for such species. Using the results of the

COMICS calculations, values of the equilibrium constant for (1) were calculated.



Equilibrium constants were corrected to zero ionic strength using the extended form of the Debye-Hückel law [ $\log \gamma_1 = -A z_1^2 I^{1/2} / (1 + I^{1/2})$ ]; errors are quoted as standard deviations derived from the multiple measurements.

The equilibrium constants were then used to calculate values of  $\Delta_f G^\circ$  (298.2K),  $\Delta_f H^\circ$  (298.2K) and  $S^\circ$  (298.2) for  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  and antlerite. Free energy data for other mineral species and component ions at 298.2K were taken from the compilation of Robie *et al.* (1978). Values of the free energy of formation of mineral species and component ions, other than brochantite, at 308.2K were calculated from enthalpy and entropy values available in the same source. The free energy of formation of brochantite at 308.2K was calculated from enthalpy and entropy data reported by Barton and Bethke (1960).

### Results and discussion

*Identity of solid phases.* A compound containing the same ratio of  $\text{Cu}^{2+} : \text{OH}^-$  as antlerite has long been known to be formed in similar titrations to ours of copper(II) sulfate solutions when a deficiency of base is used, with values approaching the 3:4 Cu:OH end-point (Posnjak and Tunell, 1929; Kheifets and Rotinyan, 1954; Balarew and Markov, 1986). The results of thermogravimetric analysis of the compound formed in such circumstances at temperatures below 30°C are given in Table 1. The compound has the stoichiometry  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ . Indeed, the infrared spectrum of this compound corresponds to that of the solid phase  $\text{CuSO}_4(\text{OH})_4 \cdot x\text{H}_2\text{O}$  noted by Balarew and Markov (1986). X-ray powder diffraction data for the phase are given in Table 2. This compound was that isolated in all titrations carried out up to the 4:3, OH:Cu end-point at temperatures between 10 and 30°C. In this temperature range, the compound was not seen to react or decompose while it remained in contact with the

aqueous solution from which it had crystallised. Subsequent desiccation at room temperature in air was however noted to cause the complete decomposition of this compound (*vide supra*). If the titration was carried out at a temperature greater than 30°C, the compound isolated was pure antlerite,  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ .

Of course, it is not possible from the results of these experiments to state categorically that, given sufficient time, the solid phase  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  will not recrystallise to antlerite in contact with solution. However, it is true that at temperatures below 30°C, any such reaction must be very slow. In the light of the synthetic results, coupled with the fact that Cu(II) is labile (certainly with respect to solution species), we conclude that antlerite is the thermodynamically stable phase above this temperature. At temperatures less than about 30°C, the dihydrate is stable *provided it remains in contact with aqueous solution*. It has been observed to be preserved in contact with the mother liquor during several weeks.

Once the 4:3 end-point for the precipitation of compounds of the stoichiometry  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4 \cdot n\text{H}_2\text{O}$  ( $n = 0$  or 2) by the slow addition of base is exceeded, both phases react rapidly to yield brochantite. If the amount of base, added quickly, is greater than that required for a 4:3 end-point, the above reactions do not occur. The solid phase formed initially in these circumstances is posnjakite,  $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$  (Komkov and Nefedov, 1967). At all temperatures used in this study, posnjakite was seen to react to give brochantite within 24 hours, if left in contact with the reaction solution. In addition, the change of relative thermodynamic stabilities of the two solid phases with 4:3 stoichiometry between room temperature and 35°C rationalises the observation of Balarew and Markov (1986) that antlerite recrystallises *via*  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot x\text{H}_2\text{O}$  to brochantite when placed in distilled water at room temperature.

*Solubility and thermodynamic calculations.* Values for the equilibrium constants  $K_a^+$  for equation (1), derived from the COMICS calculations, are given in Table 3. Fig. 1 shows these values of  $\log K_a^+$  plotted against  $1/T$ . Knowledge of which solid phase is in equilibrium with solution species at certain temperatures permits

Table 1  
Results of thermogravimetric analyses of the dihydrate.

	1	2	3	4	5*
CuO	61.1	61.2	61.1	61.07	67.28
SO <sub>3</sub>	20.5	20.4	20.5	20.49	22.57
H <sub>2</sub> O	18.4	18.4	18.4	18.44	10.15

\* 1-3: Isolated dihydrate salt; 1 4:  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ ; 5: antlerite.

Table 2  
X-Ray powder diffraction data for  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ .

d/A(meas.)	I	d/A(meas.)	I
10.71	vvs	2.201	mw
5.389	s	2.156	mw
5.155	m	2.094	w
4.407	m	2.037	w
4.125	m	1.983	vw
3.917	ms	1.903	vw
3.520	w	1.850	vw
3.351	m	1.797	vw
3.170	mw	1.734	w
2.959	w	1.585	wb
2.894	w	1.538	mw
2.793	ms	1.512	mw
2.698	m	1.479	w
2.656	m	1.450	w
2.585	ms	1.371	vwb
2.471	w	1.345	vwb
2.426	ms	1.325	vwb
2.353	m	1.238	m

Table 3  
Equilibrium constants for equation (1).

T/K	Log $K_a$	solid present
283.2	10.18(3)	$\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$
288.2	9.73(4)	"
293.2	9.41(2)	"
298.2	9.01(2)	"
303.2	8.61(2)	"
308.2	8.30(3)	antlerite
313.2	7.92(1)	"
318.2	7.60(2)	"

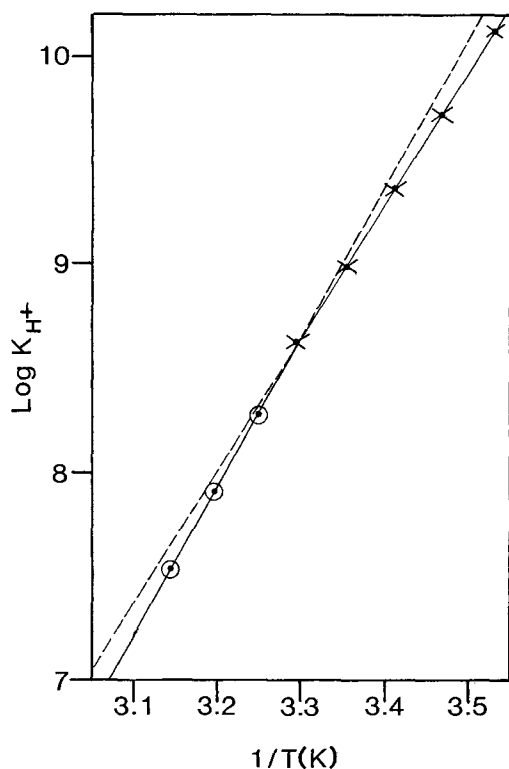
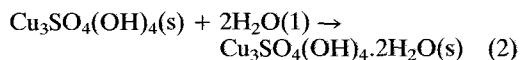


FIG. 1. Plot of  $\log K_a^+$  for equation (1) versus  $1/T(K)$ . (O) solid phase is antlerite; (X) solid phase is  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ .

the evaluation of all thermodynamic parameters for both  $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$  and antlerite, and appropriate quantities calculated at 298.2K are presented in Table 4. The errors in these energy terms are those associated with the values of  $\log K_a^+$  (one standard deviation) obtained from the pertinent least-squares derived values of  $\Delta rH^\circ$ , together with the sums of the errors in the energy terms for the component ions and water as listed by Robie *et al.* (1978). Errors in values of  $S^\circ$  are derived from the usual relation of  $\Delta fG^\circ$  and  $\Delta fH^\circ$ .

It is noted from Fig. 1 that values of  $\Delta rH^\circ$  for the two minerals with respect to equation (1) are virtually the same. Unfortunately, this fact mitigates against the estimation of an accurate temperature for the change in relative stabilities of the two solid phases because of the errors in the two least-squares plots. However, we do emphasise that antlerite is the stable phase in solution at 35°C and above, and the dihydrate at 30°C and below. We calculate  $\Delta fG^\circ$  ( $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}, s, 298.2\text{K}$ ) as being  $-1919.6(14) \text{ kJ mol}^{-1}$  (from the least-squares value for  $\log K_a^+$  at this temperature) as compared with a value for antlerite extrapolated to the same temperature of  $-1445.0(10) \text{ kJ mol}^{-1}$ . Thus at 25°C, antlerite is thermodynamically unstable with respect to the dihydrate, in the presence of  $\text{H}_2\text{O}(l)$ .  $\Delta fG^\circ$  (298.2K) for equation (2) is equal to  $-0.3 \text{ kJ mol}^{-1}$ .



*Relationships with other minerals.* Equilibrium stability field diagrams at 25°C and 35°C (Figs. 2 and 3, respectively) have been calculated to indicate the stabilities of the two compounds in relation to other common secondary copper(II) sulfates and tenorite. In order to evaluate the

Table 4  
Derived thermodynamic quantities at 298.2K.

Compound	$\Delta_f G^\circ /$ kJ mol <sup>-1</sup>	$\Delta_f H^\circ /$ kJ mol <sup>-1</sup>	$S^\circ /$ J mol <sup>-1</sup> K <sup>-1</sup>
Cu <sub>3</sub> SO <sub>4</sub> (OH) <sub>4</sub> ·2H <sub>2</sub> O	-1919.6(14)	-2303.6(41)	391(57)
Cu <sub>2</sub> SO <sub>4</sub> (OH) <sub>4</sub>	-1445.0(10)	-1726.7(60)	286(68)

significance of these results with respect to mineral formation in the oxidised zones of metal orebodies, we have taken thermodynamic data from the literature for brochantite, chalcantite and tenorite measured at 298.2K (Robie *et al.*, 1978; Barton and Bethke, 1960; *vide supra*). Fig. 2 shows the phase Cu<sub>3</sub>SO<sub>4</sub>(OH)<sub>4</sub>·2H<sub>2</sub>O to occupy a considerably smaller stability field at 298.2K than that previously allowed for antlerite (Silman, 1958), between those of the minerals chalcantite and brochantite. The range of this domain means that the compound is only stable in solution over a pH interval of about 0.5 units at any given activity of SO<sub>4</sub><sup>2-</sup> (aq). This fact can be interpreted in the light of our other observations to account for the

rarity of antlerite formed in deposits confined to temperate regions; antlerite in these circumstances could only form under equilibrium conditions *via* desiccation of initially crystallised dihydrate.

In this connection, where a description of crystal size is mentioned in the literature concerning the occurrence of antlerite in deposits of temperate environments, material has been found invariably as microcrystalline powders or crusts (Kokkoros, 1953; Hutton and McCraw, 1950; Walenta, 1975; Barwood and Hajek, 1978; Ridkosil and Povondra, 1982). Since we observe the dihydrate to decrepitate on desiccation to yield antlerite in the laboratory, the above descriptions do suggest that the mineral is formed by such a process.

In deposits in which large crystals of antlerite occur (Ungemach, 1924; Bandy, 1938; Palache *et al.*, 1951), notably at Chuquicamata, and in a number of deposits in Arizona, U.S.A. (Palache *et al.*, 1951; Anthony *et al.*, 1977), the material would be seen as having crystallised directly from solution (crystals to 10 cm are known from Chuquicamata). This could only occur at temperatures greater than 30–35°C. At 35°C, the stability field of antlerite (Fig. 3) is somewhat enlarged at the expense of those of brochantite and antlerite, as compared with the analogous case at 25°C. The argument which formed the basis of the previous estimate of  $\Delta_f G^\circ$  for antlerite (Silman, 1958), concerning the size of the deposit at Chuquicamata, would therefore seem to hold true, but for higher ambient temperatures. While it is fortuitous that the deposit is located in a hot, dry region, no information, to our knowledge, is available with respect to the climate prevailing during the development of the oxidised zone.

Finally, we would like to comment on the possible existence of the compound Cu<sub>3</sub>SO<sub>4</sub>(OH)<sub>4</sub>·2H<sub>2</sub>O as a naturally occurring species. A number of phases have been proposed as new hydrated basic copper sulfates in the past, including vernadskite (Zambonini, 1910), heterobrochantite (Buttgenbach, 1926), stelnzerite (Arzruni, 1899), and arnimitite (Weisbach, 1886; Frondel, 1949). Each has been identified subsequently as antlerite and it is impossible now to tell whether or not the material originally collected

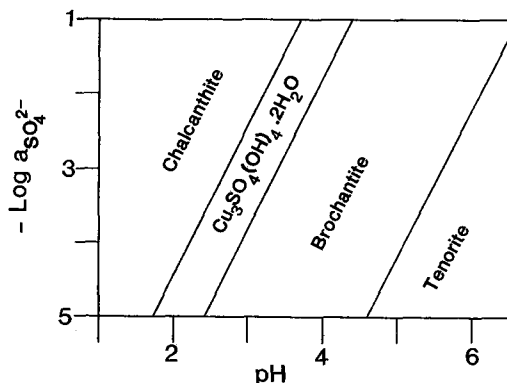


FIG. 2. Stability field diagram calculated for 25°C.

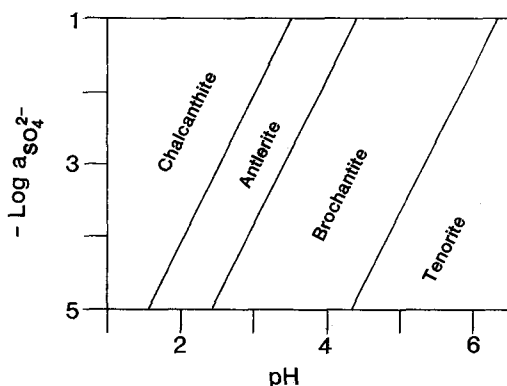


FIG. 3. Stability field diagram calculated for 35°C.

was this species. We note that the identification of the dihydrate would depend on finding the mineral in contact with the solution from which it has crystallised and performing the necessary characterisation before dehydration occurred. It does however, in our view, seem likely that the dihydrate would exist as a natural phase.

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# ANTLERITE STABILITY

365

## Appendix

Analytical and calculated results for solubilities and from the COMICS computations (see text).

T/K	[Cu] <sub>T</sub> <sup>a</sup>	[SO <sub>4</sub> ] <sub>T</sub> <sup>a</sup>	10 <sup>2</sup> [Cu] <sub>0</sub> <sup>b</sup>	10 <sup>2</sup> [SO <sub>4</sub> ] <sub>0</sub> <sup>b</sup>	pH
283.2	0.443	0.420	3.771	5.240	4.040
			3.771	5.240	4.044
			3.771	5.240	4.034
			3.771	5.240	4.030
			3.771	5.240	4.026
288.2	0.445	0.426	3.462	5.324	3.958
			3.462	5.324	3.958
			3.463	5.323	3.940
			3.463	5.323	3.933
293.3	0.443	0.420	3.462	5.324	3.952
			3.159	5.438	3.899
			3.159	5.437	3.894
298.2	0.443	0.420	3.159	5.433	3.896
			3.074	5.272	3.807
			3.073	5.274	3.813
			3.074	5.272	3.800
			3.073	5.273	3.810
303.2	0.442	0.417	3.074	5.273	3.808
			2.780	5.180	3.663
			2.782	5.181	3.670
			2.783	5.178	3.653
			2.781	5.181	3.672
308.2	0.443	0.419	2.782	5.179	3.662
			2.930	5.219	3.724
			2.930	5.219	3.727
			2.930	5.218	3.718
			2.931	5.217	3.716
313.2	0.447	0.402	2.930	5.218	3.721
			2.092	6.404	3.642
			2.092	6.402	3.636
			2.091	6.409	3.645
			2.092	6.403	3.639
318.2	0.436	0.401	2.092	6.404	3.642
			2.262	5.569	3.551
			2.263	5.567	3.547
			2.263	5.566	3.544
			2.261	5.571	3.557
			2.262	5.568	3.548

<sup>a</sup>Total concentrations in units of mol dm<sup>-3</sup>. <sup>b</sup>Equilibrium activities from COMICS calculations, and calculation of activity coefficients (see text).

Values of formation constants used in the COMICS calculations.

T/K	logK <sup>a</sup>	
	CuSO <sub>4</sub> <sup>o</sup>	H <sub>2</sub> SO <sub>4</sub> <sup>c</sup>
283.2	2.30	1.73
285.2	2.33	1.81
293.2	2.35	1.87
298.2 <sup>b</sup>	2.38	1.99
303.2	2.41	2.01
308.2	2.43	2.07
313.2	2.45	2.13
318.2	2.48	2.19

<sup>a</sup>Association constants. <sup>b</sup>Values taken from Smith and Martell (1976); all others calculated using enthalpy and entropy data from the same source.