

## The kinetics and mechanism of the thermal decomposition of tetramminecopper(II) sulphate monohydrate

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### Abstract

The results obtained in the investigation of the thermal decomposition of tetramminecopper(II) sulphate monohydrate in air atmosphere are presented. The mechanism of the process was determined by simultaneous DTA–TG–DTG, and kinetic parameters for the reactions of the defined process were obtained according to the method of Kissinger.

The enthalpy of the process and the specific heat capacity  $C_p$  of the products formed in the course of the thermal decomposition of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  were determined from the DSC measurements.

### INTRODUCTION

The thermal decomposition of tetramminecopper(II) sulphate monohydrate was studied by Wendlandt and Southern [1] and by Paulik and Paulik [2] using a comparative DTA–TG–DTG analysis at 400°C. At the same time, Paulik and Paulik analysed the gases evolved during the thermal decomposition of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ .

The studies determined that during the thermal decomposition of tetramminecopper(II) sulphate monohydrate, dehydration is followed by extraction of the studied complex. Further thermal decomposition proceeds through the decomposition of  $\text{CuSO}_4$  to  $\text{CuO}$ , which is the final decomposition product in air atmosphere. Recently, some differences in the process mechanism have been discussed [3]. It is believed that these discrepancies originate from the insufficient sensitivity of the TG and DTG measurements used by the investigators.

This paper presents the results obtained by comparative examination of the process of thermal decomposition of tetramminecopper(II) sulphate monohydrate using DTA, TG, DTG and DSC methods in air atmosphere at different heating rates. Based on the results obtained, the kinetic

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

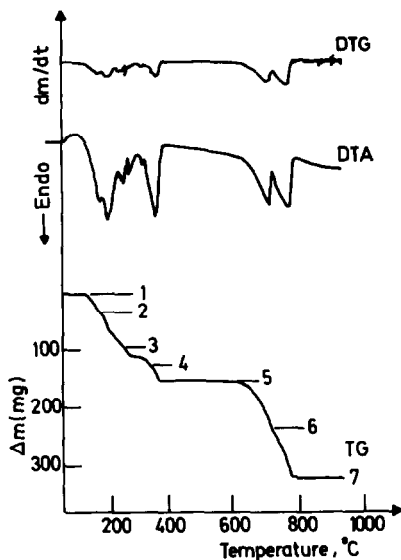


Fig. 1. The results of simultaneous DTA–TG–DTG analysis for  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  in air atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ : 1,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ ; 2,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ; 3,  $[\text{Cu}(\text{NH}_3)_2]\text{SO}_4$ ; 4,  $\text{Cu}(\text{NH}_3)\text{SO}_4$ ; 5,  $\text{CuSO}_4$ ; 6,  $\text{CuO} \cdot \text{CuSO}_4$ ; 7,  $\text{CuO}$ .

parameters for the process were determined. At the same time, the DSC measurements provided the value of the enthalpies of the processes occurring in the course of the thermal decomposition of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ , as well as the changes in the specific heat capacity  $C_p$  of the solid products of the intermediate reactions.

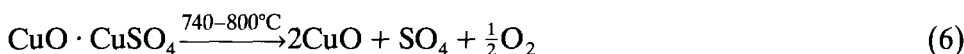
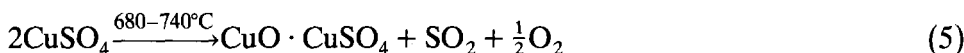
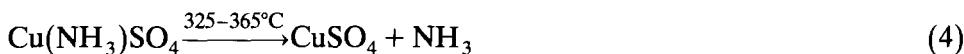
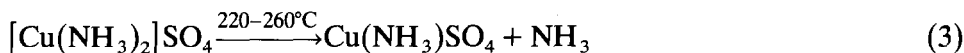
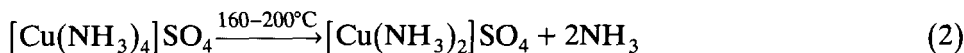
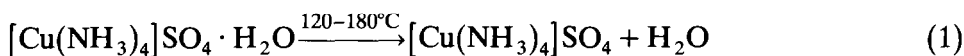
## EXPERIMENTAL

The tetramminecopper(II) sulphate monohydrate used in these investigations was synthesised in the laboratory of The Institute for Inorganic Chemistry and Metallurgy of Rare Metals in Wrocław (Poland). A MOM (Budapest) derivatograph was used for the thermal examinations and for the DSC examinations, a Netsch DSC-404 instrument was employed.

## RESULTS AND DISCUSSION

Figure 1 presents the results of a simultaneous DTA–TG–DTG analysis of tetramminecopper(II) sulphate monohydrate, obtained at a heating rate of  $10^\circ\text{C min}^{-1}$  in air atmosphere. The results indicate that the process of thermal decomposition involves six steps before the final product,  $\text{CuO}$ , is obtained.

From the result presented (Fig. 1), as well as from the results obtained at different heating rates within the range 2.5–20°C min<sup>-1</sup>, the following processes were determined.



Owing to the nature of the processes considered in eqns. (1)–(6) and to the form of the thermoanalytical curves obtained (DTA–TG–DTG), the author decided to determine the kinetic parameters of the processes using the Kissinger method [4], which requires certain DTA examinations at different heating rates. The results obtained for DTA examinations at heating rates of 2.5–20°C min<sup>-1</sup> are presented in Table 1.

The results in Table 1 were processed according to the method developed by Kissinger, or using

$$\ln[\phi/T_m^2] = C - E/RT_m^2 \quad (7)$$

where  $\phi$  is the heating rate,  $T_m$  the maximum on the DTA peak,  $E$  the activation energy,  $R$  the universal gas constant and  $C$  an integration constant.

The graphic dependence  $\ln(\phi/T_m^2) = f(1/T_m)$  for the processes defined in eqns. (1)–(6) is presented in Fig. 2, from which the values for activation

TABLE 1

DTA results ( $T_m$  (°C)) for the processes of thermal decomposition of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  at different heating rates

Process	Heating rate (°C min <sup>-1</sup> )			
	2.5	5	10	20
(1)	120	145	160	180
(2)	160	180	190	200
(3)	220	240	245	260
(4)	325	350	360	365
(5)	680	705	715	740
(6)	740	750	770	800

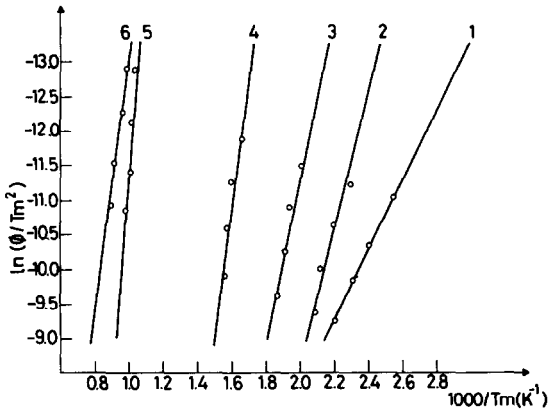


Fig. 2. The dependences,  $\ln(\phi/T_m^2) = f(1/T_m)$ , for the thermal decomposition processes of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ : 1, process (1); 2, process (2); 3, process (3); 4, process (4); 5, process (5); 6, process (6).

energy  $E$  and integration constant  $C$  can be determined; the results obtained are presented in Table 2.

The values obtained for the kinetic parameters indicate that all the processes occurring in the course of the thermal decomposition of tetramminecopper(II) sulphate monohydrate are entirely within the kinetic area, which suggests that temperature is the predominant influence on the process rate. Figure 3 presents the temperature dependence of the values obtained for activation energy  $E$  and integration constant  $C$ .

The temperature dependence obtained indicates that during the evolution of  $\text{NH}_3$ , the crystal lattice of the starting component transforms, leading to an increase in the activation energy; and the temperature influence on the rate of the processes occurring at higher temperatures becomes more pronounced.

The DSC measurements were used to determine the enthalpy of the studied processes; the results obtained are illustrated in Fig. 4. The calculated enthalpy values of processes (1)–(6), as well as the time and

TABLE 2

Values for activation energy  $E$  and integration constant  $C$  for the thermal decomposition processes of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

Process	$E$ ( $\text{kJ mol}^{-1}$ )	$C$
(1)	45	15
(2)	81	$6.2 \times 10^4$
(3)	103	$7.9 \times 10^5$
(4)	144	$2.3 \times 10^7$
(5)	657	$7.8 \times 10^{27}$
(6)	679	$8.1 \times 10^{30}$

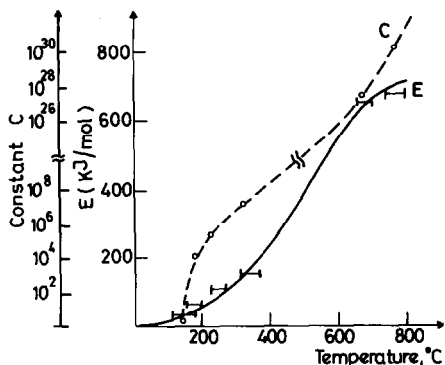


Fig. 3. The dependences  $E = f(T)$  and  $C = f(T)$  for the thermal decomposition processes of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ .

temperature limits of the individual processes occurring in the course of the thermal decomposition of tetramminecopper(II) sulphate monohydrate, are presented in Table 3.

To determine the  $C_p$  values of the solid products formed in the course of the thermal decomposition of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ , heat-flux DSC is best performed according to the ratio method [5]. Sapphire discs are preferred for the calibration. Special software was used to process the results obtained in order to calculate the  $C_p$  values of the products formed in the course of the thermal decomposition of tetramminecopper(II) sul-

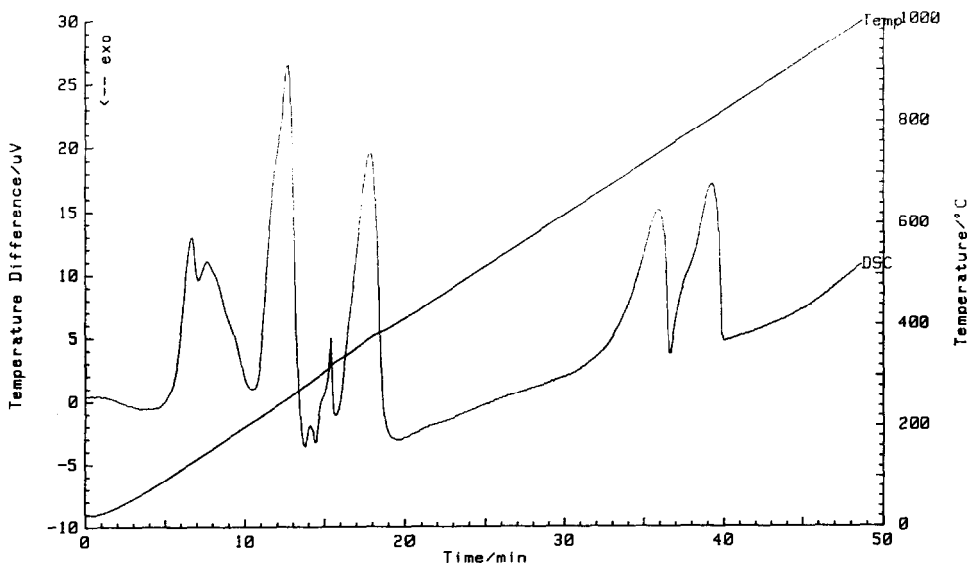


Fig. 4. DSC curve for  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  in air atmosphere at the heating rate of  $20^\circ\text{C min}^{-1}$ .

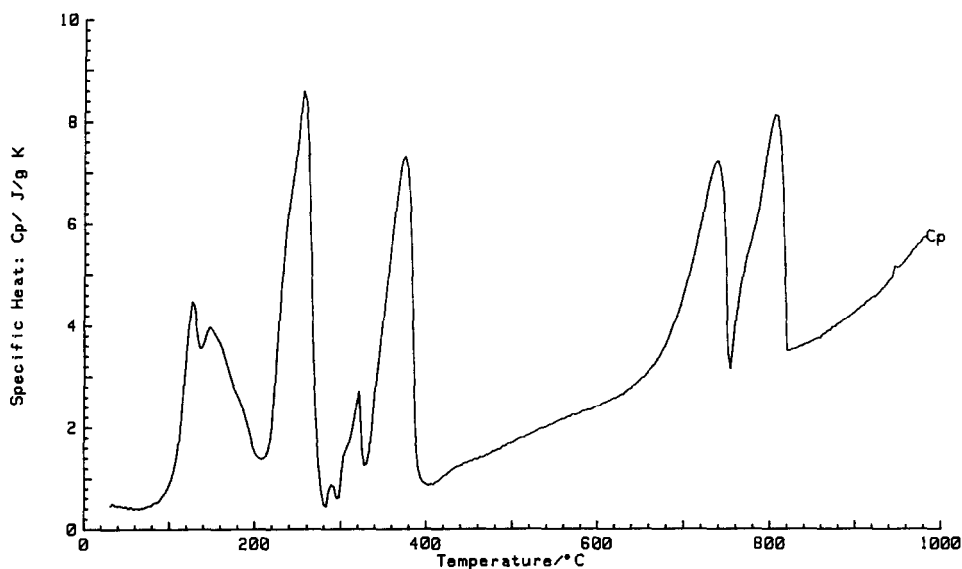


Fig. 5. The dependence of the specific heat capacity of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  on temperature.

TABLE 3

Values for enthalpies of the processes occurring in the thermal decomposition of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

Process	Enthalpy ( $\text{J g}^{-1}$ )	Temperature limit ( $^{\circ}\text{C}$ )	Time limit (min)
(1)	2.036	88.6–206.7	4.8–10.4
(2)	2.551	207.2–277.5	10.4–13.6
(3)	1.621	298.3–326.3	14.6–15.6
(4)	1.924	332.6–389.7	16.0–18.8
(5)	1.225	610.4–750.0	32.6–36.5
(6)	1.364	754.7–818.4	36.8–39.9

phate monohydrate; the results obtained for the  $C_p = f(T)$  dependence are shown in Fig. 5.

This completes the results obtained by simultaneous DTA–TG–DTG analysis, and they present a more complete picture of the process mechanism of the thermal decomposition of tetramminecopper(II) sulphate monohydrate than in the previous publications.

#### ACKNOWLEDGEMENTS

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