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Some aspects of reactivity of copper(I) sulphide with copper(II) sulphate

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The reaction of Cu_2S with $CuSO_4$ in SO_2 at $T > 710$ K proceeds forming liquid intermediates, Cu_2SO_2 and Cu_2SO_4, which decompose to solid products. Only SO_2 is a gaseous product out of all the intermediate reactions. The rate of each step is dependent, in a complex way, upon the liquid content of the reacting mixture. The relations of major importance between the rates of individual intermediate reactions, the liquid content of the reacting mixture, the composition of the liquid and the initial composition of the substrates mixtures have been discussed.

1. Introduction

The reaction of copper(I) sulphide with copper(II) sulphate – one of the products of its maximum oxidation process – is of importance for the oxidation of copper(I) sulphide, an essential process in pyrometallurgical production of copper. Although the oxidation of copper(I) sulphide at higher temperatures is well known, work dealing with this subject below 900 K is scarce and the results give only fragmentary information. It is obvious that reactions taking place at lower temperatures influence the process of copper(I) sulphide oxidation at temperatures higher than 900 K.

Besides the utilitarian aspect, the reaction of copper(I) sulphide with copper(II) sulphate exemplifies a little known type of chemical reaction in which two solid reactants form liquid intermediates being then decomposed to solid final products. Each of the reaction stages is accompanied by a gaseous product.

We have found in our earlier works [1–3] that reaction of copper(I) sulphide with copper(II) sulphate in SO_2 at 710 to 785 K runs through the following steps

$$Cu_{1.96}S_{(s)} + x\,CuSO_{4(s)} = 0.98\,Cu_2S + m\,X + y\,SO_2 \qquad (1)$$

where $x = 0.02$ to 0.04; $m = 0.01$ to 0.04; X is an unidentified reaction product; $y = 0.030$ to 0.045. Next

$$Cu_2S_{(s)} + CuSO_{4(s)} = 1.5\,Cu_2SO_{2(l)} + 0.5\,SO_{2(g)} \qquad (2)$$

$$Cu_2SO_{2(l)} + 2\,CuSO_{4(s)} = 2\,Cu_2SO_{4(l)} + SO_{2(g)} \qquad (3)$$

$$3\,Cu_2SO_{2(l)} = 2\,Cu_2O_{(s)} + Cu_2S_{(s)} + 2\,SO_{2(g)} \qquad (4)$$

$$3\,Cu_2SO_{4(l)} = 2\,Cu_2O_{(s)} + 2\,CuSO_{4(s)} + SO_{2(g)} \qquad (5)$$

Ignoring Reaction 1, which runs rapidly and to completion below 710 K, it is $CuSO_4$ and Cu_2SO_4 that are the main intermediates of the reaction considered at 710 to 785 K. A metallic copper was also found in the intermediates but its content was, each time, lower by several times than those of other components of the reaction mixture [4].

In the light of previous investigations [4], it seems that copper is a product of the total Reaction 5 which in the solid state runs via two steps

$$3\,Cu_2SO_{4(s)} = 3\,Cu_{(s)} + 3\,CuSO_{4(s)} \qquad (6)$$

$$3\,Cu_{(s)} + CuSO_{4(s)} = 2\,Cu_2O_{(s)} + SO_{2(g)} \qquad (7)$$

Under the experimental conditions, the final product of the reaction between copper(I) sulphide and copper(II) sulphate is Cu_2O, which is described by the balance reaction

$$2\,CuSO_{4(s)} + Cu_2S_{(s)} = 2\,Cu_2O_{(s)} + 3\,SO_{2(g)} \qquad (8)$$

Depending on the initial composition of the reaction mixture, each of the Reactions 1 to 5 runs at definite fractional conversion, α. The fractional conversion, α, has been calculated as a ratio of mass loss at a given instant to the maximum mass loss derived from Equation 8, whereas the initial composition denoted by Z has been defined as a number of copper(II) sulphate moles to the number of copper(I) sulphide moles present in the substrate mixture. On the basis of experimental results published earlier [3] the ranges of α were estimated for a particular composition of initial mixtures at which Reactions 1 to 5 take place. For the requirements of this work, the ranges are shown graphically in Figure 1. Individual areas α–Z have been labelled with the numbers of the reactions dominating at a given variation range. The graphic illustration of experimental results of the chemistry of the process taking place between copper(I) sulphide and copper(II) sulphate, despite its qualitative character, implies that after conversion of $Cu_{1.96}S$ into nearly stoichiometric copper(I) sulphide [3], always the first to arise, almost quantitatively, is a liquid Cu_2SO_2 (area 2). For $Z \leqslant 1$ it undergoes decomposition, in agreement with Reaction 4 (area 4). Liquid Cu_2SO_4 is formed in accordance with Reaction 3 only at the composition of initial mixtures for which $Z > 1$, but in a quantitative manner, $CuSO_4$ reacts exclusively at $Z \leqslant 2$. On the other hand, for $Z > 2$, Reaction 5 starts before Reaction 3 has been completed. For $Z = 4$ and $T < 770$ K, Reactions 3 and 5

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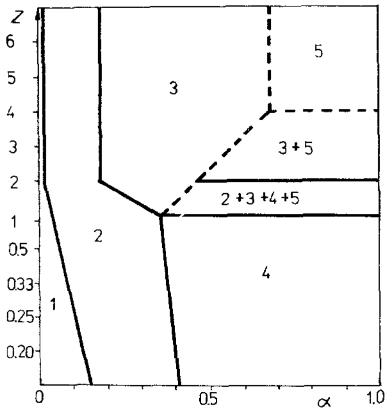

Figure 1 The participation of intermediate Reactions 1 to 5 in $Cu_{1.96}S$–$CuSO_4$ reaction as a function of the fractional conversion (α) and the initial composition. $Z = n_{CuSO_4}/n_{Cu_{1.96}S}$.

run in fact simultaneously, although it is possible to obtain an almost pure Cu_2SO_4 under precisely established conditions [5]. Therefore, the right-hand boundary of area 3 has been marked with a dotted line. For $2 \leqslant Z < 4$, the $CuSO_4$ content in the initial mixture is too small for $Cu_2SO_{2(l)}$ to react completely according to Reaction 3. However, $CuSO_4$ appears in the reaction mixture as one of the products of Reaction 5 and reacts with $Cu_2SO_{2(l)}$. As a result, Reactions 3 and 5 take place at the same time (areas 3 and 5). A similar but much more complicated process is under consideration for $1 < Z < 2$ (areas 2 + 3 + 4 + 5). A discussion with full particulars of the process chemistry was presented previously [3], whereas detailed information of intermediates, i.e. Cu_2SO_2 and Cu_2SO_4 was given previously [6]. The aim of this work was to elucidate some problems connected with the kinetics of the reaction of copper(I) sulphide with copper(II) sulphate. This has become possible because we now know the way in which this reaction takes place and we know the fundamental properties of the hitherto unknown Cu_2SO_2 and the insufficiently known Cu_2SO_4. We analysed in our previous works the chemistry of the process base on the experimental results of X-ray powder diffraction and on the investigations carried out under non-isothermal conditions. In this work we present the results of experiments carried out predominantly under isothermal conditions.

2. Experimental details

A molten copper(I) sulphide of a composition corresponding to $Cu_{1.96}S$ and anhydrous copper(II) sulphate were used for the experiments. The diameter of their particles was below 60 μm. Detailed characteristics of the substrates were given previously [7]. The substrates were mixed before preparation of the mixtures whose initial compositions corresponded to $Z = 10$, 6, 4, 3, 2, 1.33, 1 and 0.20, where $Z = n_{CuSO_4}/n_{Cu_{1.96}S}$. The relationship between time and mass changes in the mixtures was measured isothermally in SO_2 at ~ 101 kPa and from 690 to 785 K using the equipment described earlier [8, 9]. The behaviour of the samples during the process was observed visually, and selected samples were examined by means of electron scanning microscopy (ESM, Stereoscan, Cambridge). The samples were prepared by placing a silica glass plate in a powdered reaction mixture which was then heated under isothermal conditions. As soon as the desired stage of reaction was reached the specimen was quenched. The surface of the reaction mixture resulting from the sticking of the liquid to the plate was examined in the Regional Laboratory of Electron Microscopy, Technical University in Wrocław.

Measurements of mass changes (mass loss) under isothermal conditions were presented as a relationship between the process rate $d\alpha/d\tau$ and fractional conversion, α. The rate $d\alpha/d\tau$ was assigned graphically from the records of mass loss against time. Typical curves of $d\alpha/d\tau$ against α are shown in Fig. 2. The results from visual observations are given in Table I and the results from examinations by scanning electron microscopy are shown later in Figs 4 to 8 and Table II.

3. Discussion

The shape of all the curves (the rate–α shown in Fig. 2) permits one to distinguish from the curves of the investigated process two periods independent of the initial composition. In the first period, the process rate on achieving a maximum decreases rapidly, whereas in the second period, the rate is much more slower, and depending in the initial composition it remains constant or also achieves a maximum, but with a value lower than that in the first period.

A knowledge of the process chemistry (Fig. 1) permits us to state that that: (i) liquid intermediates are formed in the first period, (ii) the liquid is decomposed to final solid products in the second period.

Equations 1 to 5 suggest that the rate of all the intermediate reactions, and thus of the whole process, depends on the rate of the gaseous product transport from the inside of the reaction mixture to its surroundings. As the SO_2 transport conditions are dependent on the liquid contents of the reaction mixture, the rate of the process under study should also depend on this parameter. Moreover, the rates of Reactions 3 to 5 undoubtedly depend on composition of the liquid.

3.1. The process rate during formation of liquid

On the grounds of experimental results presented in this work and from the previous publications [1–3] one can specify at least three stages of liquid formation: (i) an initial stage at low liquid contents, (ii) a quasi-boiling stage at high liquid contents, (iii) a stage of Cu_2SO_4 formation. They do not take place within strictly established ranges but differ essentially, so they can be discussed separately.

3.1.1. The process at low liquid contents

Neglecting Reaction 1, it is Reaction 2 which results exclusively in the formation of the liquid in its initial stage. Taking the fraction of the liquid in the reaction mixture as a ratio of volume of the liquid (v_l) to volume of the solid (v_s), a relation can be written

$$\frac{v_l}{v_s} = \left[n_{Cu_2SO_2}\frac{M_{Cu_2SO_2}}{d_{Cu_2SO_2(l)}}\right] \bigg/ \left[n_{CuSO_4}\frac{M_{CuSO_4}}{d_{CuSO_{4(s)}}} + n_{Cu_2S}\frac{M_{Cu_2S}}{d_{Cu_2S_{(s)}}}\right] \qquad (9)$$

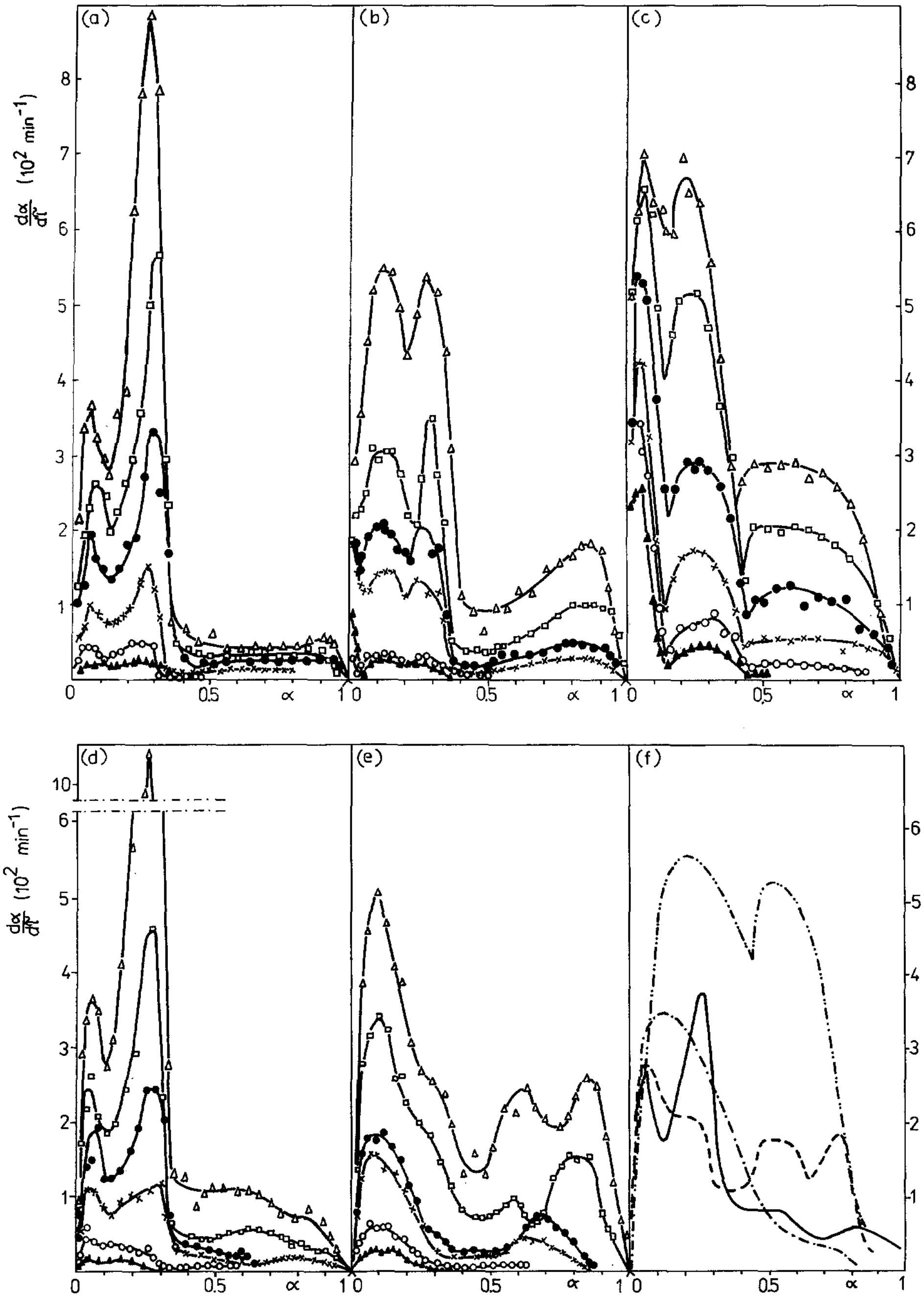

Figure 2 The affect of temperature (T) and the initial composition (Z) on the overall rate of the $Cu_{1.96}S$–$CuSO_4$ reaction ($d\alpha/d\tau$) as a function of the fractional conversion (α). (a) $Z = 1$; $-T$ (K) = (△) 782, (□) 772, (●) 763, (x) 752, (○) 738, (▲) 729. (b) $Z = 0.5$; $-T$ (K) = (△) 783, (□) 772, (●) 761, (x) 758, (○) 738, (▲) 729. (c) $Z = 0.2$; $-T$ (K) = (△) 781, (□) 771, (●) 763, (x) 753, (○) 738, (▲) 730. (d) $Z = 1.33$; for $-T$ values, see (a). (e) $Z = 4$; for $-T$ values, see (a). (f) $T = 772$ K; Z = (—··—) 10, (—·—) 6, (– – –) 3, (——) 2.

where $d_{CuSO_4} = 3.6\,g\,cm^{-3}$, $d_{Cu_2S} = 5.8\,g\,cm^{-3}$, $d_{Cu_2SO_2}$ unknown, are the density of reactants, n is the number of moles; M the molecular weight.

As $M_{Cu_2S} \cong M_{CuSO_4} = M$ and $d_{Cu_2SO_{2(l)}} = \text{constant}$ then

$$\frac{M_{Cu_2SO_2}}{d_{Cu_2SO_{2(l)}}}\frac{1}{M} = \text{constant} \qquad (10)$$

and

$$l = \frac{v_l}{v_s}\left(\frac{M_{Cu_2SO_2}}{d_{Cu_2SO_{2(l)}}M}\right)^{-1} \qquad (11)$$

or

$$l = n_{Cu_2SO_2}\Bigg/\left(\frac{n_{CuSO_4}}{d_{CuSO_4}} + \frac{n_{Cu_2S}}{d_{Cu_2S}}\right) \qquad (12)$$

Equation 12 permits the calculation of the value of l, which is a measure of the liquid content in the reaction mixture.

By definition of fractional conversion α, and from Equation 8, there results a relationship between the total number of the SO_2 moles arising from the reaction (n_{SO_2}) and the conversion

$$n_{SO_2} = 3\alpha \qquad (13)$$

As the number of SO_2 moles resulting from Reaction $2(n_{(2)SO_2})$ is lower than n_{SO_2} by the number of SO_2 moles arising by virtue of Reaction 1 ($n_{(1)SO_2}$), then

$$n_{(2)SO_2} = 3(\alpha - \alpha_1) \qquad (14)$$

where α_1 corresponds to completion of Reaction 1.

It follows from Reaction 2 that for a definite α the number of moles of particular components (n) of the

TABLE I Results of visual observations

Z	α	Description
10–0.5	0.05	The colour of the sample changed from grey to green yellow.
0.2	0.13	No changes were observed.
10, 4	0.05	A sinter of brown-red colour was formed. Volume of the sample changed considerably to achieve minimum at $\alpha = 0.4$.
3–0.50	> 0.05 < 0.2	A sinter was formed. Its volume decreased rapidly. The plastic deformation of the shape of samples was observed at $\alpha \sim 0.2$.
3–0.50	> 0.2 < 0.35	The sinter changed into dark brown liquid, foaming vigorously, with a volume several times larger than the initial sample.
3–0.50	$\geqslant 0.35$	The liquid stopped foaming.
10–0.20	1	The reaction products were solid.

reaction mixture is

$$n_{Cu_2SO_2} = 9(\alpha - \alpha_l) \quad (15)$$

$$n_{CuSO_4} = n^0_{CuSO_4} - 6(\alpha - \alpha_l) \quad (16)$$

$$n_{Cu_2S} = n^0_{Cu_2S} - 6(\alpha - \alpha_l) \quad (17)$$

where $n^0_{CuSO_4}$, $n^0_{Cu_2S}$ are the numbers of the substrate moles in the initial mixture defined by a parameter Z.

In order to simplify calculation, it was taken that in Equation 1, $X \equiv Cu_2SO_2$; $x = 0.02$; $m = 0.01$ and $y = 0.03$. By such assumption

$$\alpha_l = 0.01 \text{ at } Z \geqslant 2$$

or

$$\alpha_l = 0.02Z^{-1} \text{ at } Z \leqslant 2 \quad (18)$$

From Equations 12 to 18 it is possible to calculate l as a function of α and Z. The results from calculations are shown graphically (Fig. 3).

In order to show that in the stage under consideration, the rate of Reaction 2, determining the rate of whole process, strongly depends on the liquid content of the reacting mixture, the following procedure was followed. On the grounds of the experimental results values of α have been assigned which correspond on the curves of α–rate to the first maximum ($\alpha_{max\,l}$) and to the first minimum ($\alpha_{min\,l}$) for $\alpha > \alpha_{max\,l}$ which are cited in the α range corresponding to Reaction 2 (Figs 1 and 2).

TABLE II Results of SEM examinations

Z	
0.20	The sample possess large pores in the range $0 < \alpha < 1$.
4	Porosity of the sample decreases with the reaction progress, in order to increase above $\alpha = 0.30$–0.50.
1	Porosity of the sample decreases with increase in α to decay entirely at $\alpha \approx 0.35$; after new pores formed the sample became very porous above $\alpha \approx 0.9$.
0.20, 1, 4, 10	Cu_2O particles were observed for $\alpha \geqslant 0.5$; they were placed on the walls of pores, in each case.
2	Porosity of the sample decreases with the progress of the reaction to vanish entirely at $\alpha \approx 0.45$.

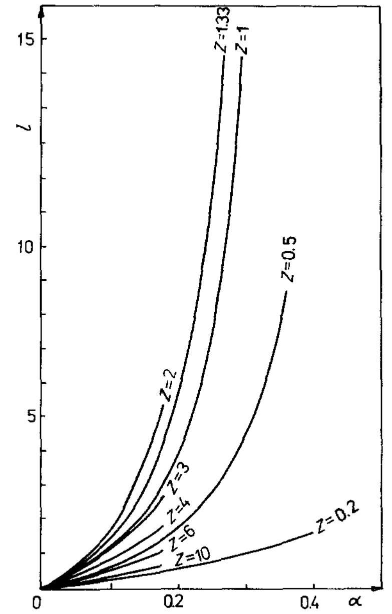

Figure 3 The calculated effect of the initial composition (Z) and the fractional conversion (α) on the liquid content of the reacting mixture within the α range corresponding to Reaction 2.

Next, from the curves shown in Fig. 3, values of l corresponding to values of $\alpha_{max\,l}$ and $\alpha_{min\,l}$ for the given Z were assigned. It has appeared that for all the $\alpha_{max\,l}$ values the values of l are equal or close to 0.6, whereas for $\alpha_{min\,l}$, $l = 1.9$. For these two values of l, the corresponding α values, ($\alpha_{0.6}$ and $\alpha_{1.9}$) were calculated from Equations 12 to 18. Results of those calculations for the given values of Z and the experimentally determined values of $\alpha_{max\,l}$ and $\alpha_{min\,l}$ are given in Table III. The data in the table are in good agreement, which confirms the correctness of interpretation of the experimental results. One can state on this basis that $\alpha_{max\,l} = \alpha_{0.6}$ and $\alpha_{min\,l} = \alpha_{1.9}$; then

$$d\alpha/d\tau < (d\alpha/d\tau)_{max\,l} \quad (19)$$

at $\alpha \leqslant \alpha_{max\,l} = \alpha_{0.6}$

$$(d\alpha/d\tau)_{max\,l} \geqslant d\alpha/d\tau \geqslant (d\alpha/d\tau)_{min\,l} \quad (20)$$

at $\alpha_{0.6} = \alpha_{max\,l} \geqslant \alpha \geqslant \alpha_{min\,l} = \alpha_{1.9}$. Thus when $\alpha < \alpha_{max\,l}$, the accelerating factors, resulting from the appearance of liquid and increase in the liquid content, determine the rate of Reaction 2. These factors are first of all favoured by a decrease in the mean distance between the substrate particles and a decrease in the length of the SO_2 transport path from the inside to the outside. On formation of the limited liquid content, i.e. when $l = 0.6$ and $\alpha = \alpha_{max\,l}$, the reaction rate is controlled by retarding factors relevant to

TABLE III The relationship between the liquid content of the reaction mixture (l) and occurrence of maxima and minima on the $d\alpha/d\tau$ against α curves

Z	$\alpha_{0.6}$	$\alpha_{max\,l}$	$\alpha_{1.9}$	$\alpha_{min\,l}$
10	0.18	0.15–0.80	–	–
6	0.12	0.11	–	–
4	0.08	0.09	–	–
3	0.07	0.07	0.15	0.15
2	0.05	0.05	0.11	0.11
1.33	0.06	0.06	0.12	0.12
1	0.07	0.07	0.14	0.14
0.50	0.11	0.11	0.21	0.21
0.20	0.25	0.25	–	–

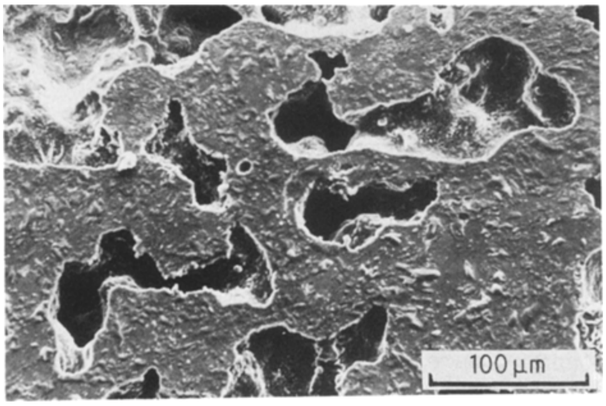

Figure 4 Scanning electron micrograph for $Z = 1$ at $\alpha = 0.136$.

further increase in the liquid content; the most important factor being the decrease in porosity of the specimen. This is supported by the SEM results (Figs 4 and 5, Table II).

3.1.2. The stage of quasi-boiling

The liquid contents arising by virtue of Reaction 2 for $Z < 0.5$ and $Z \geqslant 4$ always correspond to $l < 1.9$, because one of the substrates reacts to completion at $\alpha < \alpha_{1.9}$ (Figs 1 and 3). If $0.5 \leqslant Z \leqslant 3$ then $l > 1.9$ and the Reaction 2 rate increases considerably, a drastic change being observed in the appearance and behaviour of the specimen (Figs 2a, b, d, 3 and Table I). It was found many times that at $\alpha > \alpha_{1.9}$ the samples under study behaved as if they were an intensively boiling liquid and therefore such a process was recognized as an individual stage and called the quasi-boiling stage. The onset of the quasi-boiling stage is when $\alpha = \alpha_{\min \mathrm{I}} = \alpha_{1.9}$. Figs 2a, b, d, e and 3 show that, at $\alpha > \alpha_{1.9}$, the Reaction 2 rate increases with the progress of the reaction, that increase being particularly large when α corresponds to $l > 3$.

For $Z = 0.5$ and 1, the reaction rate achieves a second maximum at $\alpha = 0.27$ and at the same time an intensive quasi-boiling can be observed. It was found that the maximum rate for $Z = 1$ is much higher than that for $Z = 0.5$ (Figs 2a and b). At the same time, the values of l at the same values α are much larger for $Z = 1$ than those for $Z = 0.5$. It shows that in this stage the reaction rate strongly increases with increase in the liquid content. It is also confirmed by visual observations: in this stage the specimens first undergo a plastic deformation, then at $\alpha \sim 0.20$ the liquid begin to dominate and at $\alpha > 0.20$ intensively foams leading to a multiple increase in the sample volumes.

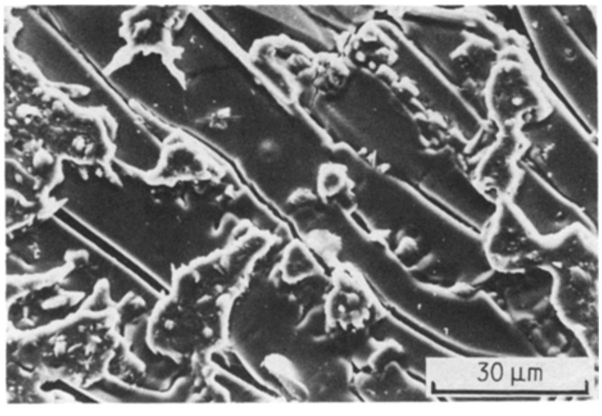

Figure 5 Scanning electron micrograph for $Z = 1$ at $\alpha = 0.347$.

It seems that the existence and the course of the quasi-boiling stage can be explained by the increase in the liquid content and by formation of a suspension of the solid substrate particles, i.e. Cu_2S and $CuSO_4$ in a liquid Cu_2SO_2. Resistance of the SO_2 flow through such a suspension should fall with increase in the liquid content and, in consequence, the Reaction 2 rate would increase with increasing α. But in the course of the reaction the amount of one of the substrates, i.e. Cu_2S for $Z \geqslant 1$ or $CuSO_4$ for $Z \leqslant 1$, falls, which makes the reaction rate decrease on achieving maximum.

That interpretation explains well the Reaction 2 kinetics for $Z = 0.5$ and 1 in this stage. However, for $Z = 1.33$ and 2 the process rate in the quasi-boiling stage increases intensively in the range of α for Reaction 2, but the position of the second maximum shifts in the α range corresponding to Reaction 3 (Figs 1, 2d, e and 3). The product of Reaction 3, Cu_2SO_4, is also a liquid under these conditions [1–3, 5]. The X-ray powder diffraction results have shown that Reaction 3 takes place only at the initial composition of mixtures with $Z > 1$ [3].

3.1.3. The stage of Cu_2SO_4 formation

The course of Reaction 3 makes the liquid content increase and simultaneously the solid phase content, $CuSO_4$, decreases. As the value of parameter Z increases, that is, when there is some excess of $CuSO_4$ with respect to Cu_2SO_2 for $Z > 1$, the Reaction 3 rate is initially proportional to the concentration of Cu_2SO_2 in the liquid. The changes in the liquid content and in the $Cu_2SO_{2(l)}$ concentration can be estimated when one assumes that the molar volumes of $Cu_2SO_{2(l)}$ and $Cu_2SO_{4(l)}$ are equal and the total volume of the liquid is the sum of the volumes of the liquid's components. Thus the value of the factor l' calculated from the following equation can be taken as a measure of the contents of the liquid in the reaction mixture

$$l' = \frac{n_{Cu_2SO_2} + n_{Cu_2SO_4}}{n_{CuSO_4}/d_{CuSO_{4(s)}}} \tag{21}$$

If Reaction 3 takes place on completion of Reaction 2 it is possible, on the basis of Equations 13 to 18, to calculate the number of moles of individual components of the reaction mixture when Reaction 3 begins, that is

$$n^0_{(3)CuSO_4} \text{ and } n^0_{(3)Cu_2SO_2} \quad (\text{for } Z > 1 \; n^0_{(3)Cu_2S} = 0)$$

and the fractional conversion α_2 related to completion of Reaction 2. These data make it possible, on the grounds of Reaction 3, to calculate for a given α the number of moles of individual components involved in this reaction

$$n_{CuSO_4} = 6(\alpha - \alpha_2) \tag{22}$$

$$n_{Cu_2SO_2} = n^0_{(3)Cu_2SO_2} - 3(\alpha - \alpha_2) \tag{23}$$

$$n_{CuSO_4} = n^0_{(3)CuSO_4} - 6(\alpha - \alpha_2) \tag{24}$$

TABLE IV The estimated values of the liquid content of the reaction mixture and the molar fractions of $Cu_2SO_{2(l)}$ in the liquid at α relevant to Reaction 3

	Z									
	1.33	2	2	3	3	3	4	4	6	10
α	0.27*	0.24*	0.29	0.18	0.28	0.45	0.40	0.52	0.51	0.68
l'	18.7*	9.5*	18.7	3.3	4.6	9.5	4.6	9.5	3.0	1.8
$x_{Cu_2SO_{2(l)}}$	0.97	0.79	0.64	1.0	0.68	0.45	0.39	0.19	0.25	0.0

*α values corresponding to maxima in the rate–α curves.

Thus, for Reaction 3, too, it is possible using Equations 21 to 24, to calculate l' as a function of α and Z. Knowing the number of moles of the components of the reaction mixture, it is possible to calculate the molar fraction, $x_{Cu_2SO_{2(l)}}$. Table IV shows the results from calculations made for the given values of α and Z.

It follows from the experimental results that in the range corresponding to Reaction 3 on the rate–α curves for $Z = 1.33$ at $\alpha = 0.27$ (Fig. 2d) and for $Z = 2$ at $\alpha = 0.24$ (Fig. 2e), very high maxima occur. From the calculations (Table IV) it is seen that at these values of α, the liquid content is very large as $l' \gg 1.9$, which enables us to state that for those initial compositions, Reaction 3 starts and runs via the quasi-boiling stage. But the maximum for $Z = 1.33$ is much higher than that for $Z = 2$, which seems to be caused by the fact that for $Z = 1.33$ the maximum $d\alpha/d\tau$ occurs at very large liquid contents and at a high concentration of $Cu_2SO_{2(l)}$ ($x_{Cu_2SO_2} = 0.97$). None the less, for $Z = 2$, the maximum occurs at the value of α for which both the value l' and $x_{Cu_2SO_{2(l)}}$ are much smaller (Table IV). For $Z = 2$, the l' value may also be 18.7 but the calculations show that then $x_{Cu_2SO_{2(l)}} = 0.64$ (Table IV) and the maximum does not occur at those values.

It means that the increasing Reaction 3 rate is accompanied by increase in the liquid content, but the drop in the concentration of Cu_2SO_2 in the liquid is retarding that rate markedly.

The results from calculations for $Z = 3$ confirm the influence of these two parameters. At those initial compositions, l' also achieves the value 9.5, but the concentrations of $Cu_2SO_{2(l)}$ are then much lower than the values of $x_{Cu_2SO_2}$ achieved for $Z = 2$ at this value of l' (Table IV). This fact explains that for $Z = 3$ (Fig. 2c) and for $Z = 4$ (Fig. 2e) on the rate–α curves in the α range corresponding to Reaction 3, the maxima do not occur. The shape of these curves and also of the curve for $Z = 6$ (Fig. 2c) show that in the α range from ~0.29, i.e. in the range corresponding to Reaction 3, its rate is decreasing. This means that at these initial compositions, the retarding factors for the Reaction 3 rate dominate, these being a drop in the $Cu_2SO_{2(l)}$ concentration and thus a slow increase in the liquid content. It can thus be concluded that the Reaction 3 rate is dependent on the liquid content in the reaction mixture in a way analogous to that for Reaction 2. But this rate is also dependent on the Cu_2SO_2 content in the liquid, which decreases during the course of Reaction 3.

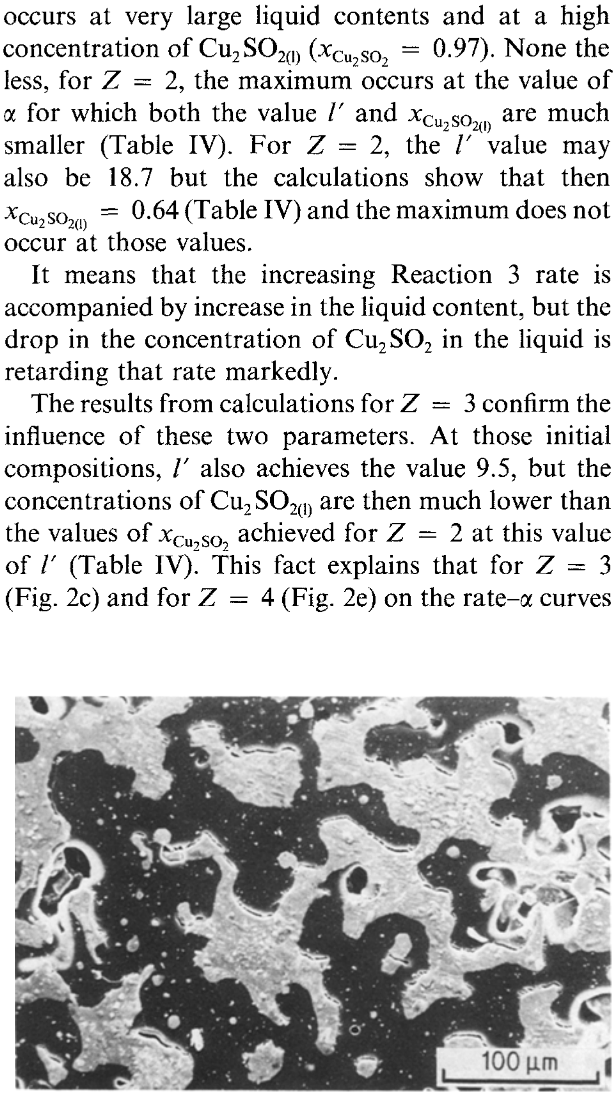

Figure 6 Scanning electron micrograph for $Z = 1$ at $\alpha = 0.873$.

3.2. The period of formation of the final solid products

Formation of the final solid products first of all results from Reactions 4 and 5. At the beginning of the stage when the composition of the initial mixtures is confined within the limits $1 \leqslant Z \leqslant 2$, the reaction mixture is, in fact, entirely liquid. On the other hand, for the other values of parameter Z, the reaction mixture, beside the liquid, also contains a solid phase, i.e. for $Z < 1$, the non-reacted Cu_2S; and for $Z > 2$, the non-reacted $CuSO_4$. Reactions 4 and 5 lead to form $Cu_2O_{(s)}$ from the liquid as well as another solid product which may be Cu_2S (Reaction 4) or $CuSO_4$ (Reaction 5), depending on the initial composition of the mixture; thus it is that component whose particles have not been reacted and exist in the reaction mixture at the start of Reactions 4 or 5. For $Z \leqslant 1$, the liquid is only Cu_2SO_2, hence for these initial compositions, Reaction 4 takes place exclusively. However, as mentioned above, for $Z > 1$, in the liquid in addition to $Cu_2SO_{2(l)}$, $Cu_2SO_{4(l)}$ also appears, the concentration of which increases with increase in the parameter Z. The presence of Cu_2SO_4 makes Reaction 5 possible, which for $Z > 1$ renders the process in the stage under study more complicated (Fig. 1). Results from the SEM examinations of rapidly quenched specimens, with the initial composition $Z = 1$ and α corresponding to the end of Reaction 2, i.e. when the samples are liquid at the temperature of measurement, have shown that their porosity is rather small (Fig. 5; Table II). One can thus state that, for this composition, Reaction 4 starts on the free liquid surface in the sample holder. However, with progress of Reaction 4 the porosity of the investigated objects increases (Figs 5 to 7; Table II). The specimens examined in the same way, but with initial composition $Z = 0.2$ and with α corresponding to the finish of Reaction 2 (Fig. 5; Table II) contain particles of unreacted Cu_2S covered with a liquid layer:

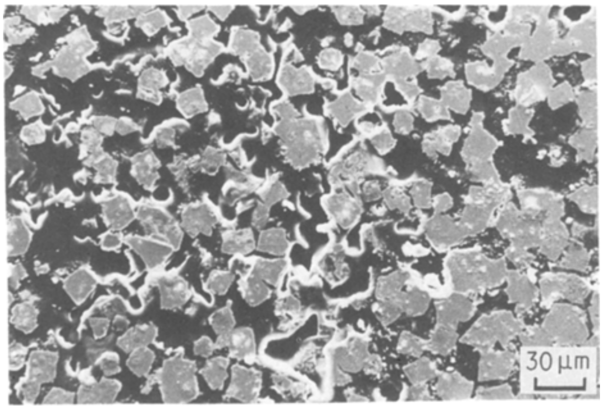

Figure 7 Scanning electron micrograph for $Z = 1$ at $\alpha = 0.986$.

$Cu_2SO_{2(l)}$. Numerous free spaces which form pores can be seen between the particles. From the fact that for $Z = 0.2$ the liquid–gas interfacial area, at the beginning of this stage, can be assumed to be related to the surface area of the non-reacted Cu_2S particles, the surface area is much larger than the area of the free liquid surface for $Z = 1$.

The SEM results (Table II) also show that, in the region of $Z \leqslant 1$, $Cu_2O_{(s)}$, being a product of Reaction 4, at these values of parameter Z, always occurs on the walls of pores [3]. It can thus be stated that Reaction 4 takes place at the liquid–gas interface at the measurement temperature. It shows that a layer of the solid products (Cu_2O and Cu_2S) arises on the surface of the liquid. Formation of such a layer must cause a considerable decrease in the SO_2 transport rate which is undoubtedly one of the agents determining the process rate in stage 2 with these compositions of the initial mixtures.

The SEM results, which permit observation of the changes in the liquid–gas interfacial area, enable us to show the influence of those changes on the rate of the period under discussion. And thus, for $Z \leqslant 1$, period 2 has the highest rate when $Z = 0.2$ (Fig. 2c). It follows from the SEM examinations (Fig. 8; Table II) that, for this initial composition, the liquid–gas interfacial area is also the largest. For $Z = 0.5$ (Fig. 2b), the Reaction 4 rate increases with its progress achieving a maximum of $\alpha = 0.86$. For this value of the parameter Z, at the beginning of the period, the surface area, on which Reaction 4 takes place, is smaller than that for $Z = 0.2$, but as the reaction progresses it increases, which accounts for the reaction rate increase. Also for $Z = 1$, the liquid–gas interfacial area should increase with the progress of Reaction 4, but for this value of the parameter Z the process rate in the period under study in fact remains constant (Fig. 2a). This can be explained by the fact that, for this initial composition, the samples do not achieve a considerable porosity before completion of the process.

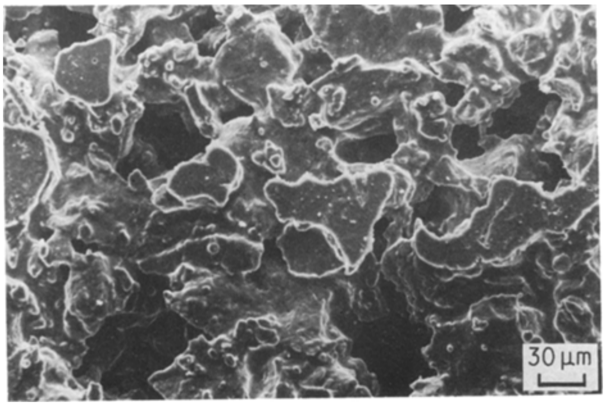

Figure 8 Scanning electron micrograph for $Z = 0.2$ at $\alpha = 0.391$.

One can thus conclude that the $Cu_2SO_{2(l)}$ decomposition rate for $Z \leqslant 1$ is controlled by the area of the gas–liquid interface on which the decomposition takes place. This area is proportional to the porosity of the sample, and also to its volume. The volume of the sample is the larger, the more of the non-reacted $Cu_2S_{(s)}$ it contains, and therefore the reaction rate increases with increase in the Cu_2S content (Figs 2a, b, c).

A similar course of kinetics in period 2 can be observed when $Z > 2$ (Figs 2c, e), leading to the rate of the process being proportional the amount of unreacted $CuSO_4$, i.e. to the value of Z. SEM examinations show (Table II) that Cu_2O (the final product of the $Cu_2SO_{4(l)}$ decomposition) also occurs on the liquid–gas interface at the measurement temperature. For these values of Z, the concentration of $Cu_2SO_{4(l)}$ grows, but Cu_2SO_2 concentration drops, which results in respective changes in rates of Reactions 4 and 5.

Period 2 is the most complex for the initial compositions for which $1 < Z < 2$ (Fig. 1) though it is not reflected in the course of the kinetic curves (Figs 2c, d).

It seems that for these initial compositions the rate of the $Cu_2SO_{2(l)}$ decomposition in the liquid approximates to that of $Cu_2SO_{4(l)}$ because $Cu_2S_{(s)}$ and $CuSO_{4(s)}$ resulting from Rections 4 and 5 are substrates of Reactions 2 and 3, which also causes these reactions to proceed in the discussed period.

3.3. Changes in the apparent activation energy

The apparent activation energy (E_a) at constant pressure of the gaseous phase and established fractional conversion can be calculated from the equation [10]

$$\ln\left(\frac{d\alpha}{d\tau}\right)_{\alpha=\mathrm{const}} = -\frac{E_a}{RT} \tag{25}$$

Using the method of least squares, calculations have been made for chosen values of α. The significance for the values of E_a obtained is above 99%, in each case. It was found that for Reaction 2, i.e. for stage 1 and thus at $\alpha \leqslant \alpha_{0.6} = \alpha_{\max I}$, the apparent activation energy for all values of parameter Z investigated is 252 to 278 $kJ\,mol^{-1}$; whereas in the quasi-boiling stage, E_a calculated for the reaction at the second maximum, i.e. at $\alpha = 0.27$ for $Z = 0.5$ and 1 is 303 to 336 $kJ\,mol^{-1}$. For Reaction 3, at $Z = 2$ and $\alpha = 0.24$ and at $Z = 1.33$ and $\alpha = 0.27$ when the formation of a liquid Cu_2SO_4 begins and continues still in the quasi-boiling stage for these initial compositions, the value of E_a is 433 to 491 $kJ\,mol^{-1}$. However, for $Z = 4$ and $\alpha = 0.27$, when the quasi-boiling stage does not occur, the apparent activation energy of Reaction 3 is much lower and is 328 kJ mol^{-1}. Thus the quasi-boiling stage is characterized by high values of the apparent activation energy both in the case of Reaction 2 and of Reaction 3.

Calculations of the apparent activation energy of the process in the second period have shown that for $Z = 0.2$ and $\alpha = 0.51$ it is 346 kJ mol^{-1}; for $Z = 0.5$ and $\alpha = 0.86$, it is 308 kJ mol^{-1}, whereas for $Z = 1$ and $\alpha = 0.60$, $E_a = 180$ kJ mol^{-1}. The calculation results confirm the interpretation of the experiments for this stage: from the $Cu_2SO_{2(l)}$ decomposition (Reaction 4), the influence of the mass transport rate on the reaction rate is highest when $Z = 1$ and the least when $Z = 0.2$.

4. Conclusions

The most important kinetic problems of the process taking place between copper (I) sulphide and copper (II) sulphate in SO_2 at 710 to 785 K were considered regarding the earlier recognized chemistry of the process [1–3].

1. It was found that in the kinetic course of the process one can distinguish at least two periods of which each is dependent on the contents of the liquid occurring in the reaction mixture as a result of formation of the liquid intermediates, i.e. $Cu_2SO_{2(l)}$.

2. The variable l, which is a measure of the liquid content in the reaction mixture and accounts for the formation of both $Cu_2SO_{2(l)}$ and $Cu_2SO_{4(l)}$ was introduced and assigned. It was found that the calculations made by using this parameter are consistent with the experimental data.

3. The SEM results permit observation of the changes in the porosity of samples depending on the molar ratio of the substrates defined by the parameter Z, and by the liquid content at given values of α. It was also possible to establish that the decomposition of the liquid intermediates takes place on the liquid–gas interface and its rate is strongly dependent on the interfacial area.

4. Calculations of the apparent activation energy, E_a, show that it achieves the highest values in the quasi-boiling stage both for the formation of Cu_2SO_2 and the liquid Cu_2SO_4. The values of E_a obtained confirm the correctness of interpretation of the process for the period of decomposition of the liquid to the final solid products.

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