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EXTRACTION METALLURGY DIVISION

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Thermodynamics of the Thermal Decomposition of Cupric Sulfate and Cupric Oxysulfate

T. R. Ingraham

The thermal decomposition of cupric sulfate and of cupric oxysulfate has been examined by determining the equilibrium gas pressure generated over each pure compound. The equilibrium data have been used to calculate the thermodynamic properties of both compounds, and the results have been combined with previously published data to establish a predominance-volume diagram for the Cu-S-O system over the normal range of roasting temperature and gas composition used in the treatment of copper minerals. Copper oxysulfate recrystallizes at 1100°K with an apparently irreversible endothermic heat requirement of 2.9 ± 0.3 kcal per mole.

WHEN mixed sulfide minerals containing copper are roasted, either of two procedures may be followed, depending on the nature of the other metals. In the first procedure, the roasting is controlled to produce a maximum amount of water-soluble copper sulfate which may be removed selectively from the water-insoluble compounds of the other metals. In the second, control is directed toward the production of water-soluble sulfates of the other metals and an insoluble salt of copper. Effective control of either of these processes would be enhanced by knowledge of the thermal stability of cupric sulfate and of cupric oxysulfate.

In this paper, established data for the thermal stability of cuprous and cupric sulfide and of cuprous and cupric oxide will be combined with new data for the thermal stability of cupric sulfate and cupric oxysulfate, to designate the volumes of stability of the significant compounds in the Cu-S-O system in the temperature range 750° to 950°K.

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Manuscript submitted April 13, 1964. EMD

EXPERIMENTAL

Materials, Apparatus, and Procedure. The copper source material used in all experiments was Fisher Certified Reagent Grade "anhydrous" cupric sulfate, for which the following analysis was supplied by the manufacturer: chloride, 0.002 pct; alkalies and earths, 0.2 pct; insoluble, 0.002 pct; iron, 0.020 pct.

Cupric oxysulfate was prepared from the normal sulfate by two procedures. In the first, equimolar quantities of cupric oxide (prepared by decomposition of the sulfate) and cupric sulfate were ground together and heated under vacuum in a sealed silica vessel at 800°C. This procedure was subject to failure because of explosion of the silica vessels due to the pressure of the final traces of water released from the sulfate on the initiation of its decomposition. The second procedure involved roasting the cupric sulfate, with frequent rabbling, in a muffle furnace at 725°C for a period of 48 hr. This produced an excellent product, which was confirmed as copper oxysulfate by X-ray and chemical analyses.

The experimental technique used was that of measuring the total pressure exerted by the sulfur trioxide, sulfur dioxide, and oxygen produced by the following reactions:

$$2\ CuSO_4 \rightleftharpoons CuO \cdot CuSO_4 + SO_3 \qquad [1]$$

$$CuO \cdot CuSO_4 \rightleftharpoons 2\ CuO + SO_3 \qquad [2]$$

$$SO_3 \rightleftharpoons SO_2 + 1/2\ O_2 \qquad [3]$$

The apparatus used in the experiments has been described previously.[1-3] Its main feature of a U-tube mercury manometer in which the mercury is protected from corrosion by enclosure in a flexible Pyrex bellows.

Before beginning a run, the interior of the apparatus, including the bellows-manometer and all connecting tubing, was thoroughly washed with hydrochloric acid and distilled water to remove any

Table I. Thermal Decomposition of Cupric Sulfate

t, °C	P, atm	t, °C	P, atm
607.0	0.0067	705.1	0.1026
631.8	0.0138	718.8	0.1406
640.8	0.0180	727.0	0.1829
649.3	0.0210	728.2	0.1787
668.4	0.0399	765.7	0.4396
677.8	0.0494	770.4	0.5120
683.1	0.0552	774.7	0.5329
704.7	0.0996	798.6	0.8905

Table II. Thermal Decomposition of Cupric Oxysulfate

t, °C	P, atm	t, °C	P, atm
695.6	0.0252	788.8	0.2209
702.7	0.0329	791.2	0.2289
716.3	0.0446	803.0	0.2985
722.1	0.0478	810.1	0.3465
723.5	0.0493	813.7	0.3779
729.3	0.0587	825.2	0.4653
740.1	0.0738	831.6	0.5324
742.5	0.0793	836.6	0.5897
751.1	0.0965	837.8	0.5924
762.9	0.1230	847.9	0.7250
766.2	0.1350	853.9	0.8117
773.8	0.1559	858.7	0.8916
782.5	0.1896	864.7	0.9902

traces of reactants or products from a previous run. The apparatus was dried by sealing and evacuating overnight at operating temperature. After cooling, the apparatus was opened and a predried sample contained in a shallow platinum boat was introduced. The apparatus was then resealed and evacuated with a rotary pump for an additional period of several hours. In the final period of 1 hr before the apparatus was isolated from the pump, the sample temperature was increased slowly until incipient decomposition had begun. This ensured both elimination of the last traces of moisture from the sample and the presence of sufficient reaction product to enhance the reversibility of the decomposition reaction. Equilibrium was established within 6 to 10 hr with either increasing or decreasing temperatures.

Results. The results obtained from the decomposition of two samples of cupric sulfate, using increasing and decreasing temperatures, are shown in Table I. Because of the volatility of cupric sulfate at temperatures above 750°C, all of the sample was not retained in the area near the temperature-measuring thermocouple immersed in the platinum boat. Since there was no reason to suspect selective absorption of SO_3, SO_2, or O_2 on the cupric sulfate, and since the cupric sulfate did not reach the manometer area, its sublimation was assumed to be without effect on the measured pressures. The results shown in Table II were obtained by the decomposition of three samples of cupric oxysulfate, using increasing and decreasing temperatures.

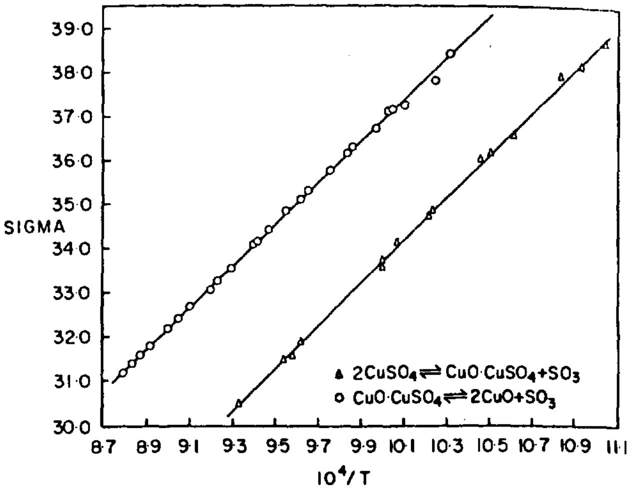

Fig. 1—Sigma vs reciprocal temperature relationship for decomposition of cupric sulfate and cupric oxysulfate.

Analysis of Results. When a metal sulfate is thermally decomposed in an evacuated space to produce a single metal oxide, and when that oxide is not oxidized or reduced by the SO_3, SO_2, or O_2, then three relationships apply to the gas phase. The total pressure is the sum of the partial pressures, the sulfur dioxide pressure is twice that of the oxygen, and the partial pressures of each gas must satisfy the equilibrium constant for the dissociation of sulfur trioxide. The foregoing argument is valid when there is no thermal segregation of the oxygen and sulfur oxides due to the temperature gradient in the apparatus.[4] From the observation[3] that there was no perceptible change in the position of the equilibrium when the gases were stagnant or in circulation, it has been concluded that any errors caused by thermal diffusion are within the normal errors of measurement in this apparatus.

The foregoing relationships lead to the following equation relating the total pressure, the equilibrium constant for sulfur trioxide dissociation, and the partial pressure of oxygen:

$$P = (2/K)p_{O_2}^{3/2} + 3\,p_{O_2} \qquad [4]$$

This equation was programmed for an IBM 1620 computer and solved using the following equation to represent the data of Evans and Wagman[5] for the dissociation of sulfur trioxide:

$$\log_{10} K = 8.8557 - 5465.5/T - 1.21572 \log_{10} T \qquad [5]$$

The values for the partial pressure of sulfur trioxide obtained from the calculation were combined with the specific-heat data of Kelley[6] for cupric sulfate, cupric oxide, and sulfur trioxide, to give the equation:

$$\Delta H_0/T + I = -4.5758 \log p_{SO_3} + 10.1314 \log T - 3.15\times 10^{-3}\,T - 1.61\times 10^{5}\,T^{-2} \qquad [6]$$

Since the heat capacity of cupric oxysulfate is not known, it was assumed to be equal to the sum of the specific heats of cupric oxide and cupric sulfate. Such an assumption is normally reliable within a few percent.[7] Because of this assumption, it was possible to apply the same specific-heat terms for both Eqs. [1] and [2].

Computer solution of Eq. [6] produced the values of sigma shown graphically in Fig. 1. Calculations of the slope and intercept include all of the results shown for cupric sulfate. However, the calculation for copper oxysulfate includes only those results obtained at temperatures below the transition temperature (1100°K). The apparently irreversible transition was detected by differential thermal analysis. From the ratio of the areas under the peaks, using the method described by Ingraham and Kellogg,[3] the following estimates were made of the heat of transition: by comparison with the K_2SO_4 transition, 3.10 kcal per mole; by comparison with $CuSO_4$ decomposition, 2.84 kcal per mole. These estimates are in agreement with 2.84 kcal per mole estimated from the change in slope of the $\log p_{SO_3}$ vs $10^4/T$ relationship at 1100°K. A value of 2.9 ± 0.3 kcal per mole has been selected as the most probable heat of transition.

The following slopes and intercepts were obtained from the computer results:

	ΔH_0	I
Cupric sulfate	47,817 cal per mole	−14.144
Cupric oxysulfate	46,859 cal per mole	−10.010

The corresponding free-energy equation and thermodynamic functions at 298.2°K are:

For cupric sulfate decomposition to cupric oxysulfate and sulfur trioxide,

$$\Delta F^\circ = 47{,}817 - 14.144\,T + 3.15\times 10^{-3}\,T^2 + 1.61\times 10^5/T - 10.1314\,T\log T$$

or

$$\Delta F^\circ = 50{,}941 + 3.516\,T\log T - 54.90\,T$$

$$\Delta F^\circ_{298} = 36{,}940 \text{ cal per mole,}$$

$$\Delta H^\circ_{298} = 49{,}920 \text{ cal per mole,}$$

$$\Delta S^\circ_{298} = 43.5 \text{ cal per mole-deg}$$

For cupric oxysulfate decomposition to cupric oxide and sulfur trioxide,

$$\Delta F^\circ = 46{,}859 - 10.010\,T + 3.15\times 10^{-3}\,T^2 + 1.61\times 10^5/T - 10.1314\,T\log T$$

or

$$\Delta F^\circ = 49{,}915 + 3.323\,T\log T - 50.12\,T$$

$$\Delta F^\circ_{298} = 35{,}985 \text{ cal per mole,}$$

$$\Delta H^\circ_{298} = 48{,}960 \text{ cal per mole,}$$

$$\Delta S^\circ_{298} = 43.5 \text{ cal per mole-deg}$$

The foregoing results were included by Kellogg[8] in his recent critical review of the work of Reinders and Goudriaan,[9] Blanks,[10] and Ahn[11] on the decomposition of cupric sulfate and cupric oxysulfate.

By combining the foregoing calculations with the heats of formation of cupric oxide and sulfur trioxide as given by Coughlin,[12] and the corresponding entropy data as given by Kelley,[13] the following estimates have been made for cupric oxysulfate:

$$\Delta H^\circ_{f(298)} = -218{,}630 \text{ cal per mole,}$$

$$\Delta S^\circ_{298} = 38.1 \text{ cal per mole-deg}$$

When these calculated results were combined with those for sulfur trioxide, the following estimates were obtained for cupric sulfate:

$$\Delta H^\circ_{f(298)} = -181{,}510 \text{ cal per mole,}$$

$$\Delta S^\circ_{298} = 27.89 \text{ cal per mole-deg}$$

The $\Delta H^\circ_{f(298)}$ value is in reasonable agreement with the −182,430 cal per mole obtained calorimetrically by Thomsen,[14] and the ΔS°_{298} value is in reasonable agreement with an estimate of 28.8 cal per mole-deg made by the Latimer method[15] using the above results for cupric oxysulfate.

The free-energy equations for Reactions [1] and [2] were used, with published free-energy data for other Cu-S, Cu-O, and S-O compounds, to calculate the equilibrium constants for the basic reactions in the Cu-S-O system between 750° and 950°K. The results of these calculations are shown in Table III. The values in Table III were used to calculate the equilibrium constants for the univariant equilibria in the Cu-S-O system between 750° and 950°K,

Table III. Basic Reactions in the Cu-S-O System between 750° and 950°K

Reaction	$\log_{10} K$				
	750°K	800°K	850°K	900°K	950°K
A) $\frac{1}{2}\,S_2 + O_2 \rightleftharpoons SO_2$[6]*	21.399	19.825	18.432	17.194	16.089
B) $SO_2 + \frac{1}{2}\,O_2 \rightleftharpoons SO_3$[6]	1.927	1.506	1.136	0.809	0.518
C) $2\,Cu + \frac{1}{2}\,O_2 \rightleftharpoons Cu_2O$[16]	8.086	7.362	6.723	6.156	5.648
D) $Cu + \frac{1}{2}\,O_2 \rightleftharpoons CuO$[16]	6.170	5.505	4.917	4.395	3.928
E) $2\,Cu + \frac{1}{2}\,S_2 \rightleftharpoons (Cu_2S)\gamma$[17]	7.578	6.994	6.482	6.027	5.623
F) $Cu + \frac{1}{2}\,S_2 \rightleftharpoons CuS$[18]	3.407	3.186	2.989	2.811	2.651
G) $2\,CuO + SO_3 \rightleftharpoons CuO{\cdot}CuSO_4$(author)	5.685	4.796	4.013	3.318	2.697
H) $CuO{\cdot}CuSO_4 + SO_3 \rightleftharpoons 2\,CuSO_4$(author)	5.055	4.149	3.350	2.642	2.009

*The sources of the data for the calculations are in the references cited.

Table IV. Equilibrium Constants for Univariant Equilibria in Cu-S-O System between 750° and 950°K

Reaction	log₁₀ K				
	750°K	800°K	850°K	900°K	950°K
1) $Cu_2S + 2\ Cu_2O \rightleftharpoons 6\ Cu + SO_2$	−2.351	−1.894	−1.496	−1.144	−0.829
2) $CuSO_4 + 3\ CuS \rightleftharpoons 2\ Cu_2S + 2\ SO_2$	+6.433	+6.387	+6.348	+6.316	+6.292
3) $2\ CuSO_4 + Cu_2S \rightleftharpoons 2\ Cu_2O + 3\ SO_2$	+1.020	+1.530	+1.976	+2.370	+2.722
4) $4\ CuSO_4 + Cu_2O \rightleftharpoons 3\ CuO \cdot CuSO_4 + SO_2$	−2.098	−1.361	−0.712	−0.140	+0.370
5) $CuO \cdot CuSO_4 + Cu_2O \rightleftharpoons 4\ CuO + SO_2$	−3.358	−2.654	−2.038	−1.492	−1.006

Table V. Equilibrium Constants for Bivariant Equilibria in the Cu-S-O System

Reaction	log₁₀ K	
	800°K	950°K
6) $4\ CuO \rightleftharpoons 2\ Cu_2O + O_2$	− 7.294	− 4.417
7) $2\ Cu_2O \rightleftharpoons 4\ Cu + O_2$	−14.724	−11.295
8) $Cu_2S + O_2 \rightleftharpoons 2\ Cu + SO_2$	+12.830	+ 9.095
9) $Cu_2S + \frac{3}{2}\ O_2 \rightleftharpoons Cu_2O + SO_2$	+20.192	+16.114
10) $Cu_2S + SO_2 + 3\ O_2 \rightleftharpoons 2\ CuSO_4$	+35.795	+24.064
11) $2\ CuS + O_2 \rightleftharpoons Cu_2S + SO_2$	+20.448	+16.410
12) $CuS + 2\ O_2 \rightleftharpoons CuSO_4$	+28.122	+20.237
13) $2\ CuSO_4 \rightleftharpoons Cu_2O + 2\ SO_2 + \frac{3}{2}\ O_2$	−15.603	− 7.949
14) $2\ CuSO_4 \rightleftharpoons CuO \cdot CuSO_4 + SO_2 + \frac{1}{2}\ O_2$	− 5.654	− 2.527
15) $CuO \cdot CuSO_4 \rightleftharpoons 2\ CuO + SO_2 + \frac{1}{2}\ O_2$	− 6.302	− 3.215
16) $CuO \cdot CuSO_4 \rightleftharpoons Cu_2O + SO_2 + O_2$	− 9.949	− 5.423

shown in Table IV, and the equilibrium constants for the bivariant equilibria at 800° and 950°K, shown in Table V. The temperature 800°K was chosen as being close to the optimum temperature for the production of cupric sulfate. At temperatures above 825°K there is a substantial possibility of forming copper ferrite in a commercial roasting operation, while at temperatures below 825°K the rate of roasting is unattractively slow. The temperature of 950°K was chosen on the basis of the roasting of ores containing copper and cobalt because commercial roasting has shown that at 950°K, in the presence of 1 pct each of sulfur dioxide and oxygen, cupric sulfate is unstable and reverts to the slightly soluble oxysulfate.

The thermodynamic relationships in Tables IV and V are illustrated in the predominance-volume graph constructed from $\log p_{SO_2}$, $\log p_{O_2}$, and $10^4/T$ data in Fig. 2. It will be noted that normal smelter gas compositions (1 to 10 pct SO_2 and O_2) lie well within the area of stability of cupric sulfate at 800°K, but 1 pct of each gas lies outside the volume of stability of cupric sulfate at 950°K but within the volume of stability of the water-insoluble cupric oxysulfate. It is of interest to observe that, when an imaginary line is drawn across Fig. 2 at $\log p_{O_2} = -2$ (*i.e.*, at 1 mole pct SO_2), it is obvious that cupric sulfide would be unstable and that during conversion of cuprous sulfide to cupric sulfate it would be reasonable to expect to detect the presence of cuprous oxide as an intermediate. If the sulfur dioxide pressure were maintained at a lower level, then there is a possibility that metallic copper and cupric oxysulfate might also be detected. It seems unlikely, however, that the roaster gas composition would fall to less than the 0.1 pct sulfur dioxide required to produce cupric oxide at this temperature. It is important to note that, notwithstanding the authoritative opinions expressed in some well-known texts on metallurgy, it is entirely unlikely that cuprous sulfide could be converted to cupric sulfate directly. Such a conversion would require sulfur dioxide pressures in excess of 30 atm.

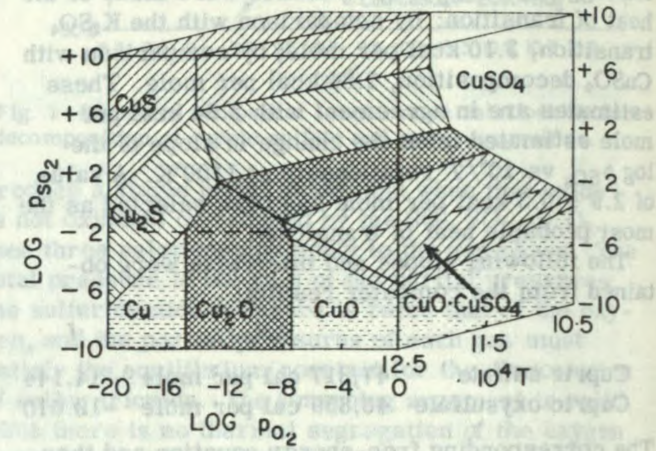

Fig. 2—Predominance-volume diagram showing volumes of stability occupied by various Cu-S-O compounds in the range of p_{SO_2} from 10^{-10} to 10^{+10} atm, p_{O_2} from 1 to 10^{-20} atm, and temperature from 750° to 950°K.

The foregoing observations are in agreement with the conclusions drawn from kinetic studies by Ong, Wadsworth, and Fassell[19] and by McCabe and Morgan.[20]

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REFERENCES

[1] N. A. Warner and T. R. Ingraham: *Can. J. Chem.*, 1960, vol. 38, pp. 196-202.

[2] S. N. Flengas and T. R. Ingraham: *Can. J. Chem.*, 1960, vol. 38, pp. 813-17.

[3] T. R. Ingraham and H. H. Kellogg: *Trans. Met. Soc. AIME*, 1963, vol. 227, pp. 1419-25.

[4] J. S. Wamer: *Trans. Met. Soc. AIME*, 1961, vol. 221, p. 591.

[5] W. H. Evans and D. D. Wagman: *J. Res.*, Nat. Bur. Std., 1952, vol. 49, p. 141.

[6] K. K. Kelly: *U.S. Bur. Mines, Bull. no. 584*, 1960.

[7] K. K. Kelley: private communication, 1963.

[8] H. H. Kellogg: *A Critical Review of Sulfation Equilibria*, Trans. Met. Soc. AIME, New York, 1964.

[9] W. Reinders and F. Goudriaan: *Verslag Amst.*, 1915-1916, vol. 24, p. 33.

[10] R. F. Blanks: PhD thesis, University of Melbourne, May, 1961.

[11] J. Ahn: unpublished senior thesis, Columbia University, May, 1960.

[12] J. P. Coughlin: *U.S. Bur. Mins, Bull. no. 542*, 1954.

[13] K. K. Kelley: *U.S. Bur. Mines, Bull. no. 592*, 1961.

[14] Thomsen: see Landolt Bomstein: *Physikalisch-chemische Tabellen*, vol. 2, pp. 1409 and 1494-1571, Julius Springer, Berlin, 1923.

[15] W. M. Latimer: *Oxidation Potentials*, Prentice Hall, Inc., New York, 1950.

[16] C. E. Wicks and F. E. Block: *U.S. Bur. Mines, Bull. no. 605*, 1961.

[17] O. Kubachewski and E. Evans: *Metallurgical Thermochemistry*, Pergamon Press, London, 1958.

[18] K. K. Kelley: *U.S. Bur. Mines, Bull. no. 406*, 1937.

[19] J. N. Ong, Jr., M. E. Wadsworth, and W. M. Fassell, Jr.: *AIME Trans.*, 1956, vol. 206, pp. 257-63.

[20] C. L. McCabe and J. A. Morgan: *AIME Trans.*, 1956, vol. 206, p. 800A.