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DEHYDRATION OF CRYSTALLINE $CoSO_4 \cdot 7H_2O$

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ABSTRACT

The thermal dehydration of crystalline cobalt sulphate heptahydrate grown at 40 ± 1°C was studied using dynamic and isothermal TG measurements. The dynamic TG measurements show that the heptahydrated cobalt sulphate dehydrates in four steps of 1 mol, 3 mol, 2 mol and 1 mol at mean temperatures of 107.5, 140, 165 and 310°C respectively. Isothermal TG measurements (dependent on temperature) show a different dehydration pattern with respect to time. In the temperature range 280–310°C, two dehydration steps (one of 6 mol and the other of 1 mol) are observed. From the dynamic and isothermal TG measurements the kinetic parameters E and Z were calculated. The general mechanism of dehydration is random nucleation and growth for the different steps in the two measurements. The study shows that E and Z values from the two measurements are not sufficient to indicate the proper form of $F(\alpha)$ which describes this mechanism.

INTRODUCTION

Crystals of cobalt sulphate grown below 40.6°C are heptahydrate in nature and those grown above this temperature are hexahydrate in nature [1]. Ben Dor and Margalith [2] have reported the sequence of dehydration steps for many polyhydrated metal sulphates as consisting of two steps. All except one molecule of water are released at a low temperature and the last molecule is evolved after a significant rise in temperature. Nandi et al. [3] have given the sequence of dehydration in $CoSO_4 \cdot 7H_2O$ and $CoSO_4 \cdot 6H_2O$ as 1 mol, 3 mol, 2 mol and 1 mol at 119.6, 161.7, 184.7 and 294.5°C and 1 mol, 2 mol, 2 mol and 1 mol at 108.8, 161.7, 187 and 301.6°C respectively. In this paper the kinetic parameters E and Z are reported from isothermal and dynamic measurements and the mechanism of dehydration is indicated.

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EXPERIMENTAL

AnalaR grade cobalt sulphate was obtained from Merck. Heptahydrated cobalt sulphate crystals were grown by slow evaporation of the aqueous solution. The temperature of the solution was maintained at 40 ± 1° C. The thermogravimetric (TG) study was carried out in the TG assembly fabricated in the laboratory; details are given elsewhere [4]. The measurement of mass loss was carried out in the temperature range 30–500° C; the heating rate was 5° C min^{-1}. The value of $\Delta m/\Delta t$, i.e. rate of change of mass (mg min^{-1}) was calculated at different temperatures. The change in mass vs. temperature (TG) and the rate of change of mass vs. temperature (differential thermogravimetry, DTG) curves were plotted. The isothermal measurements of the loss of mass were carried out over two temperature ranges, (1) 130, 140, 150 and 160° C and (2) 280, 290, 300 and 310° C; the temperature was maintained constant to within ±1° C.

RESULTS AND DISCUSSION

Figure 1 shows representative curves (TG and DTG) for the sequence of dehydration steps in crystalline $CoSO_4 \cdot 7H_2O$ grown at 40° C. The DTG maxima occur at mean temperatures of 107.5 ± 7.5, 140 ± 5, 165 ± 5 and 310 ± 5° C giving the sequence of dehydration as 1 mol, 3 mol, 2 mol and 1 mol respectively. For a crystal of mass 371 mg, the observed loss in mass corresponds to the liberation of 7 water molecules.

The dynamic TG measurements show the following scheme of dehydration in $CoSO_4 \cdot 7H_2O$ with respect to temperature.

$$CoSO_4 \cdot 7H_2O \xrightarrow{107.5^\circ C} CoSO_4 \cdot 6H_2O + H_2O$$

$$CoSO_4 \cdot 6H_2O \xrightarrow{140^\circ C} CoSO_4 \cdot 3H_2O + 3H_2O$$

$$CoSO_4 \cdot 3H_2O \xrightarrow{165^\circ C} CoSO_4 \cdot H_2O + 2H_2O$$

$$CoSO_4 \cdot H_2O \xrightarrow{310^\circ C} CoSO_4 + H_2O$$

The number of dehydration steps in $CoSO_4 \cdot 7H_2O$ observed in this study and those observed by Nandi et al. [3] agree well, although there are slight differences in dehydration temperatures. These differences may have occurred due to the different crystal mass (size) in the two studies. When crystals of different masses are studied then slight differences in dehydration temperatures are observed. This effect has also been observed by Dharwadkar and Phadnis [5].

From the mass loss α the fraction dehydrated at a particular temperature T can be calculated. Figure 2 shows an α vs. temperature plot for a crystal

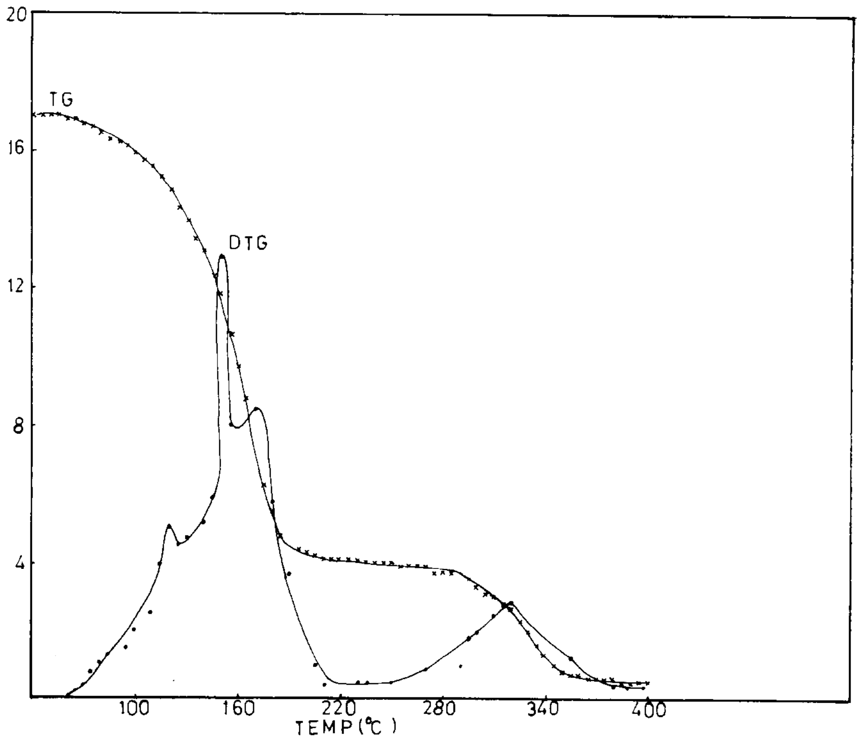

Fig. 1. TG and DTG curves of the thermal analysis of crystalline $CoSO_4 \cdot 7H_2O$.

of mass 327 mg. This curve shows four different regions with changing slopes, indicating four dehydration steps. Using the Coats and Redfern equation [6] the activation energy E and the frequency factor Z can be calculated. In the Coats and Redfern equation

$$\ln[F(\alpha)/T^2] = \ln(ZR/\phi E)[1-(2RT/E)] - (E/RT) \qquad (1)$$

T is the absolute temperature, Z is the frequency factor, R is the gas constant, ϕ is the linear heating rate and E is the activation energy. In the above equation $F(\alpha) = [-\log(1-\alpha)]^n$ (where $n = 1$, 0.66, 0.5, 0.4, 0.33 or 0.25). Figure 3 shows a typical plot of $F(\alpha)$ vs. $1/T$. It can be seen from the figure that all the functions give four linear plots again indicating the four dehydration steps. The activation energy and frequency factor calculated from these plots are given in Table 1. It can also be observed from the $F(\alpha)$ vs. $1/T$ plots that in between the third and fourth dehydration steps there is a region with an opposite slope. This linear plot has no meaning, as between the third and fourth dehydration steps there is very little loss in mass of the crystal with respect to temperature as is evident from Fig. 1.

It has been pointed out by Criado and Morales [7] from their theoretical analysis that the linearity of $-\ln[F(\alpha)/T^2]$ vs. $1/T$ in a dynamic TG study

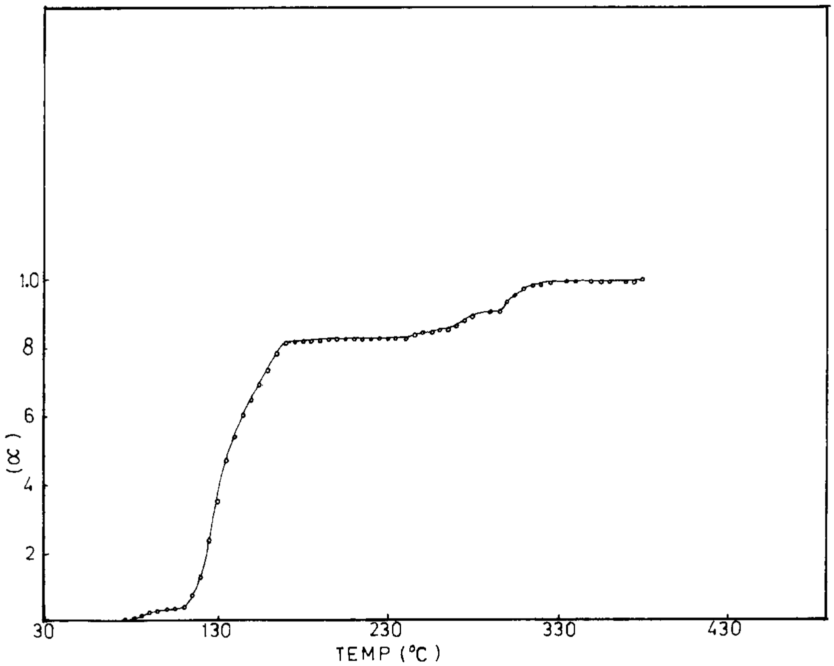

Fig. 2. Plot of α vs. T for crystalline $CoSO_4 \cdot 7H_2O$.

is a necessary, but not a sufficient criterion for assigning $F(\alpha)$. They have reiterated the necessity of recording at least one isothermal measurement of the same reaction in the temperature interval of the TG measurement in order to assign the proper form of $F(\alpha)$. The same point of view has also been expressed by other workers [7–9].

As mentioned earlier, the isothermal TG measurements were carried out over two different temperature ranges, 130–160 °C and 280–310 °C. Figure 4 shows a representative plot of α vs. time. It can be seen from Fig. 4(a) that for the loss of six water molecules the time required at 130 °C is 65 min, at 140 °C is 50 min, at 150 °C is 38 min and at 160 °C is 25 min. The higher the isothermal temperature, the shorter is the time required for the loss of six water molecules. It can also be seen from the figure that at 130 °C the curve has a slightly different shape than the curves at 140, 150 and 160 °C.

Figure 4(b) shows a plot of α vs. time in the temperature range 280–310 °C. It can be seen from this figure that after the loss of six water molecules at a very rapid rate, the seventh water molecule is lost steadily. At lower temperatures the time required for complete dehydration is greater than at higher temperatures.

The kinetic parameters E and Z can be calculated from the isothermal mass loss measurements by assuming that the equation

$$d\alpha/dt = Kf(\alpha) \tag{2}$$

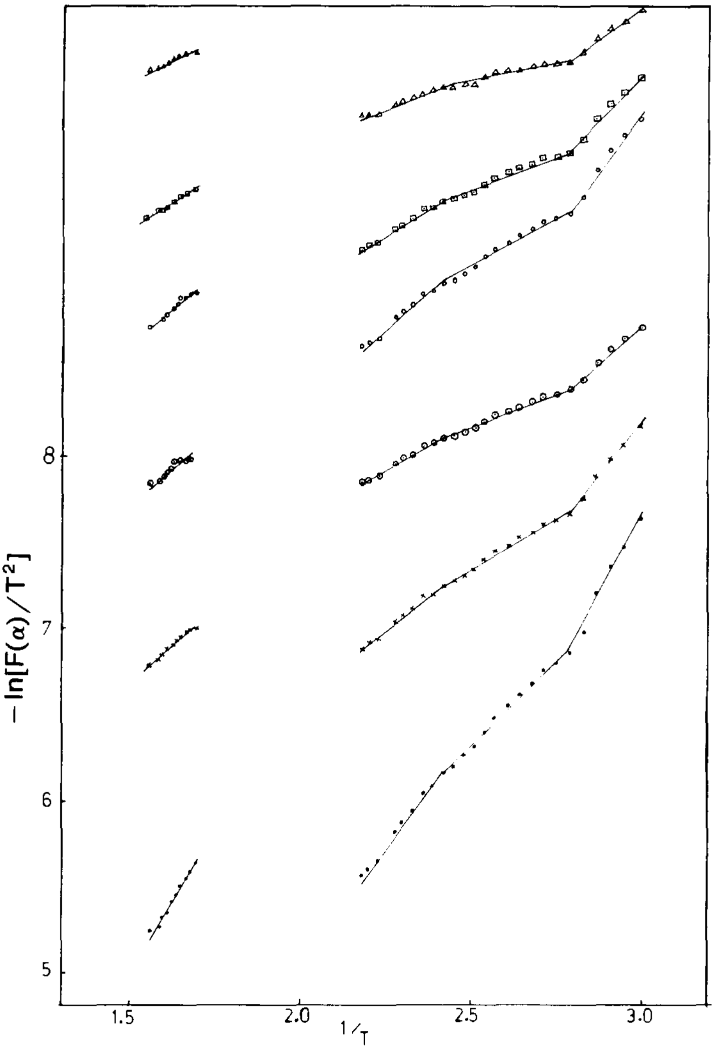

Fig. 3. Plots of $-\ln[F(\alpha)/T^2]$ vs. $1/T$ for the thermal dehydration of crystalline $CoSO_4 \cdot 7H_2O$ (dynamic): ●, $n = 1$; ×, $n = 0.66$; ⊙, $n = 0.5$; ○, $n = 0.4$; ⊡, $n = 0.33$; △, $n = 0.25$. The scale marked along the y axis is for ●; for the other functions the scale was changed appropriately to draw the remaining curves.

holds for the thermal dehydration of $CoSO_4 \cdot 7H_2O$ [10]. Here, α is the fraction of reactant dehydrated at time t and K is the rate constant. The integration of eqn. (2) gives

$$F(\alpha) = \int d\alpha/f(\alpha) = Kt = tZ\,e^{-E/RT} \qquad (3)$$

The function $F(\alpha)$ which describes the mechanism of isothermal dehydration can be determined by plotting various theoretical functions against t;

TABLE 1

Functions $F(\alpha)$ and kinetic parameters for the thermal dehydration of $CoSO_4 \cdot 7H_2O$ from dynamic TG

$F(\alpha)$	E (kcal mol^{-1})				Z (s^{-1})				Dehydration temperature (°C)			
	Step 1	Step 2	Step 3	Step 4	Step 1	Step 2	Step 3	Step 4	Step 1	Step 2	Step 3	Step 4
$-\log(1-\alpha)$	16.99 ± 0.42	16.38 ± 0.20	11.23 ± 0.71	13.76 ± 1.70	$(1.22 \pm 0.74) \times 10^{21}$	$(5.77 \pm 2.98) \times 10^{18}$	$(1.70 \pm 0.75) \times 10^{14}$	$(1.74 \pm 0.55) \times 10^{14}$	107.5	140	165	310
$-\log(1-\alpha)^{0.66}$	10.46 ± 1.36	10.22 ± 0.70	7.28 ± 0.61	10.01 ± 1.36	$(1.26 \pm 0.79) \times 10^{16}$	$(3.73 \pm 1.32) \times 10^{14}$	$(8.76 \pm 2.40) \times 10^{11}$	$(3.33 \pm 0.86) \times 10^{12}$	±7.5	±5	±5	±5
$-\log(1-\alpha)^{0.5}$	8.80 ± 0.90	7.96 ± 0.22	4.85 ± 0.40	7.39 ± 0.85	$(2.80 \pm 1.00) \times 10^{16}$	$(1.03 \pm 0.29) \times 10^{13}$	$(3.24 \pm 0.57) \times 10^{10}$	$(2.15 \pm 0.39) \times 10^{11}$				
$-\log(1-\alpha)^{0.4}$	5.31 ± 0.20	5.15 ± 1.32	3.18 ± 0.61	4.89 ± 0.57	$(6.85 \pm 2.38) \times 10^{16}$	$(1.55 \pm 0.53) \times 10^{11}$	$(3.62 \pm 0.37) \times 10^{9}$	$(8.30 \pm 0.67) \times 10^{9}$				
$-\log(1-\alpha)^{0.33}$	4.70 ± 0.20	4.55 ± 0.20	2.50 ± 0.23	5.16 ± 0.81	$(1.94 \pm 0.53) \times 10^{11}$	$(4.90 \pm 1.31) \times 10^{10}$	$(1.70 \pm 0.11) \times 10^{9}$	$(1.10 \pm 0.07) \times 10^{10}$				
$-\log(1-\alpha)^{0.25}$	3.52 ± 0.17	1.97 ± 0.81	1.82 ± 0.45	2.73 ± 0.91	$(1.97 \pm 0.40) \times 10^{10}$	$(1.59 \pm 0.09) \times 10^{9}$	$(2.37 \pm 0.56) \times 10^{9}$	$(2.82 \pm 0.37) \times 10^{9}$				

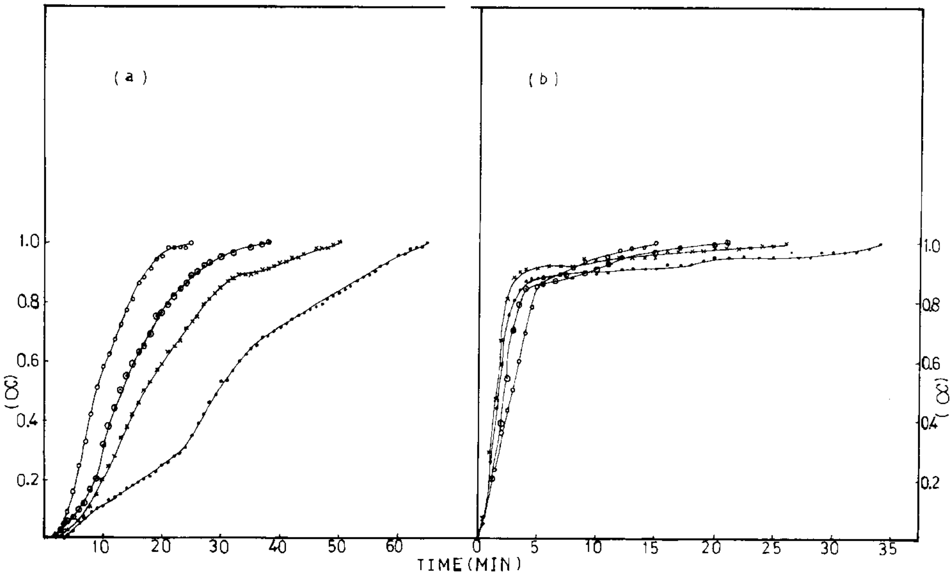

Fig. 4. Plots of fraction dehydrated vs. time: (a) ●, 130 °C; ×, 140 °C; ⊙, 150 °C; ○, 160 °C. (b) ●, 280 °C; ×, 290 °C; ⊙, 300 °C; ○, 310 °C.

the correct function should give a straight line with slope K [11]. The functions used in this study are as follows: $-\ln(1-\alpha)$; $[-\ln(1-\alpha)]^{2/3}$; $[-\ln(1-\alpha)]^{1/2}$; $[-\ln(1-\alpha)]^{2/5}$; $[-\ln(1-\alpha)]^{1/3}$; $[-\ln(1-\alpha)]^{1/4}$. Typical plots of $F(\alpha)$ vs. time at temperatures 130–160 °C and 280–310 °C are shown in Figs. 5(a) and 5(b) respectively. It can be seen from the figures that all the functions give straight line plots. In the 130–160 °C range there are two linear regions, with the exception of 130 °C where there are three linear regions. These two regions correspond to the loss of three molecules of water each. However, at 130 °C, the loss corresponds to 2 mol, 3 mol and 1 mol of water of crystallization. In the temperature range 280–310 °C there are two linear regions. The first region indicates the loss of six water molecules in one step and the second region indicates the loss of the remaining one molecule. Thus if dehydration in the temperature range 130–160 °C is considered then $CoSO_4 \cdot 7H_2O$ dehydrates with respect to time in the following fashion

$$CoSO_4 \cdot 7H_2O \xrightarrow{12\ \text{min}} CoSO_4 \cdot 4H_2O + 3H_2O \xrightarrow{6\ \text{min}} CoSO_4 \cdot H_2O + 3H_2O$$

$(T = 160\ °C)$

In the temperature range 280–310 °C the mass loss measurement with time suggests the dehydration scheme

$$CoSO_4 \cdot 7H_2O \xrightarrow{5\ \text{min}} CoSO_4 \cdot H_2O + 6H_2O \xrightarrow{8\ \text{min}} CoSO_4 + H_2O$$

$(T = 310\ °C)$

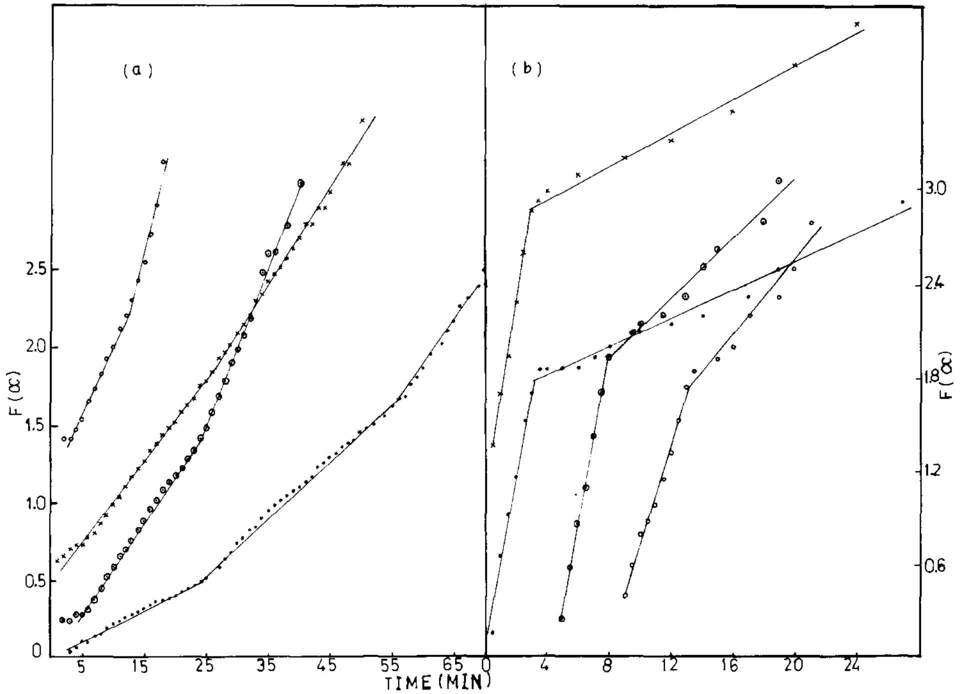

Fig. 5. Plots of $F(\alpha)$ (isothermal) vs. time for a function $F(\alpha) = [-\log(1-\alpha)]^{0.66}$ at: (a) 130, 140, 150 and 160 ° C; (b) 280, 290, 300 and 310 ° C (●, 130 and 280 ° C; ×, 140 and 290 ° C; ⊙, 150 and 300 ° C; ○, 160 and 310 ° C). The scale marked along the y axis is for ●; for the other temperatures the scale is changed appropriately. The scale along the x axis is changed appropriately in (b) for ⊙ and ○.

TABLE 2

Functions $F(\alpha)$ and kinetic parameters for the thermal dehydration of $CoSO_4 \cdot 7H_2O$ from isothermal TG

$F(\alpha)$	Step	Temperature range 130–160 ° C		Temperature range 280–310 ° C	
		E	Z	E	Z
$-\log(1-\alpha)$	1	8.69	45.2 ± 3.25	11.86	$(46.03 \pm 2.45) \times 10^1$
	2	16.20	$(62.34 \pm 3.94) \times 10^4$	32.60	$(1.12 \pm 0.08) \times 10^{10}$
$-\log(1-\alpha)^{0.66}$	1	11.46	$(10.70 \pm 2.26) \times 10^2$	5.93	1.78 ± 0.15
	2	17.97	$(36.38 \pm 1.65) \times 10^5$	27.66	$(58.40 \pm 3.95) \times 10^6$
$-\log(1-\alpha)^{0.5}$	1	11.06	$(40.72 \pm 3.09) \times 10^1$	5.93	1.28 ± 0.02
	2	11.06	$(52.85 \pm 1.95) \times 10^1$	28.65	$(8.7 \pm 0.6) \times 10^7$
$-\log(1-\alpha)^{0.4}$	1	11.26	$(49.65 \pm 5.85) \times 10^1$	5.93	1.28 ± 0.02
	2	17.97	$(15.42 \pm 1.42) \times 10^5$	20.74	$(5.64 \pm 0.25) \times 10^4$
$-\log(1-\alpha)^{0.33}$	1	10.47	$(24.20 \pm 2.41) \times 10^1$	5.93	1.24 ± 0.03
	2	11.85	$(8.45 \pm 0.07) \times 10^2$	30.62	$(2.75 \pm 0.32) \times 10^8$
$-\log(1-\alpha)^{0.25}$	1	7.70	9.21 ± 0.35	8.89	14.78 ± 0.01
	2	8.09	6.77 ± 0.1	29.64	$(9.50 \pm 0.4) \times 10^7$

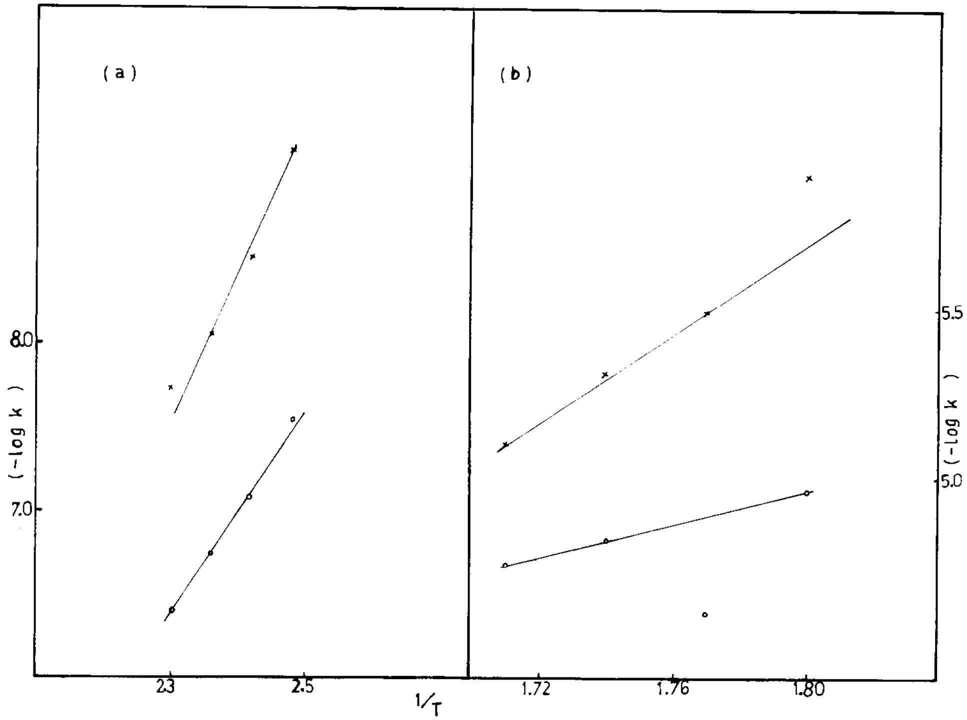

Fig. 6. The Arrhenius plots for the isothermal dehydration of crystalline $CoSO_4 \cdot 7H_2O$ for $F(\alpha) = [-\log(1-\alpha)]^{0.66}$. (a) In the temperature range 130–160 ° C; O, first dehydration step of 3 mol; ×, second dehydration step of 3 mol. (b) In the temperature range 280–310 ° C: O, first dehydration step of 6 mol; ×, second dehydration step of 1 mol (the scale marked along the y axis is for the first step; for the second step the scale is changed).

Typical plots of $-\log K$ vs. $1/T$ for the two temperature ranges are shown in Figs. 6(a) and 6(b). The activation energy E and frequency factor Z were calculated in terms of the Arrhenius equation for the different dehydration steps and are tabulated in Table 2.

As suggested earlier, to find the correct dehydration mechanism, the E and Z values from the dynamic and isothermal TG measurements are compared. It is observed that they do not agree for any step. This disagreement may be due to the following reasons: (1) the dehydration steps are different in the dynamic and isothermal measurements; (2) the time available for dehydration is different in the isothermal and dynamic studies; (3) the amount of water vapour pressure built up inside the crystal is different due to the different times available for dehydration; (4) the number of paths available for dehydration is different.

In an earlier paper [12] it was suggested that the criterion of agreement between the E and Z values obtained from isothermal and dynamic TG measurements for determining the proper form of $F(\alpha)$, and thereby the mechanism of dehydration, may not be applicable to crystals with molecules of water of crystallization numbering greater than two. The dehydration study on $CoSO_4 \cdot 7H_2O$ further substantiates this observation. However, this study shows that the possible mechanism for dehydration is random nucleation and subsequent growth. The same mechanism is described by different functions in isothermal and dynamic measurements.

CONCLUSIONS

It is concluded from the DTG study that $CoSO_4 \cdot 7H_2O$ dehydrates in four steps of 1 mol, 3 mol, 2 mol and 1 mol at mean temperatures of 107.5, 140, 165 and 310 °C respectively. In contrast the isothermal study shows that, in the temperature range 130–160 °C, there are two distinct steps of dehydration of 3 mol each. In the temperature range 280–310 °C two dehydration steps comprising 6 mol and 1 mol are observed.

For the $CoSO_4 \cdot 7H_2O$ crystal the general mechanism of dehydration for all steps is random nucleation and subsequent growth.

As mentioned earlier Ben Dor and Margalith [2] have suggested that there are only two steps of dehydration in many polyhydrated metal sulphates. Our isothermal study in the temperature range 280–310 °C also shows only two steps, which indicate the presence of only three stable phases in $CoSO_4 \cdot 7H_2O$: $CoSO_4 \cdot 7H_2O$, $CoSO_4 \cdot H_2O$ and $CoSO_4$. The other phases observed in the dynamic study may be transitional phases only.

REFERENCES

1 I. Koppel and H. Wetzel, Z. Phys. Chem., 52 (1905) 395.
2 L. Ben Dor and R. Margalith, Inorg. Chim. Acta, 1 (1967) 49.
3 P.N. Nandi, V.G. Kher and D.A. Deshpande, Thermochim. Acta, 41 (1980) 241.
4 P.N. Nandi, D.A. Deshpande and V.G. Kher, Proc. Indian Acad. Sci., Sect. A, 88 (1979) 130.
5 S.R. Dharwadkar and A.B. Phadnis, Indian J. Chem., 7 (1969) 1032.
6 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
7 J.N. Criado and J. Morales, Thermochim. Acta, 16 (1976) 312.
8 D.A. Deshpande, K.R. Ghormare and N.D. Deshpande, Thermochim. Acta, 60 (1983) 295.
9 S.R. Dharwadkar, M.S. Chandrasekharaiab and M.D. Kharkhanwala, Thermochim. Acta, 25 (1978) 372.
10 H. Tanaka, Thermochim. Acta, 43 (1981) 289.
11 K.J. Laidler, Chemical Kinetics, McGraw-Hill, New York, 1965.
12 D.A. Deshpande, S.G. Sinha and N.D. Deshpande, Thermochim. Acta, 113 (1987) 95.