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EXTRACTION METALLURGY DIVISION

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Kinetics of the Thermal Decomposition of Cupric Sulfate and Cupric Oxysulfate

T. R. Ingraham and P. Marier

When anhydrous cupric sulfate is heated in a stream of nonreactive gas, cupric oxysulfate is formed. When this reaction is complete, the cupric oxysulfate then decomposes to cupric oxide, which is the normal end product of reaction. The kinetics of each of these reactions has been studied using pellets prepared from finely divided cupric sulfate and from finely divided cupric oxysulfate. In each case, the reactant-product interface within the pellet is well-defined, and by normalizing the decrease in interfacial area with the weight fraction of the pellet decomposed it has been shown that the interface migrates into the pellet at a uniform rate at constant temperature. The activation energy estimated for the decomposition of cupric sulfate is 57 ± 7 kcal per mole and that for cupric oxysulfate is 67 ± 8 kcal per mole. The rate of interfacial reaction is flow-sensitive, increasing with increasing flow of a sweep gas in the range from 50 to 2000 cu cm per min. The rate of decomposition is retarded by sulfur trioxide in the sweep gas. The relationship between sulfur trioxide partial pressure and rate is consistent with the Langmuir Adsorption Isotherm governing the retention of sulfur trioxide in the interfacial layer.

MOST of the work reported on the thermal decomposition of cupric sulfate and of cupric oxysulfate is related to the thermodynamics of the individual decompositions.[1-4] No information is available on the rates of the individual reactions, on their activation energies, or on the effects of gas flow or of partial pressure of sulfur trioxide on the reaction rates.

Some dubious conclusions based on relative reaction rates have been drawn from studies on the oxidation of sulfides. For example, on the basis of the products observed in a quenched system, it has been suggested[5,6] that, when copper sulfide is roasted, the cupric oxide which is formed arises from the decomposition of either cupric sulfate or cupric oxysulfate. This is very difficult to reconcile with the thermodynamics of the C-S-O system,[3] which support the probability that both cuprous oxide and cupric oxide precede cupric oxysulfate and cupric sulfate in the sequence of products formed during the oxidation of cuprous sulfide.

In this paper the individual sulfate decomposition reactions will be examined and suggestions will be advanced for the mechanism of reaction. This will be based on the effects on reaction rate of changes in interfacial area, flow rate, and back-pressure of sulfur trioxide.

EXPERIMENTAL

Materials. 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 by roasting cupric sulfate for 48 hr, with frequent rabbling, in an open tray in a muffle furnace maintained at 725°C. At this temperature, cupric sulfate develops about 0.16 atm pressure of combined sulfur trioxide, sulfur dioxide, and oxygen. Cupric oxysulfate develops only about 0.05 atm pressure, and is stable until

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all of the cupric sulfate has been decomposed.[3]

Method. The technique used for making this kinetic study followed the method of using pelletized samples of powdered material which was developed earlier in these laboratories.[7,8] The technique is based on the observation that, when a mass of compacted material undergoes a decomposition reaction, that reaction occurs at a well-defined interface which migrates into the compact at a uniform rate at a constant temperature. The temperature coefficient of the rate of movement of the interface in the powder compact is identical with that in a polycrystalline solid.[8] The explanation for this behavior would seem to be related to the fact that each of the grains within the compact is surrounded by an atmosphere of the decomposition products. It is only on the surface of the pellet, where the decomposition products are free to escape, that the reaction can proceed. This argument is valid only for decomposition in a stagnant atmosphere or in a sweeping gas. The experiment is not valid under reduced pressure when each grain can react independently and the change in interfacial area cannot be conveniently correlated with the weight fraction of the material decomposed. In the type of decomposition reaction involving a solid reactant and one solid product, it is essential to relate the observed rate of reaction to the interfacial area between the reactant and product, because many of these reactions have linear kinetics and the observed reaction rate is a function of the interfacial area.

The method used in this paper for correlating the weight fraction of reaction with the continuously decreasing interfacial area was that described elsewhere by the authors[8] in a report on the decomposition of powder compacts of calcium carbonate. The reaction rate constant, k, was expressed as grams of sulfur trioxide evolved from 1 sq cm of nominal interfacial area in 1 min. A constant interfacial roughness factor was assumed but not included in the calculations.

Procedure. Cylindrical pellets of two sizes were used in the experiments. One pellet size was 0.25 in. in height and diameter and the other was 0.0234 in. in height and 0.50 in. in diameter. The pellets were prepared at a pressure of 100,000 psi, and during reaction were weighed automatically on an AMINCO Thermogravimetric Balance. To prevent decomposition of the sample before the required temperature of reaction had been attained, the samples were heated in a stream of gas in which the partial pressure of sulfur trioxide was continuously altered to maintain a sulfur trioxide pressure, slightly in excess of the decomposition pressure, at all temperatures during the preheating period. This was done by altering the percentage of nitrogen added to a 2-to-1 mixture of sulfur dioxide and oxygen. The mixed gases were preheated and passed over a platinum catalyst. Because the formation of sulfur trioxide from sulfur dioxide and oxygen is exothermic, there was no particular problem in preheating the gases, even at high flow rates.

Prevention of decomposition was relatively easy to achieve for cupric sulfate, but control of the reaction during the preheating of cupric oxysulfate was difficult. When the partial pressure of sulfur trioxide exceeded the decomposition pressure of the oxysulfate, the normal sulfate was formed. When the partial pressure did not exceed the decomposition pressure, decomposition was initiated. In most instances it was necessary to disregard the results obtained from cupric oxysulfate studies over the initial 10 pct of the decomposition, because they represented the decomposition of cupric sulfate formed during the preheating period.

When the temperature of the pellet was stable, the reaction was begun by changing the composition of the gas to a preselected partial pressure of sulfur trioxide.

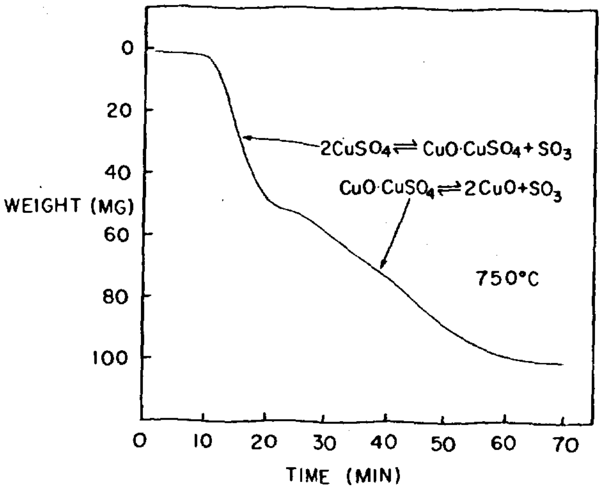

Fig. 1—Weight loss vs time relationship at 750°C showing both stages of the decomposition of anhydrous cupric sulfate in a stream of dry nitrogen flowing at 150 cu cm per min.

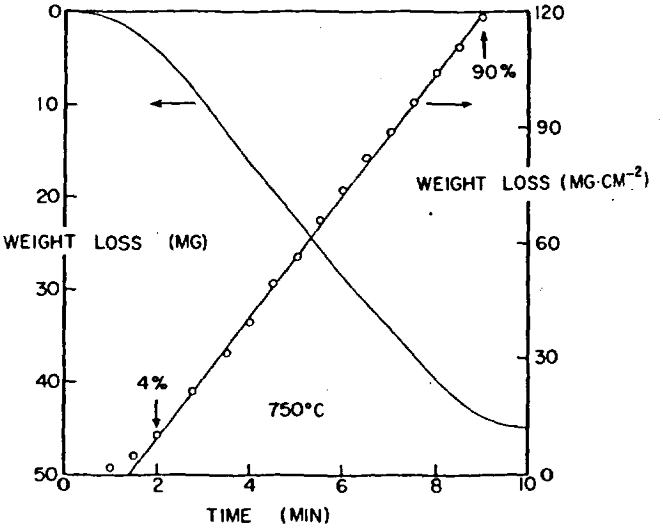

Fig. 2—Weight loss vs time relationship for first stage of cupric sulfate decomposition and weight loss of sulfur trioxide per unit of interfacial area at 750°C and a flow of 150 cu cm per min of nitrogen.

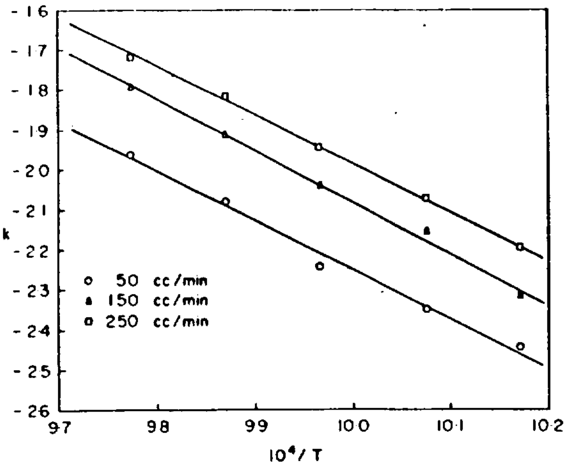

Fig. 3—Arrhenius relationship for $CuSO_4$ decomposition in nitrogen flowing at 50, 150, and 250 cu cm per min.

Table I. Equations For Rate of $CuSO_4$ Decomposition at Different Flow Rates at a Series of Temperatures

Gas Flow, cu cm per min	Equation	E, kcal per mole
50	$10.03 - 1.228 \times 10^4/T$	56 ± 11*
150	$10.82 - 1.290 \times 10^4/T$	59 ± 5*
250	$10.19 - 1.218 \times 10^4/T$	56 ± 4*

*The error was estimated on the basis of a 95 pct probability that the slope of the line would fall within ± 2 standard deviations at the top and bottom of the curve.

Table II. Initial Gas Composition, Reaction Rate, and Partial Pressure of SO_3 Used in Cupric Sulfate Decomposition Experiments at 770°C

Gas Flow, cu cm per min at 25°C				
N_2	O_2	SO_2	k	p_{SO_3}*
132	5.8	13.0	0.01042	0.0145
126	7.2	17.4	0.00518	0.0214
120	8.5	21.2	0.00350	0.0274
114	9.8	25.4	0.00136	0.0691
102	12.8	32.2	0.00037	0.0968

*Partial pressures of sulfur trioxide were calculated by successive approximation solutions of the cubic equation formed by expressing the dissociation of sulfur trioxide to sulfur dioxide and oxygen in terms of mole fractions.

Results and Discussion. In the first thermogravimetric experiment, a pellet of anhydrous cupric sulfate was preheated to a temperature of 750°C, and then its decomposition was initiated by altering the gas composition to nitrogen at 150 cu cm per min. The results of this experiment are shown in Fig. 1, from which it is evident that only one intermediate is involved in the decomposition reaction. The intermediate occurs at a composition corresponding to the loss of one half of the sulfur trioxide from cupric sulfate (*i.e.*, $CuO \cdot CuSO_4$). It is particularly important to note that the first stage of the decomposition reaction is complete before the second stage is begun.

The kinetics of decomposition of cupric oxysulfate were resolved using pellets of cupric oxysulfate prepared by the method mentioned earlier in the paper. It was not possible to make calculations directly from the second portion of the curve shown in Fig. 1 because of the high porosity of the sample, the unknown surface area, and the nonreproducible surface texture.

In a subsequent series of thermogravimetric experiments, the first stage of the decomposition was examined at various temperatures with a fixed flow rate of 150 cu cm of nitrogen. The sigmoid shape of a typical weight-loss curve is shown in Fig. 2. When the fraction of decomposition was normalized for the decrease in interfacial area accompanying reaction, and the normalized fraction of reaction converted to a weight loss of sulfur trioxide per unit area (see details of the method in Ref. 8), the linearity of the relationship between 4 and 90 pct confirmed that the reaction obeys linear kinetics. It is evident that the sigmoid shape of the weight-loss curve is due almost entirely to the geometric changes accompanying reaction. Failure of the linear relationship to pass through zero is attributed to difficulty in determining the exact time at which the dry nitrogen sweep gas reached the sample and decomposition was initiated.

The slope of the linear relationship is the reaction rate constant expressed in the units of milligrams of sulfur trioxide liberated per square centimeter of interfacial area per minute.

In the next group of experiments, the effect of gas flow rate on the rate of cupric sulfate decomposition was studied at a series of temperatures. The results of these experiments are shown in Fig. 3, from which it is evident that changes in gas flow rate have an effect on the rate of reaction. Additional flow rates selected over a wide range up to 2000 cu cm per min were used, but in no instance was it possible to observe that the reaction rate was independent of the gas flow rate.

It is evident from the almost parallel relationships shown in Fig. 3 that the effects of flow rate are probably limited to changes in the concentration coefficient factors of the decomposition. As expected, the exponential enthalpy is unaffected by flow-rate changes. The equations of each of the lines in Fig. 3 are shown in Table I. Based on a weighted average of the errors in each of the activation energies, the following equation is suggested for determining the rate of decomposition of cupric sulfate at a flow rate of 150 cu cm per min:

$$\log k_0 = 10.28 - 1.24 \times 10^4/T,$$
$$E = 57 \pm 7 \text{ kcal/mole}$$

The corresponding equation for the rate of decomposition of cupric oxysulfate as a function of temperature is:

$$\log k_0 = 11.74 - 1.45 \times 10^4/T,$$
$$E = 67 \pm 8 \text{ kcal/mole}$$

Table III. Initial Gas Composition, Reaction Rate, and Partial Pressure of SO_3 Used in Cupric Oxysulfate Decomposition Experiments at 825°C

Gas Flow cu cm per min at 25°C				
Ar	O_2	SO_2	k	P_{SO_3}*
90	9.8	25.2	0.01100	0.0302
85	11.1	29.0	0.00775	0.0367
80	12.5	32.2	0.00415	0.0430
75	13.8	35.6	0.00250	0.0498
70	15.0	38.4	0.00000	0.0561**

*See footnote in Table II.

**Sample did not gain or lose weight at this gas composition over a period of 30 min.

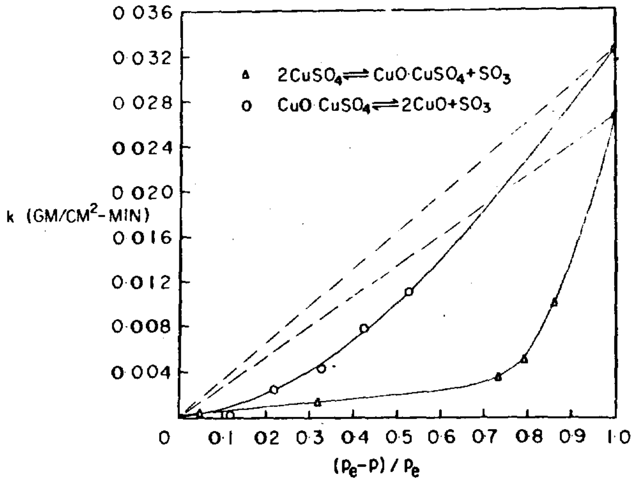

Fig. 4—Reaction rate vs partial equilibrium pressure for the decomposition of cupric sulfate and cupric oxysulfate in the presence of various partial pressures of SO_3, SO_2, O_2, and a diluent gas.

In the next group of experiments, the reaction rate was studied as a function of the partial pressure of sulfur trioxide in the sweeping gas at a fixed gas flow rate of approximately 150 cu cm per min for cupric sulfate and 125 cu cm per min for cupric oxysulfate. The gas flow rates and the calculated partial pressures of sulfur trioxide used are shown in Table II for the cupric sulfate experiments and in Table III for the cupric oxysulfate experiments.

For many heterogeneous decomposition reactions, the rate of reaction is inversely proportional to the driving force (*i.e.*, the fractional equilibrium pressure of the product gas). This has been illustrated—for ferric sulfate by Warner and Ingraham,[7] and for calcium carbonate by Ingraham and Marier[8]—by linearity of the relationship between *a*) the reaction rate and *b*) the fractional driving force that is represented by the ratio of the difference between the equilibrium and applied pressures to the equilibrium pressure. This relationship is shown in Fig. 4 for both the cupric sulfate and cupric oxysulfate systems. The substantial deviation from a linear relationship in each instance suggested that additional factors such as the presence of an intermediate, an undetected steady-state process, or adsorption might be involved. The observation that very small amounts of sulfur trioxide had a pronounced effect in decreasing the rate of the decomposition reaction favored an explanation based on adsorption. If it is assumed that θ represents the fraction of the interface covered by adsorbed sulfur trioxide, then according to the Langmuir Adsorption Isotherm,

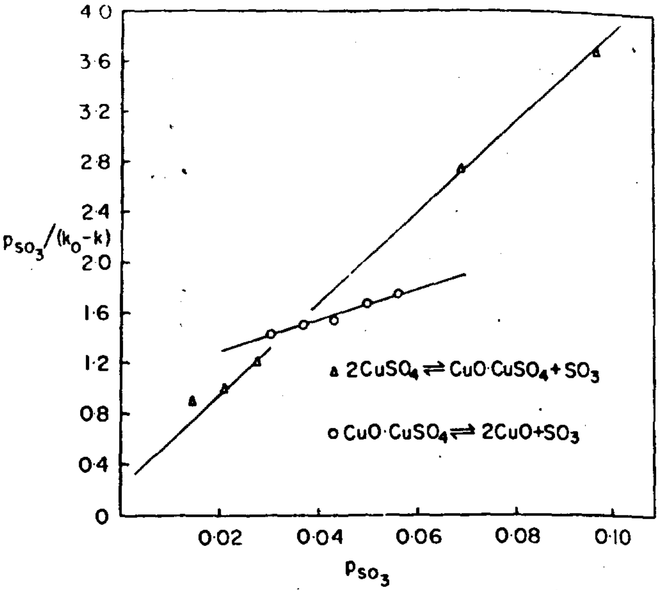

Fig. 5—Reaction rate vs partial pressure of SO_3 normalized by Langmuir Adsorption Isotherm. Cupric sulfate results obtained at 770°C, cupric oxysulfate at 825°C.

$$\theta = p/(p + c) \qquad [1]$$

where p is the partial pressure of sulfur trioxide and c is the reciprocal of the equilibrium constant for the adsorption of sulfur trioxide.

If it is also assumed that the reaction rate is proportional to the fraction of the interface not covered by sulfur trioxide, then, when $\theta = 1$, the reaction rate, $k = 0$, and when $\theta = 0$, $k = k_0$ where k_0, the reaction-rate constant, is the maximum observed reaction rate, which is presumed to represent zero retention of sulfur trioxide in the interface, it follows that

$$\theta = (k_0 - k)/k_0 \qquad [2]$$

When Eqs. [1] and [2] are equated and rearranged, it is evident that

$$p(k_0 - k) = p/k_0 + c/k_0 \qquad [3]$$

Eq. [3] represents a straight line when $p/(k_0 - k)$ is plotted against p. The slope of the line is $1/k_0$ and its intercept is c/k_0. Application of this relationship to the reaction rate and sulfur trioxide partial-pressure data for cupric sulfate and cupric oxysulfate is shown in Fig. 5. The good correlation of the data with straight lines supports the suggestion that the rate of reaction may be controlled by the concentration of sulfur trioxide adsorbed in the reaction interface.

In the accompanying study of the thermodynamics of the decomposition of cupric oxysulfate,[3] it is reported that, at 1100°K, cupric sulfate undergoes an apparently irreversible endothermic phase change involving 2.9 ± 0.3 kcal per mole. This phase change has been examined in detail by differential thermal analysis, and it has been observed that, depending on the rate of decomposition, the phase change can begin shortly before the last 30 pct of the cupric sulfate has been decomposed, or after it has all been decomposed, or shortly after the decomposition of the oxysulfate has begun. On this basis it has been presumed that the phase change does not influence the kinetics of either the decomposition of cupric sulfate or that of cupric oxysulfate.

CONCLUSIONS AND PROPOSED MECHANISM

When cupric sulfate is decomposed, two reactions are involved. In the first, cupric oxysulfate is formed and sulfur trioxide is liberated, and in the second, cupric oxide is formed and sulfur trioxide is liberated. In each reaction the loss of sulfur trioxide and the crystallization of the product leave an open and porous product layer that does not impede the liberation of sulfur trioxide from the interface. In each instance a clearly defined interface is developed between the solid reactant and the solid product. Reaction at this interface follows linear kinetics, the interface receding into the pellet at a uniform rate at constant temperature. Freshly formed cupric oxysulfate and cupric oxide are probably active adsorbents which retain a substantial quantity of adsorbed sulfur trioxide in the reaction interface. From calculations based on the Langmuir Adsorption Isotherm, the fraction of the cupric sulfate-cupric oxysulfate interface covered by adsorbed sulfur trioxide varies from about 65 pct to 100 pct, depending on the partial pressure of sulfur trioxide in the sweep gas and on the flow rate of the sweep gas.

It seems reasonable to believe that, when the flow of gas passing over the sample is increased, the equilibrium concentration of sulfur trioxide adsorbed on the interface is decreased. In effect, this increases the interfacial area by providing additional sites for the adsorption of sulfur trioxide as it is released by the decomposition reaction. Because of this effective increase in interfacial area, the rate of reaction is increased. A decrease in flow rate would be expected to have the reverse effect.

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REFERENCES

[1] W. Reinders and F. Goudriaan: *Verslag Amst.*, 1915-16, vol. 24, p. 33.

[2] R. F. Blanks: PhD Thesis, University of Melbourne, May, 1961.

[3] T. R. Ingraham: *Trans. Met. Soc. AIME*, 1965, vol. 233, pp. 359-63.

[4] H. H. Kellogg: *Trans. Met. Soc. AIME*, 1964, vol. 230, pp. 1622-34.

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

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

[7] N. A. Warner and T. R. Ingraham: *Can. J. Chem. Eng.*, 1962, vol. 40, pp. 263-67.

[8] T. R. Ingraham and P. Marier: *Can. J. Chem. Eng.*, 1963, vol. 41, pp. 170-73.