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Kinetic of Dehydration of $CuSO_4{\cdot}5H_2O$

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Thermal decomposition of $CuSO_4{\cdot}5H_2O$ was studied under non-isothermal conditions in air. The kinetic of particular stages of $CuSO_4{\cdot}5H_2O$ decomposition were evaluated from the dynamic weight loss data by the means of integral method and differential method. The values of the activation energy E, the pre-exponential factor A of each stages of the thermal decomposition were calculated. The entropy of activation ($\Delta S^{\neq}$), the enthalpy of activation ($\Delta H^{\neq}$), the free energy of activation ($\Delta G^{\neq}$) and kinetic compensation effect were also studied.

Key Words: Dehydration, Copper sulphates pentahydrate, Kinetic parameter, Kinetic compensation effect.

INTRODUCTION

The thermal decomposition of copper sulphate has been studied as a part of the program to investigate the thermal dissociation of metal sulphate of the fourth period of Mendeleev's classification. In addition to academic interest they have an important role in metallurgy and pesticide.

In this paper, the thermal characteristics of $CuSO_4{\cdot}5H_2O$ is studied using TG-DTG-DTA technique, together with all the dehydration kinetic analysis results of their decomposition, such as the reaction mechanism and the Arrhenius parameters, the entropy of activation (ΔS^*), the enthalpy of activation (ΔH^*) and the free energy of activation (ΔG^*).

In view of general complexity in the process involved in solid-state reactions[1-4], two thermal analysis kinetic methods were jointly employed in this paper to process the TG, DTG data to determine parameters, *i.e.* the activation energy (E) and the pre-exponetial factor (A) for the compound studied. The entropy of activation (ΔS^*), the enthalpy of activation (ΔH^*) and the free energy of activation (ΔG^*) were also studied. Furthermore, the kinetic compensation effect is also studied. The rate of a reaction under non-isothermal conditions has been expressed by the relation[5]:

$$d\alpha/dt = k(T){\cdot}f(\alpha) \qquad (1)$$

where α represents the transformation degree at time t, $f(\alpha)$ the conversion function dependent on mechanism of the reaction, the k(T) the rate constant as a function of temperature. After integrating eq. 1, we have:

$$d\alpha/g(\alpha) = f(\alpha) \qquad (2)$$

k(T) can be describes by the Arrhenius equation:

$$k(T) = A\cdot\exp(-E/RT) \tag{3}$$

where A is the pre-exponetial factor, E the activation energy and R the gas constant or, by an equation of the Eyring type:

$$K(T) = k_B T/h\cdot\exp(\Delta S^*/R)\cdot\exp(-\Delta H^*/RT) \tag{4}$$

where 'k_b' is the Boltzmann constant, 'h' the Plank constant, ΔS^* the entropy of activation and ΔH^* the enthalpy of activation. In case of Wertera and Zenera type:

$$K(T) = \nu \exp(-\Delta G^*/RT) \tag{5}$$

where ν is the Einstein vibration frequency and ΔG the free energy of activation.

In the present study, the kinetic of dehydration of $CuSO_4\cdot 5H_2O$ was followed by the integral method and differential method. The two methods are as follow:

Achar-Brindly-Sharp(A-B-S) equation[6]:

$$\ln [g(\alpha)/T^2] = \ln (AR/\beta E) - E/RT \tag{6}$$

Coats-Redfern (C-R) equation[7]:

$$\ln [(d\alpha/dt)/f(\alpha)] = \ln A - E/RT \tag{7}$$

the algebraic express of integral g(α), differential f(α) functions for the most common mechanism used in kinetic of solid-state decomposition tested in this work are listed in Table-1.

TABLE-1
SOME INTEGRAL AND DIFFERENTIAL COEFFICIENT KINETIC FUNCTION

Symbol	Integral kinetic function	Differential coefficient kinetic function	Mechanism
D1	α^2	$1/(2\alpha)$	1-Dimensional diffusion
D2	$\alpha+(1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$	2-Dimensional diffusion
1D3	$1-(2/3)\alpha-(1-\alpha)^{2/3}$	$3/2[(1-\alpha)^{1/3}-1]^{-1}$	3-Dimensional diffusion (cylindrical symmetry)
2D3	$[1-(1-\alpha)^{1/3}]^2$	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	3-Dimensional diffusion (spherical symmetry)
3D3	$[(1+\alpha)^{1/3}-1]^2$	$3/2(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	3-Dimensional diffusion
4D3	$[1/(1-\alpha)^{1/3}-1]^{1/2}$	$3/2(1-\alpha)^{4/3}[1/(1-\alpha)^{1/3}-1]^{-1}$	3-Dimensional diffusion
A1	$-\ln(1-\alpha)$	$(1-\alpha)$	Random nucleation and nuclei growth (n=1)
A1.5	$[-\ln(1-\alpha)]^{2/3}$	$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	Random nucleation and nuclei growth (n=1.5)
A2	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	Random nucleation and nuclei growth (n=2)
A3	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	Random nucleation and nuclei growth (n=3)
A4	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	Random nucleation and nuclei growth (n=4)

Symbol	Integral kinetic function	Differential coefficient kinetic function	Mechanism
R2	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	Contracting sphere (cylindrical symmetry)
R3	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	Contracting sphere (spherical symmetry)
P1	α	1	Exponential nucleation
P2	$\alpha^{1/2}$	$2\alpha^{1/2}$	Exponential nucleation
P3	$\alpha^{1/3}$	$3\alpha^{2/3}$	Exponential nucleation
P4	$\alpha^{1/4}$	$4\alpha^{3/4}$	Exponential nucleation
C2	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$	Chemical reaction
C1.5	$(1-\alpha)^{-1/2}$	$2(1-\alpha)^{3/2}$	Chemical reaction

The following parameters were calculated to aid the selections of the f(α), g(α) function which best describes the experimental results: (i) the correlation coefficient (r) and (ii) standard error of estimation (s).

EXPERIMENTAL

Thermal experiments were performed in a TGA/SDTA851e (Mettler-Toledo Instruments). This apparatus allows TG and DTG measurements to be taken simultaneously. Crucibles were made from alumina. The instrument was previously calibrated against standard substance provide by Mettler-Toledo Instruments Corp. All the tests were carried out under non-isothermal conditions at heating rate (β) of 10ºC min^{-1}, in flowing (20 mL min^{-1}) nitrogen of 99.99 % using samples within the range 5-10 mg which were gently crushed with a pestle and mortar before measured. Simulated TG-DTG-DTA curves were obtained 30-250ºC

RESULTS AND DISCUSSION

The thermal analysis curves of the copper sulphate pentahydrate (Fig. 1) show several peaks. The weight decreased was stabilized at 285ºC. The TG curve for this salt shows three temperature regions in which there are weight loss with maximum rate at 89.99, 120.24, 255.93ºC in the DTG curve (Table-2). The DTA curve shows that the three steps of decomposition is endothermic.

TABLE-2
THERMAL ANALYSIS DATA OF $CuSO_4{\cdot}5H_2O$

Stage	Temperature range (K)	DTG peak temperature (K)	Experimental loss (%)	Theoretical loss (%)
1	318.15-378.60	363.14	14.36	14.40
2	378.60-403.15	393.39	14.41	14.40
3	403.15-588.15	529.08	7.40	7.20

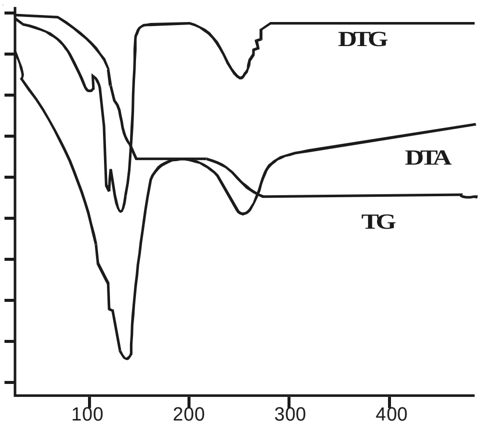

Fig. 1. TG-DTG-DTA curve of $CuSO_4{\cdot}5H_2O$

On the basis of this study, we find that the following dehydration reaction occur in the course of the thermal decomposition of $CuSO_4{\cdot}5H_2O$

$CuSO_4{\cdot}5H_2O \rightarrow CuSO_4{\cdot}3H_2O + 2H_2O$
$CuSO_4{\cdot}3H_2O \rightarrow CuSO_4{\cdot}1H_2O + 2H_2O$
$CuSO_4{\cdot}H_2O \rightarrow CuSO_4 + H_2O$

The thermal stability sequence was in a good agreement with the previous results[8]. The thermal characteristics of each reactions studied are summarized in Table-3.

TABLE-3
KINETIC AND STATISTICAL PARAMETERS VALUES FROM DYNAMIC TG EXPERIMENT

Step	Mecha-nism	A	E (KJ mol^{-1})	ΔH* (KJ mol^{-1})	ΔS* (J mol^{-1})	ΔG* (KJ mol^{-1})	R^2	SD
First step	R2	1.89×10^6	84.04	81.02	867.74	-237.74	0.9999	0.6648
Second step	D2	4.43×10^{47}	328.36	325.09	1666.98	-330.56	0.9971	0.7090
Third step	2D3	6.83×10^{29}	174.17	169.77	1323.70	-530.57	0.9933	0.7333

From the mass loss-temperature dependence observed in the TG curve, the α-T relations for the particular steps were estimated (Figs. 2-4).

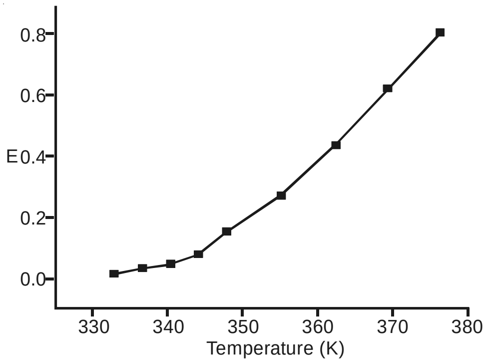

Fig. 2. First stage of dehydration of $CuSO_4{\cdot}5H_2O$

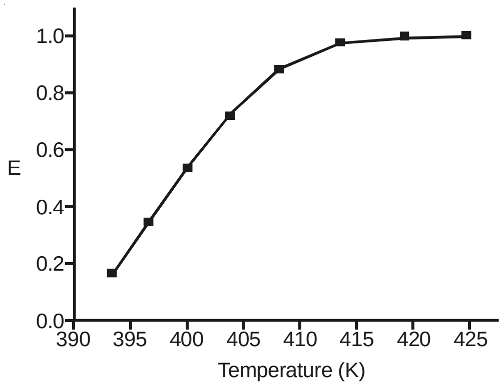

Fig. 3. Second stage of dehydration of $CuSO_4 \cdot 5H_2O$

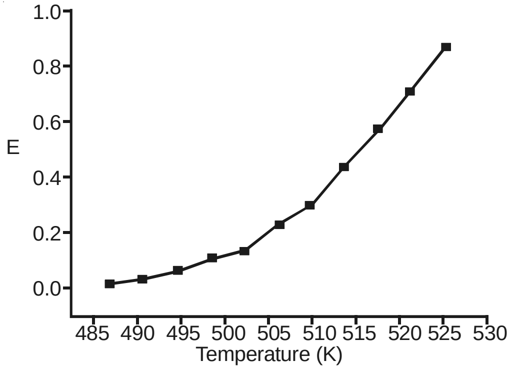

Fig. 4. Third stage of dehydration of $CuSO_4 \cdot 5H_2O$

The f(α), g(α) functions from well-known model (Table-1), which best described the experimental results of the decomposition were chosen. Average values of the apparent activation energy (E), the pre-exponential factor (A), linear regression coefficient (r), the standard error of estimation (s), the entropy of activation (ΔS*), the enthalpy of activation (ΔH*) and the free energy of activation (ΔG*) obtained from analysis of seven dynamic TG on the basis eqn. 6, are listed in Table-3. The values in Table-3 were obtained from those tested equations which best fit the experimental TG curves.

From the Table-3, it can be seen that the best fit for the first stage of $CuSO_4 \cdot 5H_2O$ dehydration is Contracting sphere (cylindrical symmetry) model with an activation energy of 84.04 KJ mol^{-1}. The second stage of dehydration were described by two-dimensional diffusion model, with an activation energy of 328.36 KJ mol^{-1}. The last stage of dehydration were described by three-dimensional diffusion model, with an activation energy of 174.17 KJ mol^{-1}.

Using kinetic compensation effect equation[8,9] : $\ln A = aE + b$ (a,b is compensation parameter) and the data of integral and differential kinetic in Table-4, a plot of ln A *vs.* E gives a straight line by PLS. We obtained a = 0.2268, b

= -4.3863 (integral); a = 0.2283, b = 13.1276 (differential) in the first step; a = 0.2268, b = -4.3863 (integral); a = 0.3028, b = 11.1901 (differential) in the second step; a = 0.2805, b = -3.3903 (integral); a = 0.3282, b = 11.6151 (differential) in the first step So the six kinetic compensation effect equation as follows:

TABLE-4

$CuSO_4·5H_2O$ DEHYDRATION COMPENSATION EFFECT EQUATION OF INTEGRAL AND DIFFERENTIAL KINETIC

Step	Integral	R^2	SD	Differential	R^2	SD
I step	ln A = 0.2268E - 4.3863	0.9998	0.6647	ln A = 0.2283E + 13.1276	0.9975	2.6438
II step	ln A = 0.2347E - 3.9084	0.9997	0.7105	ln A = 0.2283E + 11.1901	0.9999	0.7090
III step	ln A = 0.2805E - 3.3903	0.9995	0.7332	ln A = 0.3282E + 11.6151	0.9992	1.0408

In conclusion, the dehydration of $CuSO_4·5H_2O$ occurs in three steps. The elimination of water takes places at temperature below 280ºC in three stages. The first step of dehydration is governed by contracting, the remaining steps by diffusion. These stages have activation energy, the first 84.04 KJ mol^{-1}, the second 328.36 KJ mol^{-1} and the last 174.17 KJ mol^{-1}.

The entropy of activation (ΔS^*), the enthalpy of activation (ΔH^*) and the free energy of activation (ΔG^*) were studied. The kinetic compensation effects of three steps in dehydration were also studied. They represent reaction themselves[8].

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