KINETICS OF DEHYDRATION REACTIONS—A COMPARISON BETWEEN ISOTHERMAL AND NON-ISOTHERMAL STUDIES

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ABSTRACT

A comparison of results for the kinetics of dehydration of copper sulphate monohydrate from TG, DTA, DSC and isothermal weight-change measurements indicated that differences in impedance to diffusion of water vapour affected conclusions regarding the reaction mechanism. Isothermal studies indicated that the mechanism is in accordance with Jander's model for three-dimensional diffusion. Non-isothermal studies, on the other hand, suggested that Mampel's model for random nucleation and growth of nuclei without overlap was valid. The effect of impedance in the non-isothermal studies was an increase in the activation energy and the pre-exponential factor. When impedance to dehydration was low, non-isothermal measurements yielded activation energy values and pre-exponential factors in good agreement with those obtained from isothermal measurements, notwithstanding disagreement in the reaction mechanism. The distinction between 'crystalline' copper sulphate monohydrate and the species produced in situ by the dehydration of higher hydrates of copper sulphate, reported by Langfelderova et al., has been shown to be only apparent, and is due to the effect of water vapour from dehydration of $CuSO_4 \cdot 5H_2O$ and/or $CuSO_4 \cdot 3H_2O$ on the subsequent dehydration of $CuSO_4 \cdot H_2O$.

INTRODUCTION

The variability of kinetic parameters calculated from thermoanalytical data obtained under different experimental conditions has been the subject of a number of papers [1–4]. However, these studies were concerned mostly with experiments using comparatively large samples which provided long diffusion paths for the gaseous products of reaction. The resulting higher partial pressure of product gases in the environment of the decomposing sample particles at progressively longer times delayed the overall decomposition reaction and hence altered the shapes of the corresponding thermoana-

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lytical curves. Further, the methods used for data analysis [2] were limited in application as a number of models relevant to solid state kinetics could not be tested. A reassessment of the validity of non-isothermal methods in kinetics on the basis of measurements using small samples and the analysis of results employing the modified method of Zsako [5,6] is therefore desirable. Some relatively simple dehydration and decomposition reactions have been examined by TG, DTA, DSC and isothermal weight-change determination from this point of view in our laboratory.

The dehydration of copper sulphate monohydrate takes place at a relatively high temperature [7] and is well separated from the previous dehydration steps involving the pentahydrate and trihydrate. Hence, in the presence of a moderate flow (10–15 ml min^{-1}) of a dry inert carrier gas around the sample, copper sulphate monohydrate produced in situ from copper sulphate pentahydrate may be expected to undergo dehydration in an atmosphere free of water vapour, especially if the sample size is small. Furthermore, the anhydrous copper sulphate formed from this dehydration step in the temperature range 498–548 K is stable up to 873 K. The dehydration of copper sulphate monohydrate can, therefore, be considered as a simple reaction, at least from a thermoanalytical point of view, and has been chosen as a model for dehydration reactions for the purpose of the study reported here.

EXPERIMENTAL

Isothermal weight-change measurements and thermogravimetric (TG) studies were carried out using a Cahn RG Electrobalance. Use of a 16 mm i.d. silica hang-down tube and a micro-TG sample-pan assembly (platinum) provided by the manufacturer permitted measurements at a sensitivity of 100 μg in^{-1}. A nichrome-wound furnace and a temperature controller-programmer (M/s. Indotherm Instruments Pvt. Ltd., Bombay, Model 457) permitted the sample temperature to be increased at a desired rate or maintained at a desired value. A Perkin–Elmer Differential Scanning Calorimeter, DSC-1B, was used for recording the DSC curves. A home-made differential thermal analyser [8] modified by facilitating measurements in controlled non-corrosive atmospheres and using calibrated Platinel II thermocouples was used for the DTA studies.

Copper sulphate pentahydrate (Guaranteed Reagent) obtained from M/s. Sarabhai Merck was used without further purification. Alumina (B.D.H. AnalaR) was heated over a flame for half an hour and cooled in a desiccator before being used as reference material or diluent.

Isothermal weight-change data were recorded with samples weighing about 5 mg at temperatures in the range 463–503 K in dry argon flowing at the rate of 10 ml min^{-1}. The samples were initially heated to 423 K and maintained at this temperature for nearly 15 m to flush out the water vapour

evolved from the in situ dehydration of copper sulphate pentahydrate to the corresponding monohydrate. The sample was then quickly raised to the desired temperature.

DSC measurements were carried out in open aluminium pans covered only with a dome-shaped cover (supplied by the manufacturer) for ensuring matched heat losses from the sample and reference holders. DSC curves were recorded under various conditions of sample weight and heating rate while the specimen holder assembly was flushed with commercial nitrogen (M/s. Indian Oxygen Ltd., Bombay) flowing at a constant rate. As these measurements did not indicate any pronounced effect of sample weight on the activation energy of the dehydration, calculated by the modified method of Zsako (loc. cit.), the TG and DTA studies were carried out with samples of a fixed mass (~ 5 mg for TG and ~ 25 mg for DTA) at various heating rates in dry argon flowing at the rate of 10 ml min^{-1}. Three measurements were usually carried out at each heating rate to determine the reproducibility of the activation energy values.

A separate set of three TG measurements were carried out with the sample contained in sealed sample holders in order to draw inferences on the reversibility of the reaction. These measurements were carried out at a fixed heating rate of 4.3 K min^{-1}, but with sample weight varying in the range 2–10 mg. The aluminium pan-lid assemblies used with the DSC-IB were employed for this purpose. The sample was weighed into the aluminium pan which was covered with the lid and then crimped mechanically. The crimped sample holder was loaded directly onto the sample carrier system of the thermobalance and the TG curves were recorded.
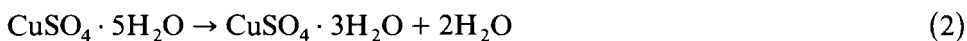
RESULTS AND DISCUSSION

Isothermal studies

The fraction dehydrated before the attainment of the desired temperature was within 0.1 for the highest temperature data and, therefore, the time at which weight loss was first detected was taken as zero-time. A computer program, written in FORTRAN IV and executed on a Norsk-Data Computer, ND 560, was used for the calculations. The program enabled the selection of an appropriate reaction mechanism from among twenty-three possible cases [5] on the basis of the minimum value of the relative standard deviation, R_σ, defined as
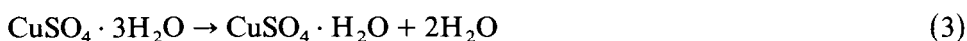
$$R_\sigma = \frac{\sigma_i^2}{m} \tag{1}$$

where m is the slope of a line obtained by the least-squares fit of $g(\alpha)$ versus time, $g(\alpha)$ being a function [5] of α, the fraction dehydrated at

time t. σ_i is the standard deviation of m. The data in the reaction range 10–90% only yielded consistent results by the least-squares analysis and hence all the calculations were carried out for the corresponding range of α. The results of the analysis of isotherms recorded at 478, 483, 488, 494 and 501 K indicated that the reaction mechanism is in accordance with Jander's model for three-dimensional diffusion (Fig. 1). The isotherm at 465 K, however, showed agreement with the Ginstling–Brounshtein model for three-dimensional diffusion. The Arrhenius plot (Fig. 2) of the rate constants conforming to Jander's diffusion equation gave values of 129.7 kJ mol^{-1} and 2.5×10^{11} s^{-1} for the activation energy, E, and the pre-exponential factor, Z, respectively. The value of the activation energy is in good agreement with the value of 126.9 kJ mol^{-1} reported by Langfelderova et al. [9] for the activation energy of dehydration of 'crystalline' copper sulphate monohydrate. However, for copper sulphate monohydrate prepared in situ by the dehydration of the corresponding pentahydrate, as in the present study, Langfelderova et al. (loc. cit.) reported an activation energy of 216.9 kJ mol^{-1} and suggested that the latter value was the sum total of the activation energies for crystallization and dehydration. It appears from the present studies that the so-called 'crystalline' copper sulphate monohydrate is not essentially different from that obtained in situ from the dehydration of the pentahydrate. Langfelderova et al. obtained a higher activation energy value for the latter species probably because of the presence of water vapour from the dehydration of the pentahydrate in the sample environment while the dehydration of the monohydrate was proceeding. In the present study, care was taken to flush out the water vapour resulting from the reactions

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

and

$$CuSO_4 \cdot 3H_2O \rightarrow CuSO_4 \cdot H_2O + 2H_2O \tag{3}$$

before initiation of the dehydration of the monohydrate and, hence, the activation energy for the latter reaction corresponded to the lowest value obtained by Langfelderova et al. in a moisture-free atmosphere.

Jander's model for three-dimensional diffusion is usually interpreted on the basis of diffusion of reactant lattice sites across a product layer when the reactant particles have a spherical shape and one of the reactants is in the form of a fine powder dispersed on the surface of the other reactant. Such a situation is rather difficult to visualize in the case of a dehydration reaction involving only a single reactant. Jander's model may, however, be appropriate in the case of a hydration reaction. It is likely that because of the reversibility of the dehydration process, water vapour liberated by material in the bulk of the sample rehydrates particles of anhydrous copper sulphate while diffusing out of the sample layer. These rehydrated particles will of course immediately be dehydrated because of the ambient temperature. The
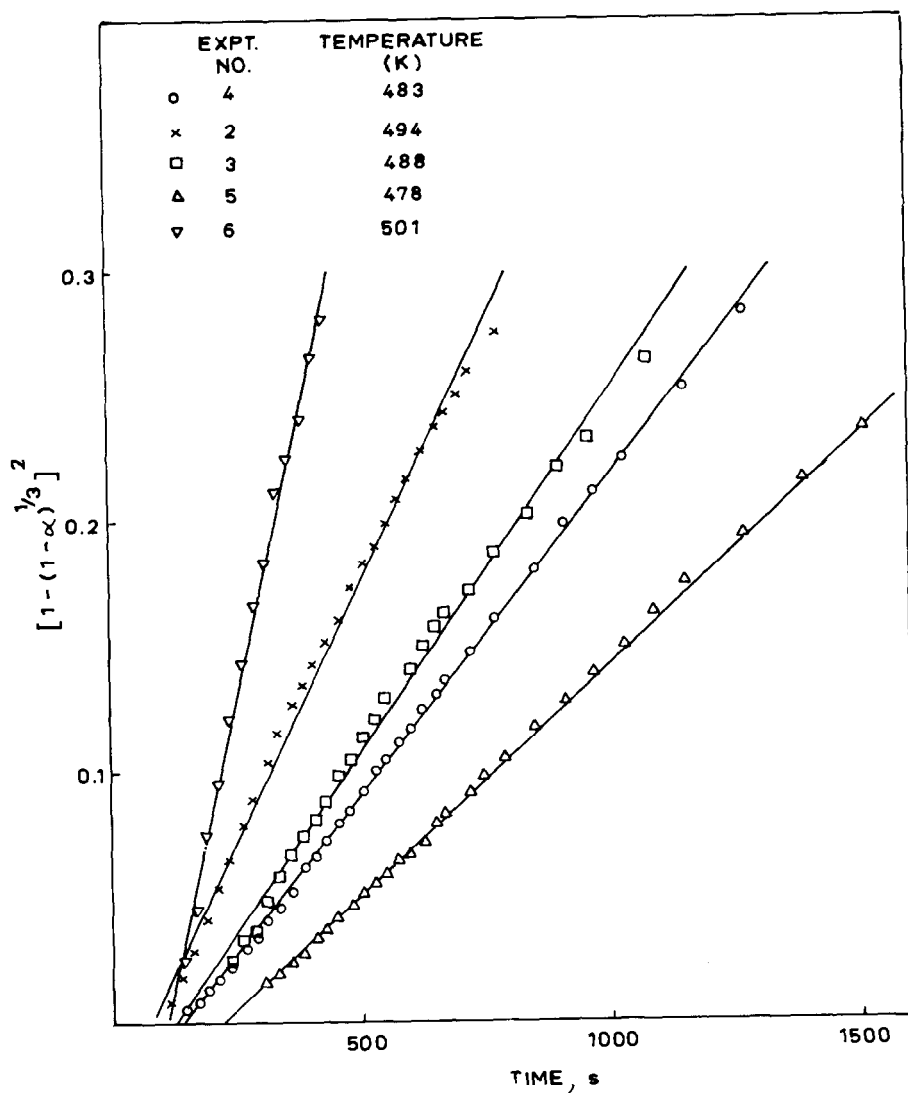
Fig. 1. Isothermal studies on dehydration of copper sulphate monohydrate.

endothermicity of the dehydration process will also contribute to such rehydration processes by lowering the temperature of the sample and, hence, the equilibrium vapour pressure of water over the hydrate. Thus, the overall dehydration reaction in an isothermal study may be proceeding through a multitude of dehydration and rehydration steps. The three-dimensional diffusion mechanism observed in this study may be indicative of the effects of rehydration and of the consequent impedance [10] to the diffusion of water vapour away from the sample particles on the shape of the isotherm.
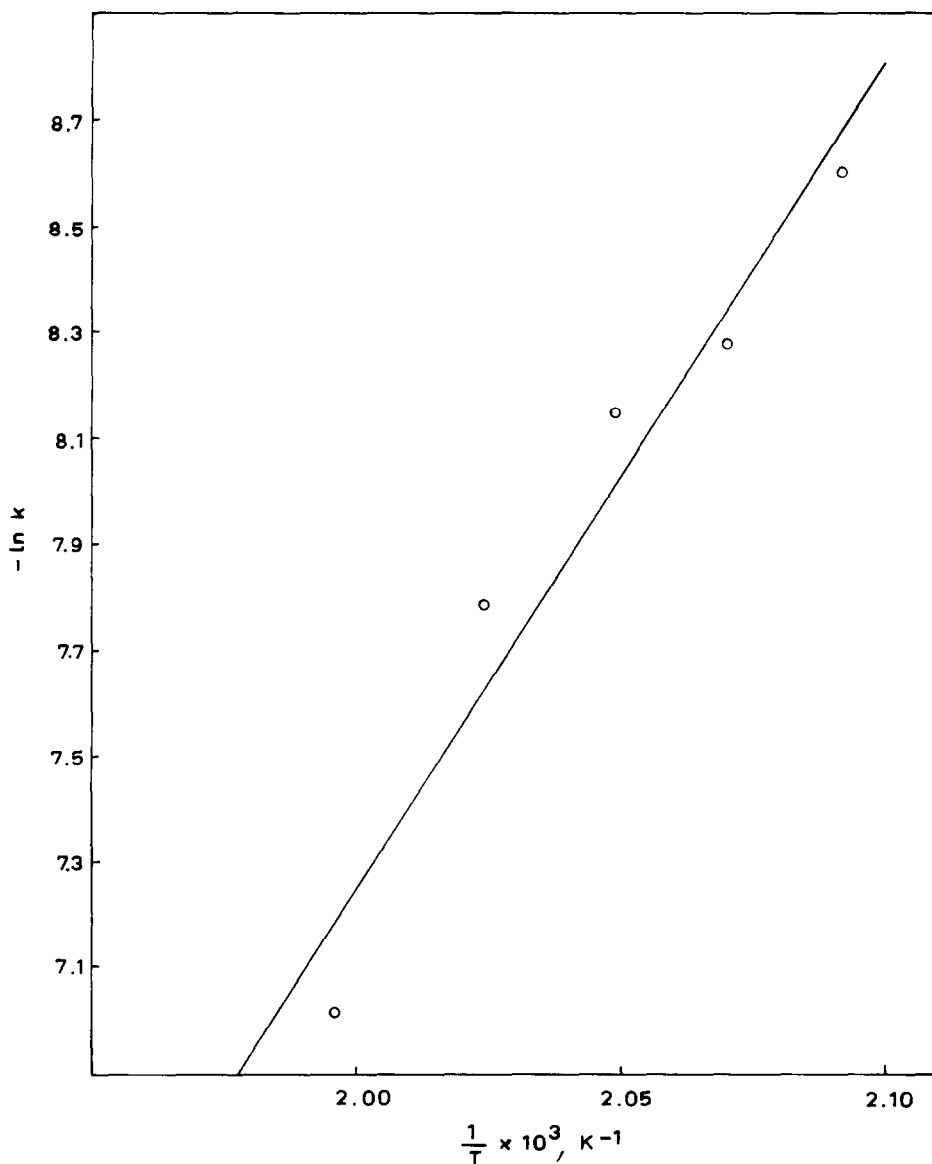
Fig. 2. Arrhenius plot from isothermal data for dehydration of copper sulphate monohydrate.

Non-isothermal studies

Typical DSC, TG and DTA curves for the reaction

$$CuSO_4 \cdot H_2O \rightarrow CuSO_4 + H_2O \qquad (4)$$

are presented in Fig. 3. The modified method of Zsako (loc. cit.) was used for analysis of all non-isothermal data.
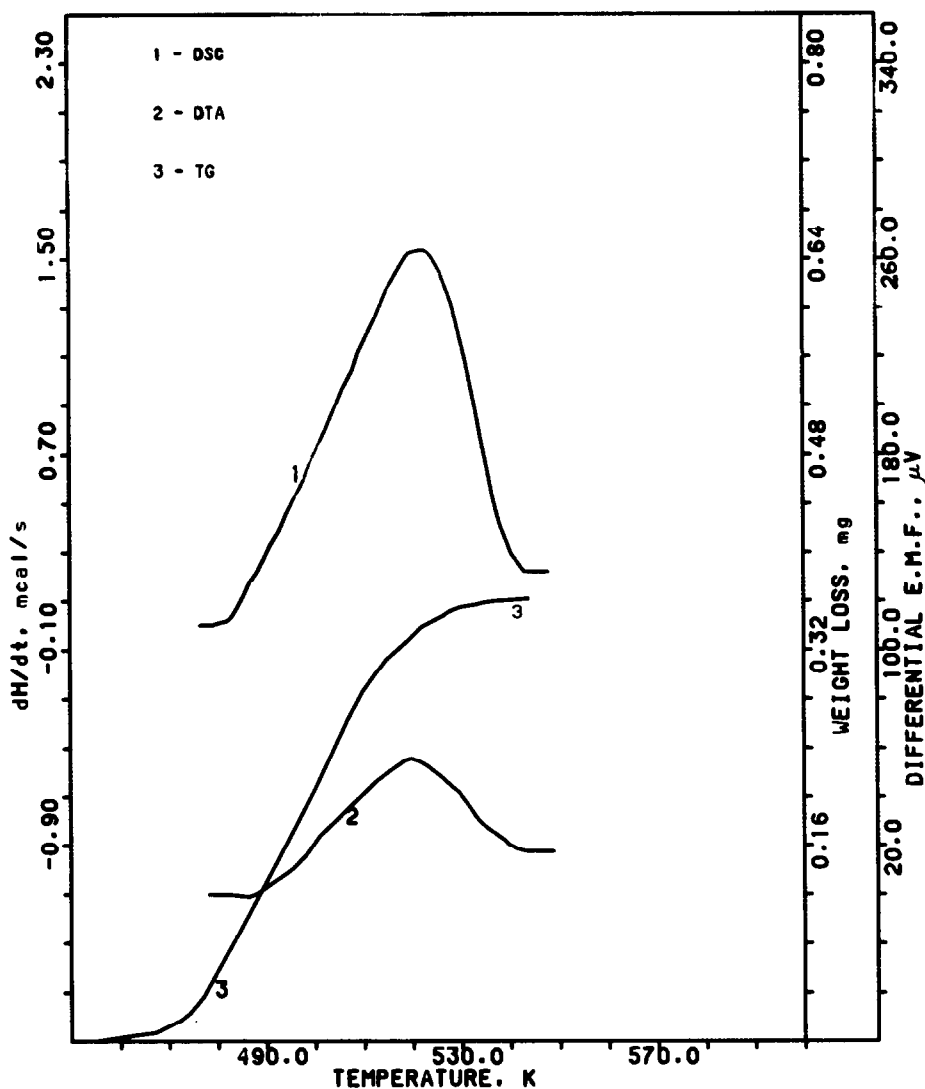
Fig. 3. DSC, DTA and TG curves for the dehydration of $CuSO_4 \cdot H_2O$.

DSC studies

The results from DSC studies are presented in Table 1. The reproducibility of the measurements was fairly good as indicated by the constancy of peak area per unit weight. The observed scatter in results may be due to poorly defined thermal contact between sample holder, sample pan and sample. The value of σ, given in the 7th column, corresponds to the minimum value of standard deviation of the difference $[\ln g(\alpha) - \ln p(x)]$, and serves as an index of agreement between experiment and theory [5], its value being ideally equal to zero for complete agreement. The variation of σ with different choices of reaction mechanism and activation energy in the

TABLE 1

Kinetic parameters for the dehydration of $CuSO_4 \cdot H_2O$—DSC study in flowing nitrogen

Sample weight [a] (mg)	Heating rate (K min^{-1})	Peak area (mJ)	Modified method of Zsako				Method of Piloyan et al.	
			E (kJ mol^{-1})	log Z [b]	$g(\alpha)$	σ	E (kJ mol^{-1})	log Z [b]
5.0	4.2	1230	205.9	18.86	$-\ln(1-\alpha)$	0.1836	256.1	24.11
5.0	8.5	1312	199.6	18.08	$-\ln(1-\alpha)$	0.0546	182.8	16.23
5.1	16.9	1255	189.5	17.08	$-\ln(1-\alpha)$	0.0667	187.4	16.79
10.1	4.2	2637	244.3	22.72	$-\ln(1-\alpha)$	0.0841	242.3	22.40
10.1	8.5	2693	181.2	15.99	$-\ln(1-\alpha)$	0.1016	184.9	16.28
10.0	16.8	2281	199.6	17.88	$-\ln(1-\alpha)$	0.0953	211.7	19.00
15.1	4.2	3930	218.4	19.91	$-\ln(1-\alpha)$	0.1305	233.5	21.40
15.0	8.4	4030	196.2	17.61	$-\ln(1-\alpha)$	0.1302	230.5	21.04
15.0	17.0	4133	213.0	19.18	$-\ln(1-\alpha)$	0.1075	222.6	21.40

[a] Initial weight of $CuSO_4 \cdot 5H_2O$.
[b] Z expressed in s^{-1}.

neighbourhood of E determined by the method of Piloyan and Novikova [11] is illustrated in Fig. 4. The theoretical and experimental values of α for experiments giving the lowest and highest values of σ are compared in Fig. 5.

The results (Table 1) show that the scatter in the E values is less if E is calculated by the modified method of Zsako (205.3 ± 18.5 kJ mol^{-1}) rather than by the method of Piloyan and Novikova (216.9 ± 26.8 kJ mol^{-1}). Values of E appear to be independent of sample weight and heating rate. The average value of the pre-exponential factor was 3.9×10^{18} s^{-1}. As the specimens were covered with the dome-shaped covers, interaction of the carrier gas (nitrogen) with the sample environment was not efficient and hence the copper sulphate monohydrate produced in situ from the corresponding pentahydrate would have dehydrated in the water-vapour-rich atmosphere resulting from the reactions represented in eqns. (2) and (3). It is interesting to note in this context that the activation energy calculated from the DSC curves is in good agreement with the value of 215.9 kJ mol^{-1} reported [9] for the dehydration of copper sulphate monohydrate produced in situ from the corresponding pentahydrate.

The results derived from the DSC studies are different from those obtained from isothermal studies, possibly because of the differences in impedance to dehydration under non-isothermal and isothermal conditions. The continually increasing temperature in the non-isothermal studies increases the equilibrium dissociation pressure of the hydrate and hence does not favour the rehydration reaction. In the isothermal studies, however, the equilibrium dissociation pressure is constant because of constant tempera-

b

SYMBOL $\quad g(\alpha)$

$\circ \quad -\ln(1-\alpha)$

$\square \quad 3\left[1-(1-\alpha)^{1/3}\right]$

$\triangledown \quad 2\left[1-(1-\alpha)^{1/2}\right]$

$\bullet \quad \alpha^{3/2}$

$\times \quad \left[-\ln(1-\alpha)\right]^{2/3}$

$\triangle \quad \dfrac{3}{2}\left[(1+\alpha)^{1/3}-1\right]^{2}$
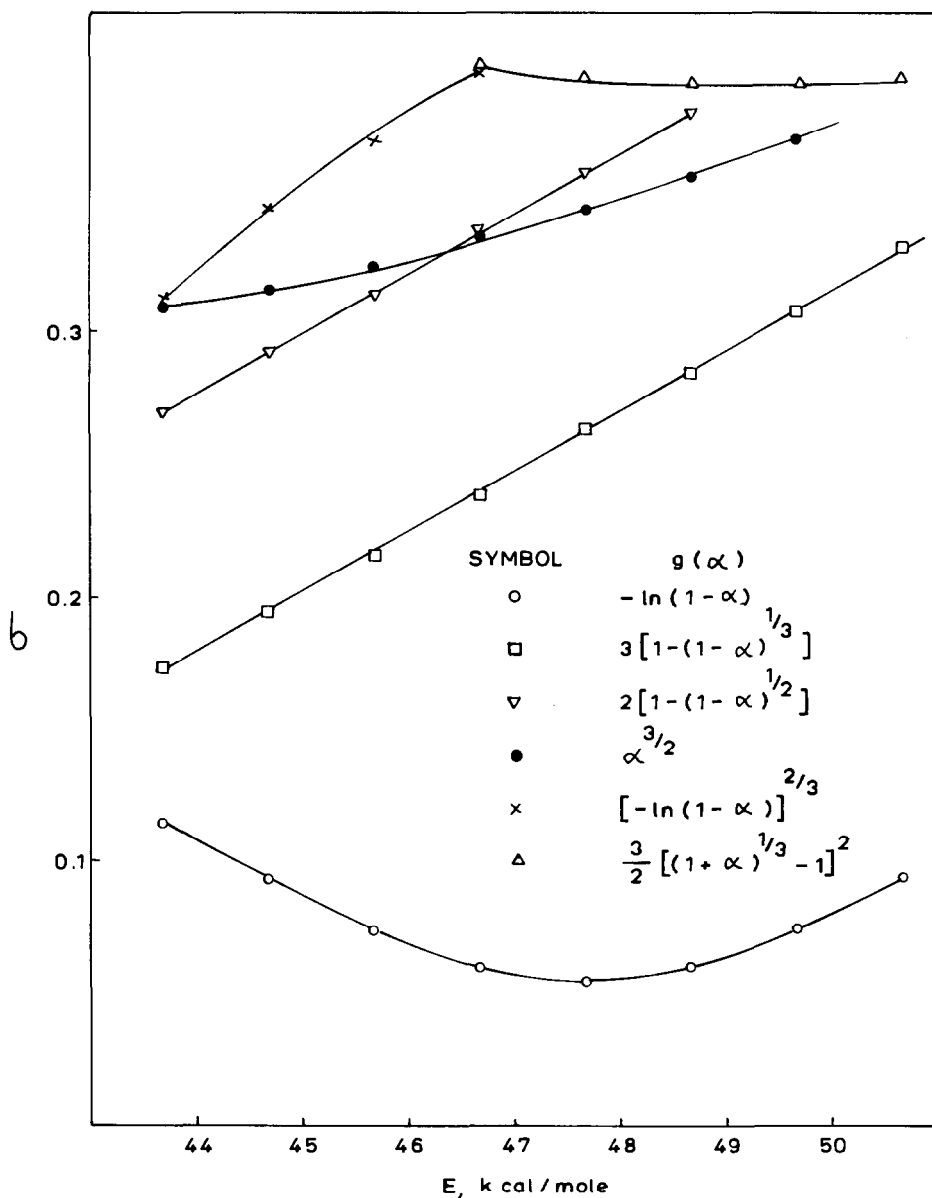
$E,\ kcal/mole$

Fig. 4. Variation of σ with activation energy and reaction mechanism—DSC study.

ture; unless the vapour pressure of water over the dehydrating particles is reduced below the equilibrium vapour pressure by diffusion away from the reaction interface or rehydration of already dehydrated particles (because of local temperature fluctuations due to the reaction), the reaction front cannot advance into the bulk of the particle.
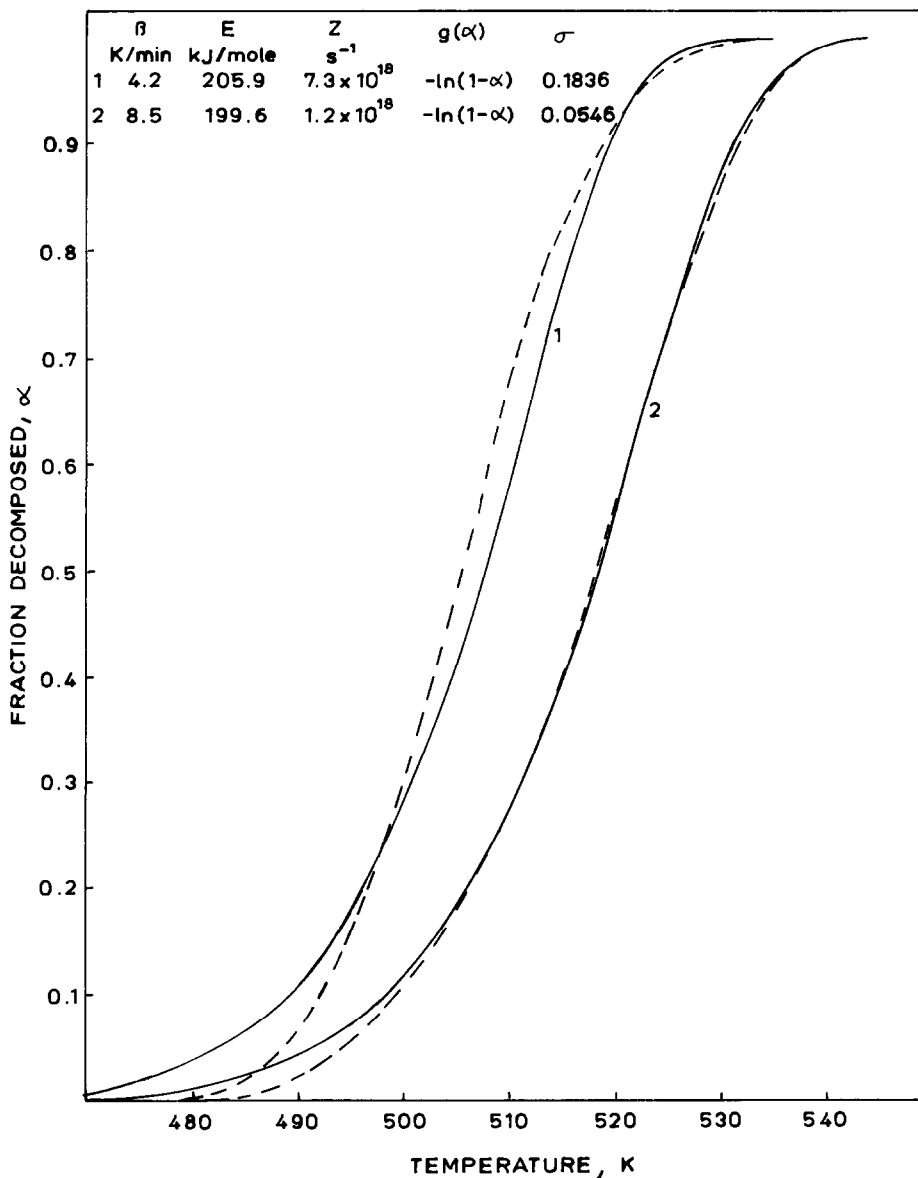
Fig. 5. Comparison between theoretical (full lines) and experimental (broken lines) curves for the dehydration of copper sulphate monohydrate—DSC study.

TG studies

The results of the thermogravimetric studies are summarized in Table 2. The analysis of data was restricted to the reaction range of 10–90%. The values of the kinetic parameters appear to be independent of the heating rate. Although the values of E (129.9 ± 10.9 kJ mol^{-1}) and Z (2.1 × 10^{11} ± 17.4 s^{-1}) calculated by the modified method of Zsako were in excellent

TABLE 2

Kinetic parameters for the dehydration of $CuSO_4 \cdot H_2O$—TG study in flowing argon

Sample weight [a] (mg)	Heating rate (K min^{-1})	Modified method of Zsako				Method of Piloyan et al.	
		E (kJ mol^{-1})	log Z [b]	$g(\alpha)$	σ	E (kJ mol^{-1})	log Z [b]
5.053	1.8	116.7	9.75	$-\ln(1-\alpha)$	0.1501	143.1	12.64
5.136	1.8	120.9	10.26	$-\ln(1-\alpha)$	0.1688	161.5	14.79
4.593	1.8	117.2	9.79	$-\ln(1-\alpha)$	0.1110	171.5	15.85
5.001	4.0	134.3	11.81	$-\ln(1-\alpha)$	0.1258	151.9	13.67
5.094	4.0	123.4	10.63	$-\ln(1-\alpha)$	0.0913	169.5	15.65
5.149	4.1	137.7	12.18	$-\ln(1-\alpha)$	0.1500	162.3	14.86
4.905	7.5	146.4	13.20	$-\ln(1-\alpha)$	0.1489	168.6	15.58
5.004	13.3	137.2	12.23	$-\ln(1-\alpha)$	0.1489	164.8	15.18
5.299	13.4	135.1	12.04	$-\ln(1-\alpha)$	0.0982	136.4	12.08
5.298 [c]	1.8	232.6	21.23	$-\ln(1-\alpha)$	0.1793	316.3	30.92

[a] Initial weight of $CuSO_4 \cdot 5H_2O$.
[b] Z expressed in s^{-1}.
[c] Experiment in static air atmosphere.

agreement with those obtained from isothermal studies, the TG curves, like the DSC curves, indicated that the reaction mechanism conformed with the model for random nucleation followed by growth of nuclei with only one nucleus on each particle. The better interaction between the sample and carrier gas as compared to that in the DSC studies, in view of the use of an open sample holder, ensured the efficient removal of the water vapour resulting from dehydration of higher hydrates and, hence, the activation energy derived from TG measurements was lower than that from DSC measurements. This was further confirmed by the data for a TG measurement carried out in static air (Table 2) which predictably yielded an activation energy value in close agreement with the results from DSC measurements.

The results of analysis of the TG curves recorded using sealed specimen holders are given in Table 3. The activation energy values derived from these studies were higher than those obtained from measurements with open sample holders, confirming the reversibility of the reaction. However, much significance could not be attached to these results because of the overlap of the dehydration of copper sulphate trihydrate with the monohydrate dehydration. The sample weight contained in the sealed holders seemed to markedly affect the shape of the TG curves. The value of the activation energy and the reaction mechanism obtained was in better agreement with those from DSC measurements when the sample weight was comparatively large. The mechanism of the reaction also seemed to be affected by the impedance to diffusion of water vapour.

TABLE 3

Kinetic parameters for the dehydration of $CuSO_4 \cdot H_2O$ in partially sealed sample holders. Atmosphere, argon flowing at 10 ml min^{-1}; heating rate, 4.3 K min^{-1}

Sample weight [a] (mg)	Modified method of Zsako				Method of Piloyan et al.	
	E (kJ mol^{-1})	log Z [b]	$g(\alpha)$	σ	E (kJ mol^{-1})	log Z [b]
2.1	387.0	37.04	$3/2[1-(1-\alpha)^{1/3}]^2$	0.3168	336.4	32.99
4.5	239.7	21.94	$3[1-(1-\alpha)^{1/3}]$	0.0456	261.9	25.69
9.5	235.1	21.75	$-\ln(1-\alpha)$	0.1005	249.8	23.18

[a] Initial weight of $CuSO_4 \cdot 5H_2O$.
[b] Z expressed in s^{-1}.

DTA studies

The data, presented in Table 4, indicated that the DTA measurements were fairly reproducible. The peak area (expressed in K s) per unit weight is a constant except for the last three entries corresponding to measurements with a different instrument (Netzsch Thermal Analyser, Model STA 409). The activation energy values and the pre-exponential factor calculated from the DTA curves varied inversely with the heating rate (Table 5). The DTA curves recorded at the fastest heating rate (14 K min^{-1}) indicated better agreement in the values of E and Z with those derived from TG and

TABLE 4

Kinetic parameters for the dehydration of $CuSO_4 \cdot H_2O$—DTA study in flowing argon

Sample weight [a] (mg)	Heating rate (K min^{-1})	Peak area (K s)	Modified method of Zsako				Method of Piloyan et al.	
			E (kJ mol^{-1})	log Z [b]	$g(\alpha)$	σ	E (kJ mol^{-1})	log Z [b]
24.2	13.7	253.1	151.5	12.52	$-\ln(1-\alpha)$	0.1398	190.4	12.24
24.8	14.0	342.6	165.7	14.04	$-\ln(1-\alpha)$	0.1397	203.3	14.18
25.0	14.4	272.5	169.0	11.84	$-\ln(1-\alpha)$	0.0902	176.6	11.83
25.0	7.1	325.5	236.0	21.51	$-\ln(1-\alpha)$	0.1079	251.0	20.43
25.2	7.5	266.0	215.1	19.63	$-\ln(1-\alpha)$	0.0417	214.2	15.93
25.0	7.6	306.8	232.6	21.20	$-\ln(1-\alpha)$	0.1092	248.5	19.18
24.8	7.7	239.4	239.7	22.18	$-\ln(1-\alpha)$	0.0486	228.4	17.36
25.2 [c]	1.9	546.1	259.4	23.94	$-\ln(1-\alpha)$	0.1337	297.9	24.85
24.9 [c]	2.0	499.1	278.7	26.00	$-\ln(1-\alpha)$	0.1026	291.6	24.23
24.9 [d]	1.8	567.1	337.6	33.04	$-\ln(1-\alpha)$	0.0686	324.7	28.34

[a] Initial weight of $CuSO_4 \cdot 5H_2O$.
[b] Z expressed in s^{-1}.
[c] Experiment with Netzsch Thermal Analyser, sample diluted with calcined Al_2O_3.
[d] Experiment with Netzsch Thermal Analyser, sample not diluted.

TABLE 5

Dependence of kinetic parameters calculated from DTA curves for the dehydration of $CuSO_4 \cdot H_2O$ on heating rate. Atmosphere, argon flowing at 10 ml min^{-1}; initial sample weight, 25 ± 0.2 mg; method of analysis, the modified method of Zsako

Heating rate (K min^{-1})	Average values of kinetic parameters			
	E (kJ mol^{-1})	Standard deviation of E (kJ mol^{-1})	log Z [a]	Standard deviation of log Z
14.0	162.1	9.3	12.82	1.12
7.5	230.9	10.9	21.13	0.09
1.9	269.1	13.6	24.97	1.44

[a] Z expressed in s^{-1}.

isothermal studies than did the curves recorded at the slowest heating rate (2 K min^{-1}). The results from experiments at a given heating rate demonstrated that the internal consistency of the data was comparable to that in the TG and DSC studies.

The results of an experiment carried out without using a diluent (calcined alumina) indicated (Table 4) that mixing of the sample ($\sim$ 25 mg) with alumina ($\sim$ 175 mg) reduced the activation energy of dehydration presumably because alumina acted as an adsorbent for water vapour and brought down the partial pressure of water vapour in the immediate vicinity of unreacted particles of copper sulphate monohydrate. Thus, it is apparent that the variation of activation energy and pre-exponential factor observed in DTA, in contrast with DSC or TG, is due to a more pronounced variation in the partial pressure of water vapour in the immediate vicinity of the dehydrating sample particles. The use of comparatively large samples inhibiting the diffusion of water vapour produced by the dehydration of sample in the lower layers is a possible reason for such a marked variation in the partial pressure of water vapour.

One of the consequences of a decrease in the heating rate is the decrease in the temperature span of the reaction. In other words, within a given temperature interval, more sample is dehydrated at a slow heating rate than at a fast heating rate. Hence, if the non-isothermal curve is considered as a sum total of a number of infinitesimal isothermal steps [12], these component isotherms, especially those corresponding to the decay portion of a DTA curve obtained at a slow heating rate, will have to be recorded at a higher partial pressure of water vapour than the component isotherms of a DTA curve recorded at a high heating rate. Dehydration under a higher partial pressure of water vapour will, in turn, result in a higher activation energy and hence it is not surprising that the DTA curves recorded at slow heating rates lead to higher activation energy values in comparison to those

recorded at fast heating rates. However, such effects will only be manifested if the size and layer thickness of the sample are sufficiently large to impede the diffusion of water vapour evolved away from the immediate vicinity of unreacted particles.

CONCLUSIONS

It is apparent from the studies reported here that non-isothermal methods do not necessarily yield the same kinetic parameters as derived using isothermal methods. In the present study on the dehydration of copper sulphate monohydrate, the reaction mechanism inferred from the various non-isothermal studies was invariably random nucleation in accordance with Mampel's law for unimolecular decay. The isothermal measurements, on the other hand, indicated that the reaction mechanism was three-dimensional diffusion in accordance with Jander's law. The analysis of experimental data reported here indicates that such discrepancies arise because of the differences in impedance to the removal of water vapour from the reaction interface under isothermal and non-isothermal conditions. The impedance, resulting from the possibility of a recombination reaction, will be less in a non-isothermal than in an isothermal experiment because of the continuous increase in the equilibrium vapour pressure of product gas in dynamic temperature studies.

In the case of non-isothermal studies, the following seem to be the conditions necessary for a fairly consistent set of kinetic parameters independent of heating rate: the use of small samples in open specimen holders; the use of an inert carrier gas to efficiently flush out the gases produced from the immediate vicinity of the reacting particles; and the use of the modified method of Zsako (loc. cit.) for the data analysis. These conditions can be best satisfied in thermogravimetric measurements using a sensitive thermobalance.

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