

STUDIES OF THE REACTION MECHANISM BETWEEN COPPER(I) SULPHIDE AND EXCESS COPPER(II) SULPHATE

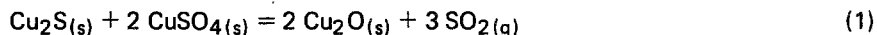
H. Debiński and J. Walczak

DEPARTMENT OF FUNDAMENTAL CHEMISTRY, THE TECHNICAL UNIVERSITY OF SZCZECIN, AL. PIASTÓW 42, 71-065 SZCZECIN, POLAND

The reaction between copper(I) sulphide and excess copper(II) sulphate in the temperature range 600–750 K was investigated by methods of thermal analysis as well as by measuring the phase composition as a function of the fractional conversions. The reaction proceeds in four stages. The transient products are Cu_2S , a Cu_2SO_2 phase and Cu_2SO_4 , and the final product is Cu_2O with the non-defect structure. The initial composition of the substrate mixture strongly influence the reaction kinetics.

The reaction between copper(II) sulphates and copper(I) sulphide has been the subject of many investigations. However, the reported results are highly contradictory [1–3].

In this paper an attempt has been made to establish the reaction process occurring between copper(I) sulphide and excess copper(II) sulphate. Measurements were carried out using the same substrates and the same methods as described in [4], where this reaction was investigated for the case of an excess of copper(II) sulphide. Mixtures with initial compositions $z = 2/1, 3/1, 4/1, 6/1$ and $10/1$ ($z =$ the ratio of the number of moles of copper(II) sulphate to that of copper(I) sulphide ($\text{Cu}_{1.96}\text{S}$)) were prepared. Changes in mass and related thermal effects were measured under conditions of a linear increase of temperature. Some typical results, obtained for $z = 1/1, 3/1$ and $4/1$, are presented in Figs 1–3 as the variations of $d\alpha/dT$ and DTA with α and T . The fractional conversion α was calculated according to the equation:



The phase composition of the reaction products as a function of α and z was determined by means of X-ray diffraction and scanning electron microscopy. From the measured changes in intensity of the diffraction lines characteristic of a given phase, the changes in the concentrations of these phases were determined.

Table 1 lists the values of α for which a given phase began to appear, when a complete reaction or its content reached a minimum (denoted by α_{min}), and the values of α for which the content of a given phase reached a maximum (denoted by α_{max}).

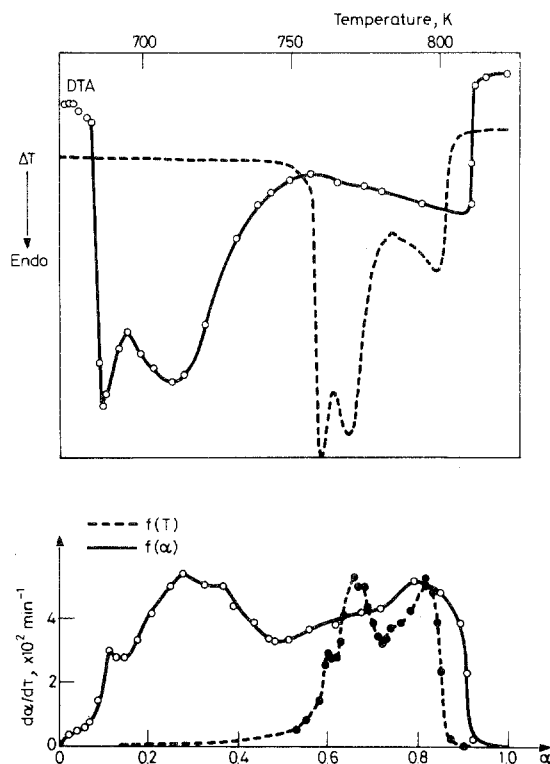
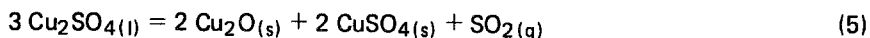
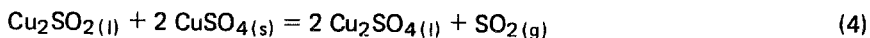
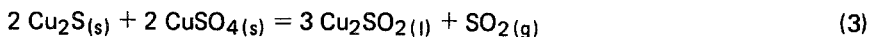
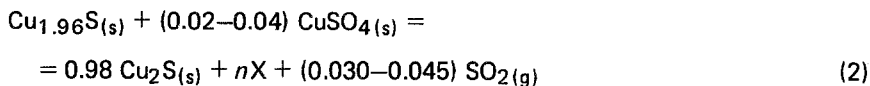


Fig. 1 TG and DTA curves of the mixture $2 \text{CuSO}_4 + \text{Cu}_2\text{S}$

The results revealed that at $730 < T < 800$ K for $\alpha = 1.00$ (Eq. 1) is merely the overall equation; in reality, the investigated reaction proceeds in four steps, described by the following equations:



The first step occurs for $\alpha = 0.01-0.015$ and $650 < T < 700$ K (Eq. 2), whereas the second step is dominant for $0.18 < \alpha < 0.24$ and at $T \geq 710$ K. The steps described by (2) and (3) are equivalent to the two first ones if the reaction proceeds in an excess of copper(I) sulphide [4].

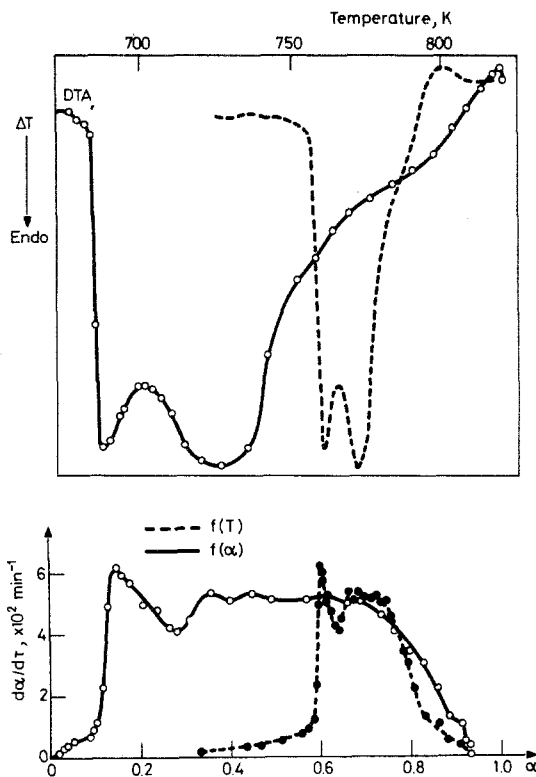


Fig. 2 TG and DTA curves of the mixture 3 CuSO₄ + Cu₂S

Table 1 Values of α at which the content of a given phase in the reaction products reaches a minimum (α_{min}) or maximum (α_{max})

α	z phase	CuSO ₄	Cu ₂ S	Cu	Cu ₂ SO ₄	Cu ₂ O	Cu ₂ SO ₂
α _{min1}	4/1	0.34	0.20	0.13	0.20	0.20	0.02
	3/1	0.54	0.24	0.14	0.18	0.33	0.03
	2/1	0.45	0.18	0.11	0.18	0.21	0.03
α _{max1}	4/1	0.00	0.02	0.35	0.63	1.00	0.20
	3/1	0.00	0.03	0.30	0.50	1.00	0.22
	2/1	0.00	0.03	0.30	0.45	1.00	0.20
α _{min2}	4/1	1.00	—	1.00	1.00	—	1.00
	3/1	—	—	1.00	1.00	—	1.00
	2/1	—	—	1.00	1.00	—	1.00
α _{max2}	4/1	1.00	—	—	—	—	—
	3/1	1.00	—	—	—	—	—
	2/1	—	—	—	—	—	—

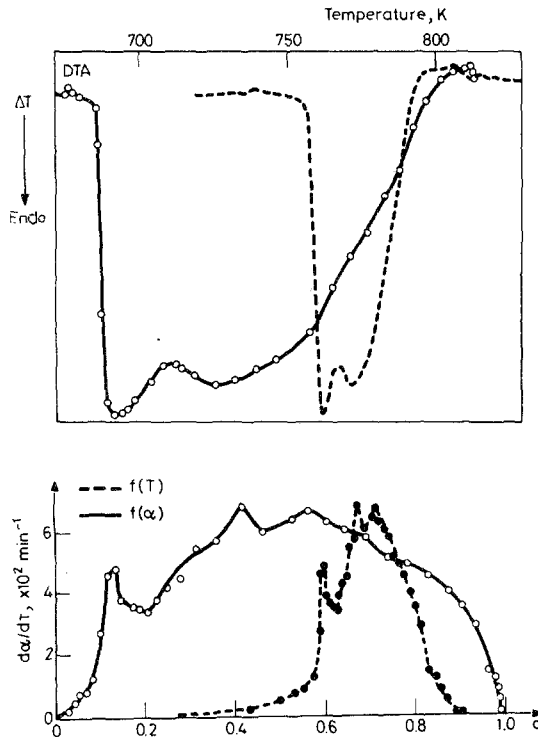


Fig. 3 TG and DTA curves of the mixture $4 \text{CuSO}_4 + \text{Cu}_2\text{S}$

In the third step (Eq. 4), which is dominant in the range $0.45 < \alpha < 0.63$, the main product is copper(I) sulphate, which is liquid under these conditions [5]. In the fourth step (Eq. 5), in the range $0.45 < \alpha < 0.63$ with $z > 2/1$, not only Cu_2O but also CuSO_4 is finally formed, which indicates that Cu_2O is a product of the decomposition of Cu_2SO_4 . The Cu_2O formed under these conditions has a non-defect structure compared to the Cu_2O obtained as a decomposition product of Cu_2SO_2 [4]. The decomposition of Cu_2SO_4 proceeds simultaneously with its formation. The rate of decomposition compared to the rate of its formation increases substantially in the range of α greater than that corresponding to the maximum content of Cu_2SO_4 , and also with the increase of the CuSO_4 content in the initial mixture of substrates.

A considerable amount ($\sim 10 \text{ mol}\%$) of metallic copper appears in the range $0.11 < \alpha < 0.35$. This is most probably caused by the decomposition of Cu_2SO_4 to Cu and CuSO_4 .

References

- 1 R. Schenk and E. Hempelmann, *Z. Angew. Chem.*, 26 (1913) 685.
- 2 W. Reinders and R. Goudrian, *Z. Anorg. Allg. Chem.*, (1923) 85.
- 3 J. V. Margulis and V. P. Ponomarev, *Izv. Akad. Nauk., Ser. met. obog. ogneup.*, 3 (1958) 9.
- 4 H. Debiński and J. Walczak, *J. Thermal Anal.*, 29 (1984) 977.
- 5 N. Jacinto, M. Nagamori and H. Y. Sohn, *Met. Trans.*, 13B (1982), 515.

Zusammenfassung — Die Reaktion zwischen Kupfer(I)-sulfid und überschüssigem Kupfer(II)-sulfat im Temperaturbereich von 600–750 K wurde mittels thermoanalytischer Methoden und durch Ermittlung der Phasenzusammensetzung in Abhängigkeit von der Konversion untersucht. Die Reaktion verläuft in vier Schritten. Als Zwischenprodukte treten Cu_2S , eine Cu_2SO_2 -Phase und Cu_3SO_4 auf, Endprodukt ist ein Cu_2O mit ungestörter Struktur. Die Reaktionskinetik wird stark von der Ausgangszusammensetzung des Substratgemisches beeinflusst.

Резюме — Реакция между сульфидом одновалентной меди и избытком сульфата двухвалентной меди была исследована в области температур 600–750 К методом термического анализа, а также определением фазового состава в зависимости от фракционированного превращения. Реакция протекает в четыре стадии. Переходными продуктами были Cu_2S , Cu_2SO_2 + фаза и Cu_3SO_4 , а конечным продуктом — Cu_2O с упорядоченной структурой. Исходный состав смеси компонентов оказывает большое влияние на кинетику реакций.