Journal of Thermal Analysis, Vol. 29 (1984) 977–981

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

H. Dębiński and J. Walczak

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

The reaction process between $CuSO_4$ and excess Cu_2S in the temperature range 650–750 K was investigated by methods of thermal analysis and by studying the phase contentss of the products as a function of the fractional conversion. The reaction proceeds in three steps, with Cu_2S and a new phase described by the formula Cu_2SO_2 as intermediates. This new phase is liquid under the conditions of the reaction. The final product of the reaction is a defective crystalline Cu_2O.

A number of literature data [1–3] give evidence that the reaction between $CuSO_4$ and Cu_2S in the temperature range $675 \leqslant T \leqslant 960$ K under an equilibrium SO_2 pressure $P_{SO_2} = 0.1$ MPa proceeds according to the following formula:

$$2\,CuSO_{4(s)} + Cu_2S_{(s)} = 2\,Cu_2O_{(s)} + 3\,SO_{2\,(g)} \tag{1}$$

It is claimed by other authors that the products of this reaction may be Cu_2SO_4 and some phases of general formula Cu_xSO_y which are not included in the reports on the thermodynamic properties of the Cu–S–O system [4–8].

Within the framework of studies on the reaction mechanism of this reaction, measurements in argon and SO_2 atmospheres in the temperature range $600 \leqslant T \leqslant 850$ K have been undertaken. The measurements were carried out using mixtures of the substrates with $z = 2/2$, $2/4$ and $2/10$, where z is the initial ratio of the number of moles of $CuSO_4$ to that of Cu_2S. These mixtures were prepared from anhydrous $CuSO_4$ and Cu_2S (exclusively the $Cu_{1.96}$ S phase, as confirmed by chemical analysis, X-ray diffraction and thermogravimetric methods).

During thermal measurements the substrates also contained 30–10 wt. % SiO_2, which prevented ejection of the contents of the crucible. With a home-built apparatus, changes in mass and related thermal effects (DTA) were measured during linear temperature increase at a rate of 2 deg/min. The phase composition of the reaction products, obtained under isothermal conditions, was determined using X-ray diffraction phase analysis methods. This composition was determined as a function of the fractional conversion α, defined as the ratio of the mass loss to the maximum loss resulting from Eq. (1). The results are presented in Figs 1–3, which show the variations of $d\alpha/d\tau$ and DTA with α and T.

Some illustrative X-ray diffraction patterns of the reaction products, for $z = 2/2$ with $\alpha = 0.025$ and $\alpha = 0.363$, are presented in Fig. 4.

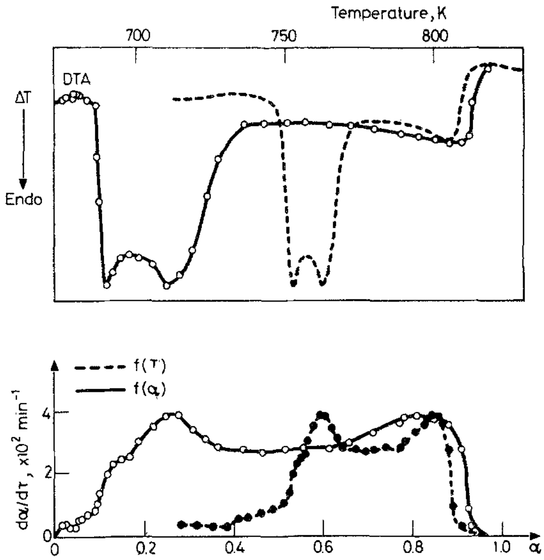

Fig. 1 TG and DTA curves of the mixtures 2 $CuSO_4$ + 2 Cu_2S

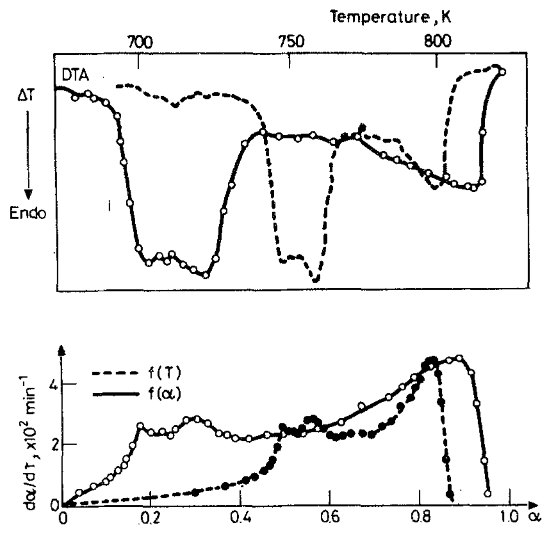

Fig. 2 TG and DTA curves of the mixtures 2 $CuSO_4$ + 4 Cu_2S

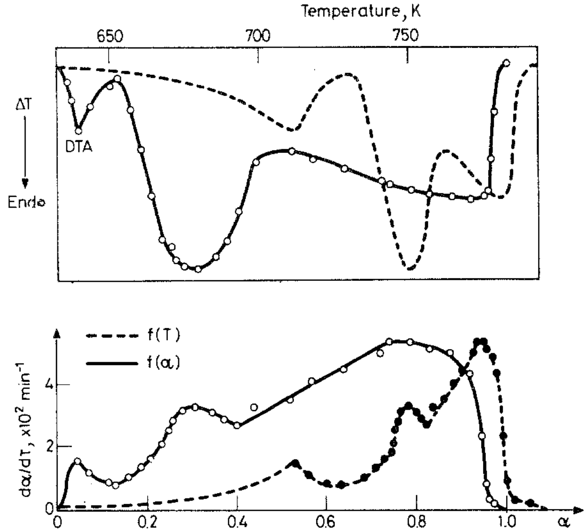

Fig. 3 TG and DTA curves of the mixtures 2 $CuSO_4$ + 10 Cu_2S

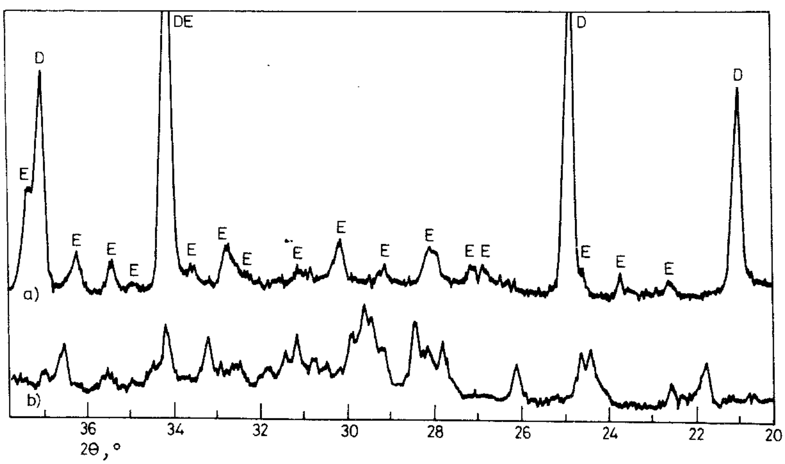

Fig. 4 X-ray diffraction patterns with Cu–K_α radiation of reaction products for $z = 2/2$: D = $CuSO_4$, E = Cu_2S. (a) $\alpha = 0.025$, (b) $\alpha = 0.363$

From the results, it has been established that the reaction between copper(II) sulphate and excess copper(I) sulphide proceeds in three steps:

$$Cu_{1.96}S_{(s)} + (0.02\text{–}0.04)\ CuSO_{4(s)} =$$

$$= 0.98\ Cu_2S_{(s)} + nX + (0.030\text{–}0.045)\ SO_{2\,(g)} \qquad (2)$$

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

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

The first step occurs in the range $\alpha \leqslant (0.02\text{–}0.03)\,z^{-1}$ and at temperatures $650 < T < 700$ K. It has not been possible to establish whether other solid products (X) apart from Cu_2S are present in this step and Eq. (2) results from the mass balance.

In the next step (Eq. 3), proceeding at $T > 710$ K and $\alpha \cong 0.36\text{–}0.40$, $CuSO_4$ reacts completely and the content of Cu_2S reaches a minimum. For $z = 2/2$ and $\alpha = 0.36$ the products contain less than 2 mol % $CuSO_4$ and 5 mol % Cu_2S. The X-ray diffraction pattern of the main product consists of a set of lines which could not be ascribed to any of the known phases in the Cu–S–O system. From the results of chemical analysis it was concluded that the chemical formula Cu_2SO_2 can be ascribed to this new phase. Under the conditions of this reaction, Cu_2SO_2 is liquid: for $z = 2/2$ and 2/4 with $0.05 < \alpha < 0.20$, and for $z = 2/10$ with $0.15 < \alpha < 0.40$, the products undergo sintering, whereas for $z = 2/2$ and 2/4 with $\alpha > 0.20$ the products are completely liquefied.

In the third step (Eq. 4), for $\alpha > 0.64\text{–}0.40$; the product contains not only Cu_2S, but also copper(I) oxide with a strongly defective crystalline structure; this is manifested in a strong broadening of the appropriate diffraction lines, as well as in a strong shift of their positions towards lower diffraction angles.

In the range $0.10 < \alpha < 0.80$ a slight content of metallic copper is also present in the reaction products. This fact has not been included in the discussion in this investogation.

References

1 J. Walczak, Prace Nauk, Pol. Szczec., nr 50, (1975).
2 T. R. Ingraham, Trans. Met. Soc. AIME, 233 (1965) 359.
3 W. Reinders and F. Goudrian, Z. Anorg. Allg. Chem., (1923), 85.
4 R. Schenck and E. Hempelmann, Z. Angew. Chem., 26 (1913), 685.
5 J. V. Margulis and V. D. Ponomarev, Izv. Akad. Nauk., Ser. met. obog. i ogneup., 3 (1958) 9.
6 J. V. Margulis, Sb. Nautch. Tr. Vses. Nautch.-Issled. Gornomet. Inst. Cvet. Met., 17 (1968) 5.
7 M. Nagamori and F. Habashi, Met. Trans., 5 (1974) 523.

Zusammenfassung — Der Verlauf der Reaktion zwischen $CuSO_4$ und überschüssigem Cu_2S im Temperaturbereich von 650–750 K wurde mittels thermoanalytischer Methoden und durch Ermittlung der Phasenzusammensetzung in Abhängigkeit von der Konversion untersucht. Die Reaktion verläuft in drei Schritten mit Cu_2S und einer neuen Phase der Zusammensetzung Cu_2SO_2 als Zwischenproduke. Die neue Phase ist unter den Reaktionsbedingungen eine Flüssigkeit. Endprodukt der Reaktion ist nicht völlig kristallines Cu_2O.

Резюме Реакционной процесс между $CuSO_4$ и избытком Cu_2S был исследован в области температур 650–750 K методом термического анализа и изучением фазового состава продуктов в зависимости от фракционированного превращения. Реакция протекает в три стадии с образованием промежуточных продуктов Cu_2S и новой фазы, описываемой формулой Cu_2SO_2 и которая в условиях реакции является жидкой. Конечным продуктом реакции является кристаллическая Cu_2O с нарушенной структурой.