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THERMAL DECOMPOSITION OF COPPER /I/ SULFATE

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ABSTRACT

The thermal decomposition of Cu_2SO_4 is a three-stage process, Cu and $CuSO_4$ being the main decomposition products at the first stage, and consequently being reacted to Cu_2O at the following ones. A part of Cu_2SO_4 decomposes directly to Cu_2O.

INTRODUCTION

Thermodynamic calculations revealed Cu_2SO_4 to be a stable phase in the Cu-S-O system, only at temperatures between 500 and 700 K for $P/SO_2/ \cong 101$ kPa [1,2] whereas, the formation of Cu_2SO_4 during the hydrogen reduction of $CuSO_4$ was established at 373 to 773 K [2,3].

From the investigations of Cu_2SO_4 decomposition in argon, Cu_2SO_4 was found to decompose entirely above 600 K, according to equation /1/. At 600 K traces of copper were detected in decomposition products [4].

$$3\ Cu_2SO_4 = 2\ Cu_2O + 2\ CuSO_4 + SO_2 \qquad /1/$$

It was, found [5] that Cu_2SO_4 melts at T = 696 K but heated from room temperature upwards decomposes below its melting point. Cu_2SO_4 may be an intermediate or final product of the reactions proceeding below 800 K, in the Cu-S-O system [6]. For this reason it was necessary to elucidate the mechanism of thermal decomposition of Cu_2SO_4.

MEASURING METHODS

The Cu_2SO_4 used in this study was prepared from Cu_2O and $/CH_3/_2SO_4$ [7]. The chemical and X-ray analysis indicated that this material contained 93,54 ∓ 2,04 % of pure Cu_2SO_4.

The investigations were carried out on apparatus of our own construction in SO_2 atmosphere $/P/SO_2/ \cong 100$ kPa/ with simultaneous recording of the mass changes /TG/ and thermal effects /DTA/ at the temperature rising linearly at a rate of 2; 4; 10 K/min from 298 to 850 K. The samples heated at the rate of 4 K/min were analysed by

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X-ray method after reachng $T = 563$; 698; 844 K; moreover products of Cu_2SO_4 decomposition, obtained under isothermal conditions, at the range of temperatures from 443 to 775 K, were analysed by X-ray method, too.

RESULTS AND DISCUSSION

The results of thermal analysis /TG and DTA/ are depicted in Fig. 1., and those from X-ray analysis of products obtained under isothermal conditions are tabulated in Table 1.

The values of mass loss have been taken as the values of fractional conversion /α/. The values of α have been calculated from the mass losses, according to equation /1/. The intensities of diffraction lines, characteristic of individual phases have been given in arbitrary units /au/. The products of Cu_2SO_4 decomposition obtained at $T \geqslant 673$ were sintered, the more strongly the higher the temperature of reaction. At 775 K traces of liquid phase were observed in the decomposition products.

The results inferred from the thermal decomposition of Cu_2SO_4 implies that this process consists of three endothermal stages. At the first of these above 420 K, Cu_2SO_4 decomposes to Cu and $CuSO_4$ preferentially. Only a negligible amount of Cu_2O accompanied by a fairly small mass loss is observed at 575 K.

The second stage is associated with a vehement decrease in Cu and $CuSO_4$ contents in the products, accompanied by a considerable mass loss with immediate in crease in the Cu_2O content. Fig. 1 indicates the rate of this stage to be insignificant in the range of 575 - 646 K and to be increasing rapidly with temperature above 646 K. It should be noticed that, after completion of the reaction at the second stage, Cu and Cu_2SO_4 remain unreacted; it is only the third stage of reaction proceeding above 726 K at which they will entirely be reacted. The course of the reaction at this stage is also responsible for the mass loss, the value of which is remarkably small as compared with that the preceding stage. The maximum mass loss of samples heated isothermally and non-isothermally, at temperatures above 750 K was, at each instance higher by 25 % of the mass loss calculated in accordance with equation/1/.

It may be inferred from the results presented that decomposition of Cu_2SO_4 should proceed according to equations /2/ and /3/ which summed up equal to equation/1/

$$3\ Cu_2SO_4 = 3\ Cu + 3\ CuSO_4 \qquad /2/$$

Table 1.

X-ray diffraction analysis of product of Cu_2SO_4 decomposition obtained under isothermal conditions.

T	t		Intensity			
/K/	/min/		$CuSO_4$ /a u/	Cu_2SO_4 /a u/	Cu_2O /a u/	Cu a u
443	30	0.00	72	848	?	50
485	30	0,00	260	384	?	190
517	30	0.00	434	76	?	282
517	120	0.12	640	40	66	330
575	30	0.19	624	24	46	382
637	30	0.58	572	20	484	110
637	120	0.67	540	24	468	16
683	30	0.74	544	24	680	8
701	30	0.89	660	16	848	13
775	30	1.22	544	-	1090	-

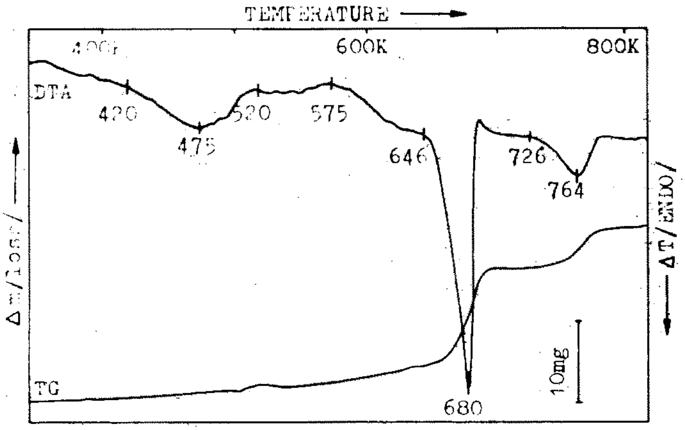

Fig.[illegible].TG and DTA results of the Cu_2SO_4 decomposition;m =20[illegible].5mg;heating rate 4K/min

$3\ Cu + CuSO_4 = 2\ Cu_2O + SO_2$ /3/

The exessive maximum mass loss proves that Cu_2SO_4 may in part decompose in accordance with equations/4/and/5/which added up equal to equation/1/ too.

$3\ Cu_2SO_4 = 3\ Cu_2O + 3\ SO_2 + 1{,}5\ O_2$ /4/

$Cu_2O + 2\ SO_2 + 1{,}5\ O_2 = 2\ CuSO_4$ /5/

It means also that the reaction /4/ is considerably faster than the reaction /5/. This mechanism seems to be more probable than the former in terms of equilibria of the Cu-S-O system but as it has been found the contributions of the reactions /4/ and /5/ to the whole process are relatively small.

CONCLUSIONS

According to equations/2/and/3/the decomposition of Cu_2SO_4 proceeds essentially in two steps Cu and $CuSO_4$ being the intermediate products.

Some of Cu_2SO_4 decomposes directly to Cu_2O in accordance with equation/4/.

At the third stage of decomposition taking place above 726 K Cu and Cu_2SO_4 which have remained unreacted react completely.

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