

## **THE REACTION OF COPPER(I) SULPHIDE WITH A PRODUCT OF ITS OXIDATION COPPER(II) SULPHATE**

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The course of the reaction between copper(I) sulphide and copper(II) sulphate in  $\text{SO}_2$  at 710–785 K was studied by the TG method under isothermal and non-isothermal conditions, as well as by the DTA method, X-ray analysis and scanning electron microscopy. It was established that the reaction is essentially dependent upon the initial composition of the substrate mixture,  $\text{Cu}_2\text{SO}_2$  and  $\text{Cu}_2\text{SO}_4$  being the chief intermediates in the reaction. Copper(I) oxide appears as the permanent final product of the reaction of interest. The reaction network, with the intermediate stages depending on the initial compositions in the temperature range studied, has been demonstrated.

It was shown earlier that copper(I) sulphide reacts with copper(II) sulphate at 101 kPa  $\text{SO}_2$  pressure, at a reaction rate not measurable below 730 K [1–3].  $\text{Cu}_2\text{SO}_2$  and  $\text{Cu}_2\text{SO}_4$  were found to be the main intermediates in the reaction. Significant, though quite small amounts of copper were also detected in the course of the process. Copper(I) oxide appeared as the final product of the reaction. The  $\text{Cu}_2\text{SO}_2$  phase had not been reported before. We recently published its X-ray diffraction pattern [3] and its thermal characteristics and reactivity towards some phases occurring in the Cu—S—O system [4].

$\text{Cu}_2\text{SO}_2$  exists as a liquid above 605–610 K, whereas  $\text{Cu}_2\text{SO}_4$  does not pass into the liquid state until 696 K [4, 5]. As the reaction between copper(I) sulphide and copper(II) sulphate proceeds to yield liquid above 700 K, there is reason to believe that  $\text{Cu}_2\text{SO}_2$  and  $\text{Cu}_2\text{SO}_4$  are the components of the liquid. The course of the reaction is strongly dependent upon the composition of the starting mixture [1, 2]. Accordingly, the quantitative composition of the liquid will be influenced by this parameter.

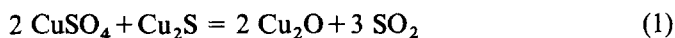
The purpose of this work is to elucidate the processes involved in the reaction, since it is of importance that the mechanism of  $\text{Cu}_2\text{S}$  oxidation below 850 K should

be fully understood. On the assumption that  $\text{CuSO}_4$  is the final product of  $\text{Cu}_2\text{S}$  oxidation in this temperature range, the pathway in this reaction will determine the further steps in the  $\text{Cu}_2\text{S}$  oxidation process.

## Experimental

A molten copper(I) sulphide with granulation below 60  $\mu\text{m}$ ,  $\text{Cu}_{1.96}\text{S}$ , and a pure grade anhydrous copper(II) sulphate with the same granulation, were used. From these reagents, mixtures were prepared with their initial compositions determined by the mole ratio of  $\text{CuSO}_4$  to  $\text{Cu}_2\text{S}$ , denoted as  $Z$ . Mixtures were investigated with  $Z = 10/1, 6/1, 4/1, 3/1, 2/1, 2/1.5, 2/2, 2/4$  and  $2/10$ .

The process under study always proceeded with mass loss,  $\text{Cu}_2\text{O}$  being the final product in each case. On this basis, we assumed the maximum mass loss to be that resulting from the following reaction:



The fractional conversion  $\alpha$  was taken to indicate the advance of the reaction, calculated as the ratio of the mass loss from an individual measurement to the total mass loss from Eq. (1). The differential of the fractional conversion  $\alpha$  with respect to time ( $d\alpha/d\tau$ ), graphically obtained from the mass loss vs. time records, was taken as a measure of the reaction rate.

The course of the reaction was judged by measuring isothermally, at 690–785 K, the mass losses of samples with initial compositions in the range  $2/10 \leq Z \leq 10/1$ . Additionally, for the same compositions, thermal (DTA) and thermogravimetric (TG) analyses were performed at 290–900 K, the temperature rising linearly at a rate of 2 deg/min. The apparatus for isothermal measurements was described in [6], and that for non-isothermal measurements in [7].

The phase composition modifications in the range of fractional conversion  $0.0 < \alpha < 1.0$  for the respective compositions were determined by phase X-ray analysis (DRON-3,  $\text{CuK}_\alpha$ ) and, in certain selected cases, by scanning electron microscopy coupled with X-ray microanalysis (Stereoscan, Cambridge).

## Results and discussion

The patterns of typical curves  $\text{DTA} = f(\alpha)$  and  $d\alpha/d\tau = f(\alpha)$  obtained from measurements under non-isothermal conditions are shown in Fig. 1; and those of curves  $d\alpha/d\tau = f(\alpha)$  resulting from measurements under isothermal conditions in Fig. 2. The curves exhibit numerous maxima and minima, and many sudden

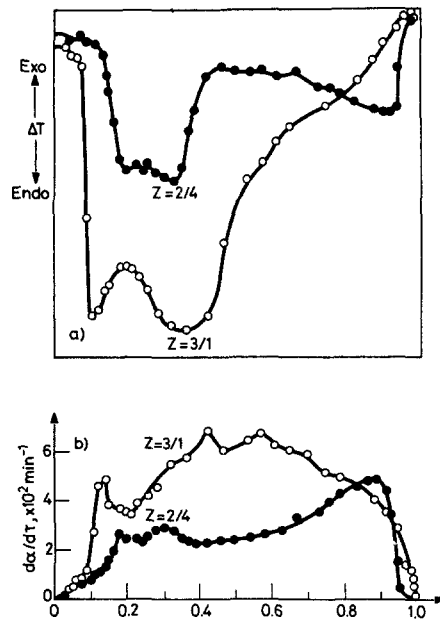


Fig. 1 The results of non-isothermal measurements at the heating rate 4 deg/min. (a) DTA vs.  $\alpha$ , (b)  $d\alpha/dt$  vs.  $\alpha$

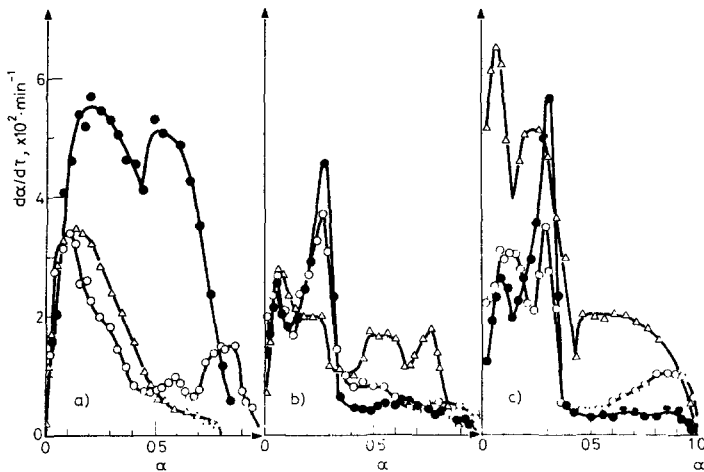


Fig. 2 The rate of reaction  $d\alpha/dt$ , as a function of the fractional conversion,  $\alpha$ , at 772 K.  
 (a) ● Z = 10/1, △ Z = 6/1, ○ Z = 4/1; (b) △ Z = 3/1, ○ Z = 2/1, ● Z = 2/1.5;  
 (c) ○ Z = 2/4, ● Z = 2/2, △ Z = 2/10

Table 1 Values  $\alpha_{min}$  determined from isothermal ( $\alpha_{min}^i$ ) and non-isothermal ( $\alpha_{min}^T$ ) measurements

	$Z$									
	10	6	4	3	2	2	2	2	2	2
$\alpha$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$	$\bar{1}$
$\alpha_{min}^i$	0.014	0.014	0.014	0.014	0.014	0.014	0.021	0.03	0.05	0.13-0.15
$\alpha_{min}^T$	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.02	0.02-0.04	0.03-0.06	0.10-0.12
$\alpha_{min}^i$	0.24-0.42	0.16-0.26	0.22-0.28	0.15-0.18	0.11	0.11	0.11-0.13	0.14	0.21	0.40-0.44
$\alpha_{min}^T$	0.25-0.31	0.18-0.22	0.27	0.18	0.16	0.16	0.18	0.17	0.23	0.38-0.40
$\alpha_{min}^i$	---	---	0.34-0.47	0.30-0.40	0.40-0.53	0.40-0.53	0.34-0.36	0.36	0.38	---
$\alpha_{min}^T$	0.59-0.70	0.50-0.63	0.49	0.47	0.48	0.48	0.34	0.38	0.39	---
$\alpha_{min}^i$	---	---	0.53-0.73	0.60-0.65	---	---	---	---	---	---
$\alpha_{min}^T$	---	---	---	0.70	0.68	0.64	---	---	---	---
$\alpha_{min}^i$	---	---	---	---	---	---	---	---	---	---

changes in  $d\alpha/d\tau$ . These facts argue that the reaction is a process involving several steps. The end of one stage in the reaction and the start of the following one should correspond to a minimum in  $d\alpha/d\tau$ , or to a sudden decrease in the rate of decrease of  $d\alpha/d\tau$ , these phenomena being related to a given value of  $\alpha$ , denoted  $\alpha_{min}$ . The isothermally and non-isothermally determined  $\alpha_{min}$  for particular initial compositions are tabulated in Table 1. It follows from the compilation that the process of interest is, in each instance, at the very least three-staged, its kinetics being strongly dependent upon the initial composition.

Phase X-ray analysis has indicated that for mixtures with different initial compositions, the contents of particular phases in the reactant mixture will show typical maxima and minima, occurring at the respective fractional conversions, designated  $\alpha_{max}^R$  and  $\alpha_{min}^R$ . The values of  $\alpha_{min}^R$  are also related with those values of  $\alpha$  at which the given phase undergoes reaction proceeding to completion, or at which the phase begins to occur in the reaction mixture. Values of  $\alpha_{min}^R$  and  $\alpha_{max}^R$  are given in Table 2. X-ray analysis permitted establishment of the quantitative contents of the

**Table 2** Values  $\alpha$  at which the content of the reacting substance in the products, determined by x-ray method, gains minimum ( $\alpha_{min}^R$ ) or maximum ( $\alpha_{max}^R$ )

$\alpha$	Reacting substance	Z						
		$\frac{4}{1}$	$\frac{3}{1}$	$\frac{2}{1}$	$\frac{2}{1.5}$	$\frac{2}{2}$	$\frac{2}{4}$	$\frac{2}{10}$
$\alpha_{min1}^R$	Cu <sub>1.96</sub> S	0.01*	0.03*	0.03*	0.05*	0.02*	0.05*	0.13*
	Cu <sub>2</sub> S	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	CuSO <sub>4</sub>	0.20-0.48	0.54	0.45	0.45*	0.38*	0.38*	0.45*
	Cu <sub>2</sub> SO <sub>2</sub>	0.01	0.03	0.03	0.05	0.02	0.05	0.13
	Cu <sub>2</sub> SO <sub>4</sub>	0.20	0.18	0.18	0.23	—	—	—
	Cu <sub>2</sub> O	0.20	0.33	0.21	0.33	a	a	a
	Cu	0.13	0.14	0.11	0.08	0.07	0.10	a
$\alpha_{max1}^R$	Cu <sub>1.96</sub> S	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Cu <sub>2</sub> S	0.01	0.03	0.03	0.05	0.02	0.05	0.13
	CuSO <sub>4</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Cu <sub>2</sub> SO <sub>2</sub>	0.20	0.22	0.20	0.27	0.37	0.37	a
	Cu <sub>2</sub> SO <sub>4</sub>	0.63	0.50	0.45	0.33	—	—	—
	Cu <sub>2</sub> O	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	Cu	0.35	0.30	0.30	0.33	0.37	0.37	a
$\alpha_{min2}^R$	Cu <sub>2</sub> S	0.20*	0.24*	0.18*	0.29*	0.37	0.33	0.45
$\alpha_{cat}$	—	0.18	0.18	0.18	0.27	0.36	0.38	0.41

At  $\alpha_{min2}^R = 1.00$  — Cu<sub>2</sub>SO<sub>2</sub>, Cu<sub>2</sub>SO<sub>4</sub> and Cu are liable to complete reaction irrespective of the initial composition, whereas CuSO<sub>4</sub> reacts to completion at  $Z = 2/1$

At  $\alpha_{max2}^R = 1.00$  — Cu<sub>2</sub>S gains maximum content at  $Z < 2/1$ , and CuSO<sub>4</sub> at  $Z > 2/1$

\* the reacting substance reacts to completion

a no X-ray patterns

phases in the reactant mixtures within the ranges  $4/1 \leq Z \leq 2/1$  and  $0 < \alpha < 1$ , and likewise within the ranges  $2/4 \leq Z \leq 1.5$  and  $0 < \alpha < \alpha_{max}^R$  ( $\text{Cu}_2\text{SO}_2$ ). With modifications in the compositions at  $2/4 \leq Z \leq 2/1.5$  and  $\alpha > \alpha_{max}$  ( $\text{Cu}_2\text{SO}_2$ ), it is possible to show them only in the form of relative changes in the intensity of the X-ray diffraction lines determining the given phase. The results from quantitative analyses of mixtures for which  $Z = 3/1$  or  $2/4$  are depicted in Figs 3 and 4.

X-ray analysis proved  $\text{Cu}_2\text{O}$  to be the sole final product from any reaction of copper(I) sulphide with copper(II) sulphate. However,  $\text{Cu}_2\text{O}$  with its X-ray

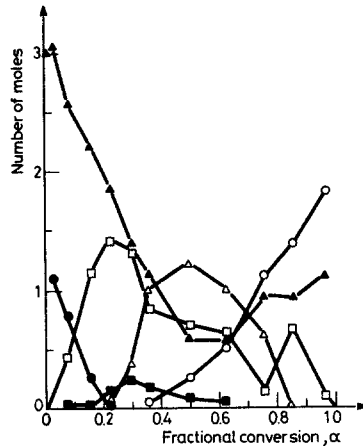


Fig. 3 The composition of reaction products as a function of the fractional conversion at  $Z = 3/1$   
 ▲  $\text{CuSO}_4$ , ●  $\text{Cu}_2\text{S}$ , □  $\text{Cu}_2\text{SO}_2$ , △  $\text{Cu}_2\text{SO}_4$ , ■  $\text{Cu}$ , ○  $\text{Cu}_2\text{O}$

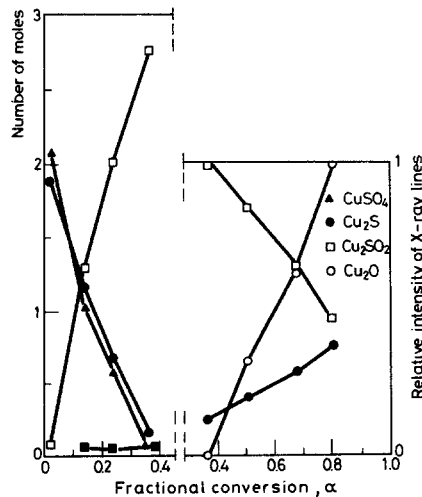


Fig. 4 The composition of reaction products as a function of the fractional conversion at  $Z = 2/4$

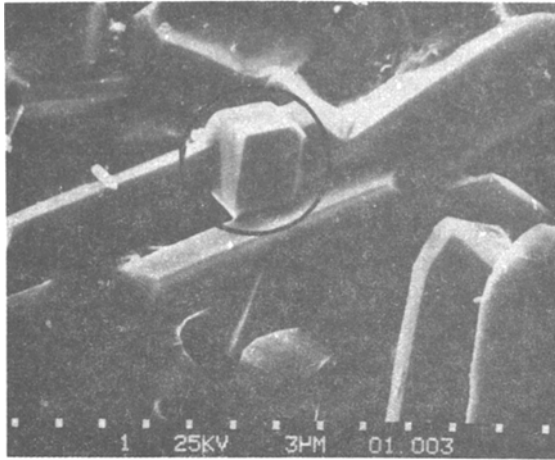
diffraction pattern true to the standard and with relatively large linear dimensions of its crystallites, i.e. with X-ray diffraction lines which do not show marked broadening, was obtained only from mixtures with initial compositions with  $Z \geq 2/1$ . By contrast, at  $Z < 2/1$ ,  $\text{Cu}_2\text{O}$  produces X-ray diffraction lines significant in their considerably lower intensity and appreciable broadening, as proof of the smaller linear dimensions of its crystallites. Moreover, the positions of the lines are evidently shifted towards lower diffraction angles as compared with the  $\text{Cu}_2\text{O}$  standard. The results from analysis of the profiles and positions of the X-ray diffraction lines of  $\text{Cu}_2\text{O}$  are given in Table 3, together with the positions of

**Table 3** Position of  $\text{Cu}_2\text{O}$  diffraction lines, their intensities referred to the pure component and the linear dimension of the  $\text{Cu}_2\text{O}$  crystallite

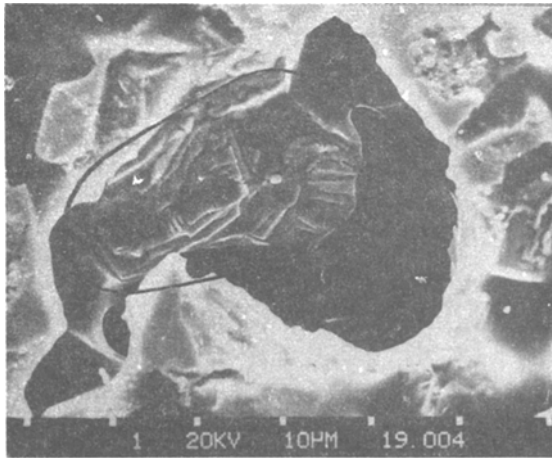
Z	Diffraction angle, °			Intensity, arbit. units	Linear dimension, nm $\times$ 0.1
	$2\theta_1$	$2\theta_2$	$2\theta_3$		
$\frac{10}{1}; \frac{6}{1}; \frac{4}{1}; \frac{3}{1}; \frac{2}{1}$	42.25	61.30	73.40	820–890	200–300
$\frac{2}{1.5}$	41.70–41.90	60.52–60.90	72.40–72.95	625	70–120
$\frac{2}{2}$	41.12–41.20	60.12–60.60	71.55–71.90	300	50–90
$\frac{2}{4}$	41.22–41.92	59.70–60.75	71.30–73.10	430	70–100
$\frac{2}{10}$	41.52	60.60	—	—	100–110

diffraction lines of intensities associated with the 100% content of  $\text{Cu}_2\text{O}$ ; the estimated linear dimensions of crystallites have also been included in this Table. The differences involved were supported by results from scanning electron microscopy, exemplified by a particle of  $\text{Cu}_2\text{O}$  with high regularity in its shape at  $Z = 4/1$  (Fig. 5), as opposed to a particle of  $\text{Cu}_2\text{O}$  remarkable for its considerably deformed shape at  $Z = 2/2$  (Fig. 6).

The results indicate that in the temperature range from 710 to 785 K,  $P_{\text{SO}_2} \cong 101$  kPa, the reaction between copper(I) sulphide and copper(II) sulphate proceeds with the participation of intermediates in accordance with the reaction network shown in Fig. 7. In the first stage in the reaction, the  $\text{Cu}_{1.96}\text{S}$  phase is converted into the  $\text{Cu}_2\text{S}$  phase. Since we found no other solid product ( $X$ ) from the reaction under discussion, Eq. 2 (Fig. 7) is an equation of stoichiometric coefficients evaluated from the mass balance of the first reaction stage. The experimental results proved that in the second stage (Eq. 3, Fig. 7) the reaction between  $\text{CuSO}_4$  and  $\text{Cu}_2\text{S}$  progresses completely to  $\text{Cu}_2\text{SO}_2$ . This implies that the reaction of  $\text{Cu}_2\text{S}$  at



**Fig. 5** The particle of  $\text{Cu}_2\text{O}$ , circled, at  $Z = 4/1$  and  $\alpha = 0.59$ ;  $\times 3200$



**Fig. 6** The particle of  $\text{Cu}_2\text{O}$ , circled, at  $Z = 2/2$  and  $\alpha = 0.99$ ;  $\times 1800$

$Z \geq 2/2$  and the reaction of  $\text{CuSO}_4$  at  $Z \leq 2/2$  proceed to completion at fractional conversion values  $\alpha_{max1}^R$  ( $\text{Cu}_2\text{SO}_2$ ), related to the maximum content of the  $\text{Cu}_2\text{SO}_2$  phase in the reactant mixture (Table 2, Fig. 4). These facts were supported by the results of calculation of  $\alpha$  values associated with the end of the second reaction stage on the assumption that reactions 2 and 3 proceed quantitatively. The calculated values ( $\alpha_{cal}$ ) differ imperceptibly from the corresponding  $\alpha_{max1}^R$  ( $\text{Cu}_2\text{SO}_2$ ) and  $\alpha_{min1}^R$  ( $\text{CuSO}_4$ ) at  $Z \leq 2/2$  and from  $\alpha_{min2}^R$  ( $\text{Cu}_2\text{S}$ ) at  $Z > 2/2$  (Table 2). As for Eq. 3,  $\text{Cu}_2\text{SO}_2$



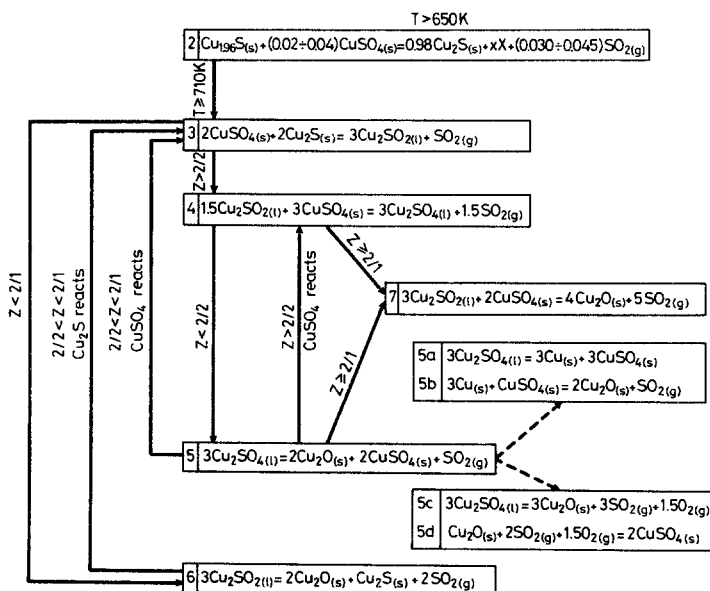


Fig. 7 The network of the reaction between copper(I) sulphide and copper(II) sulphate

was assumed to exist in the liquid state, since the melting temperature of the phase is 605 K [4, 7], far lower than the temperature at which the process was studied.

Accordingly, reaction [4] takes place to produce  $\text{Cu}_2\text{SO}_4$ , which must also be a liquid as its melting point is 696 K [5]. Further, copper(I) sulphate undergoes decomposition to  $\text{Cu}_2\text{O}$  and  $\text{CuSO}_4$  by virtue of reaction 5. The mechanism of this reaction is not clear. The presence of metallic copper detected in the course of the reaction suggests that the composition follows Eqs 5a and 5b. However, as ascertained in another experiment [8], relating to the thermal decomposition of  $\text{Cu}_2\text{SO}_4$  in a  $\text{SO}_2$  atmosphere, it is not unlikely that the decomposition of  $\text{Cu}_2\text{SO}_4$  proceeds as in Eqs 5c and 5d.

It follows from Eqs 3 and 4 that the initial composition,  $Z = 4/1$  permits complete reaction of the substrates to  $\text{Cu}_2\text{SO}_4$ . Nonetheless, all our attempts to attain a chemically pure  $\text{Cu}_2\text{SO}_4$  ended in failure, though the preparation of such an entity has been reported [5]. The different conditions under which we obtained the  $\text{Cu}_2\text{SO}_4$  were presumably responsible for this result: our experiments were carried out at lower temperatures and considerably lower  $\text{SO}_2$  pressure. X-ray analysis has revealed that for initial compositions with  $Z \leq 2/2$  no  $\text{Cu}_2\text{SO}_4$  (Table 2) is to be found in the reaction products. Nevertheless, at such  $Z$  values  $\text{Cu}_2\text{O}$  appears as the other final product of the reaction (Table 2).

Analysis of X-ray diffraction patterns (Table 3) and of the results of scanning

electron microscopy has proved that a  $\text{Cu}_2\text{O}$  with performed structure is involved in the reaction at  $Z \leq 2/2$ , distinguishable from the  $\text{Cu}_2\text{O}$  produced in the reaction under discussion when  $Z \geq 2/1$ , the latter  $\text{Cu}_2\text{O}$  variety preserving its crystalline structure non-deformed. The experiments permit the assumption that the essential difference lies primarily in the nature of the intermediate from which the product of interest is produced. It seems plausible that, at  $Z \geq 2/1$ ,  $\text{Cu}_2\text{O}$  should be the exclusive product of  $\text{Cu}_2\text{SO}_4$  decomposition. However, in the range  $2/1 \leq Z < 4/1$  this would be admissible only if  $\text{CuSO}_4$  (the product of  $\text{Cu}_2\text{SO}_4$  decomposition (Eq. 5)) reacted with  $\text{Cu}_2\text{SO}_2$  until  $\text{Cu}_2\text{SO}_2$  was depleted. Through such a process of  $\text{Cu}_2\text{O}$  formation, the balance of Eq. 5 would be satisfied.

It results from the stoichiometry of Eqs 3, 4, 5 and 7 that at  $2/2 < Z < 2/1$  it is impossible for  $\text{Cu}_2\text{SO}_2$  to be converted completely into  $\text{Cu}_2\text{SO}_4$ . For these initial compositions,  $\text{Cu}_2\text{O}$  should be the product of decomposition of both  $\text{Cu}_2\text{SO}_2$  and  $\text{CuSO}_4$ . Analysis of profiles and the positions of the diffraction lines of  $\text{Cu}_2\text{O}$  at  $Z = 2/1.5$  reveals that the average shift in their positions is much lower, while the intensities of these lines are marked higher, compared with those of the lines of the  $\text{Cu}_2\text{O}$  arising in  $\text{Cu}_2\text{SO}_2$  decomposition. At the same time, the X-ray diffraction lines of the  $\text{Cu}_2\text{O}$  from  $\text{Cu}_2\text{SO}_2$  decomposition and those of the  $\text{Cu}_2\text{O}$  from  $\text{Cu}_2\text{SO}_4$  decomposition are quite distinct from each other in their positions and profiles. The above facts provide unequivocal evidence that  $\text{Cu}_2\text{O}$  is actually a product of decomposition of both  $\text{Cu}_2\text{SO}_2$  and  $\text{Cu}_2\text{SO}_4$  at  $Z = 2/1.5$ . Accordingly, a reaction might well be postulated in which  $\text{CuSO}_4$  (the product of  $\text{Cu}_2\text{SO}_4$  decomposition) reacts at  $2/1 > Z > 2/2$  with  $\text{Cu}_2\text{S}$  produced in the  $\text{Cu}_2\text{SO}_2$  decomposition. On this assumption, the sharing of particular  $\text{Cu}_2\text{O}$  forms produced from reactions 5 and 6 would depend on the ratio of the reaction rates.

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**Zusammenfassung** — Der Verlauf der Reaktion von Kupfer(I)-sulfid mit Kupfer(II)-sulfat wurde in  $\text{SO}_2$  bei 710–785 K durch isotherme und nichtisotherme Thermogravimetrie sowie DTA, Röntgenanalyse und Scanning-Elektronenmikroskopie untersucht. Es wurde festgestellt, daß die Reaktion wesentlich von der Ausgangszusammensetzung des Substratgemisches abhängt, wobei  $\text{Cu}_2\text{SO}_2$  und  $\text{Cu}_2\text{SO}_4$  die vorherrschenden intermediären Produkte der Reaktion sind. Kupfer(I)-oxid tritt als Endprodukt auf. Der die intermediären, im untersuchten Temperaturbereich von der Ausgangszusammensetzung abhängigen Reaktionsschritte in sich einschließende Reaktionsverlauf wird dargelegt.

**Резюме** — При температуре 710–785 K в атмосфере двуокиси серы изучена реакция между сульфидом одновалентной меди и сульфатом двухвалентной меди с помощью изотермического и неизотермического ТГ метода, ДТА, рентгеноструктурного анализа и сканирующей электронной микроскопии. Установлено, что реакция существенно зависит от состава исходной смеси. Главными промежуточными продуктами реакции являются  $\text{Cu}_2\text{SO}_2$  и  $\text{Cu}_2\text{SO}_4$ , тогда как конечным продуктом реакции является закись меди. Показано, что в изученной области температур реакция является цепной по отношению к промежуточным стадиям.