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DEHYDRATION OF CRYSTALLINE $MnSO_4 \cdot 4H_2O$

S.G. SINHA and N.D. DESHPANDE

Physics Department, Institute of Science, Nagpur 440 001 (India)

D.A. DESHPANDE

Physics Department, V.M.V. Commerce, J.M.T. Arts and J.J.P. Science College, Wardhamannagar, Nagpur 440 008 (India)

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ABSTRACT

Tetrahydrated manganese sulphate crystals have been grown by slow evaporation of an aqueous solution maintained at 40 ± 1°C. The thermal dehydration of this crystal has been studied by dynamic and isothermal TG measurements. It is observed from dynamic TG that the tetrahydrated Mn sulphate dehydrates in two steps releasing two molecules each at mean temperatures of 172 and 340°C. Isothermal TG measurements, dependent upon temperature, show different dehydration patterns with respect to time. From isothermal and dynamic TG measurements, the kinetic parameters E and Z have been calculated. It is observed that the general mechanism of dehydration in this crystal for both steps is random nucleation and growth. The proper form of the $F(\alpha)$ function which describes this mechanism is different in isothermal and dynamic studies.

INTRODUCTION

It has been found previously from solubility measurements [1] that manganese sulphate exists in four different phases at room temperature: mono-, tetra-, penta- and heptahydrate. If the saturated solution is maintained above 27°C, tetrahydrated manganese sulphate is formed. When hydrated manganese sulphate is heated to redness it forms the anhydrous salt. Thorpe and Watts [2] found that the anhyddrous salt is formed when the hydrate is heated to 280°C and Krepelka and Rejha [3] have shown that the salt is anhydrous at 450°C. A literature survey shows that very little work has been carried out on the dehydration of manganese sulphate in general and mechanism of dehydration in particular. The present paper deals with the dehydration of manganese sulphate tetrahydrate and its mechanism of dehydration.

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EXPERIMENTAL

AR grade manganese sulphate was obtained from M/s E Merck. Tetrahydrated manganese sulphate crystals were grown by slow evaporation of its aqueous solution. The temperature of the solution was maintained at 40 ± 1°C.

A thermogravimetric (TG) study was carried out using the TG assembly fabricated in the laboratory, details of which are given elsewhere [4]. The measurement of mass loss was carried out in the temperature range 30–500°C. The crystals were heated at a rate of 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 versus temperature (TG) and rate of change of mass versus temperature (differential thermogravimetry, DTG) curves were plotted.

Isothermal thermogravimetry measurements were carried out by maintaining the temperature constant within ± 1°C. Measurements of loss in mass were made in two temperature ranges: (1) 160, 170, 180 and 190°C; and (2) 330, 340, 350 and 360°C.

Kinetic parameters, namely activation energy, E, and frequency factor, Z, were calculated by using both the dynamic and isothermal TG methods.

RESULTS AND DISCUSSION

Figure 1 shows representative curves (TG and DTG) for the sequence of dehydration steps in the $MnSO_4 \cdot 4H_2O$ crystal grown at 40°C. It is seen from the Figure that there are two DTG maxima at mean temperatures of 172 and 340°C, giving two dehydration steps of two moles each. The TG curve also shows a change of slope in the two temperature ranges [(1) 120–190°C; and (2) 280–380°C] which is indicative of two dehydration steps. It is observed that, for a crystal of mass 183 mg, the observed total loss in mass corresponded to 4 water molecules (temperature range (1), 34 mg; temperature range (2), 55 mg).

The thermogravimetric measurements suggest that $MnSO_4 \cdot 4H_2O$ dehydrates in the following fashion (with respect to temperature):

$$MnSO_4 \cdot 4H_2O \xrightarrow{172^\circ C} MnSO_4 \cdot 2H_2O + 2H_2O$$

$$MnSO_4 \cdot 2H_2O \xrightarrow{340^\circ C} MnSO_4 + 2H_2O$$

Isothermal TG measurements were carried out in two different temperature ranges 160–190°C and 330–360°C at intervals of 10°C. Figure 2 shows the results of the isothermal TG measurements at 160, 170, 180 and 190°C. Here, the fraction dehydrated, α, at time t is plotted against time. The

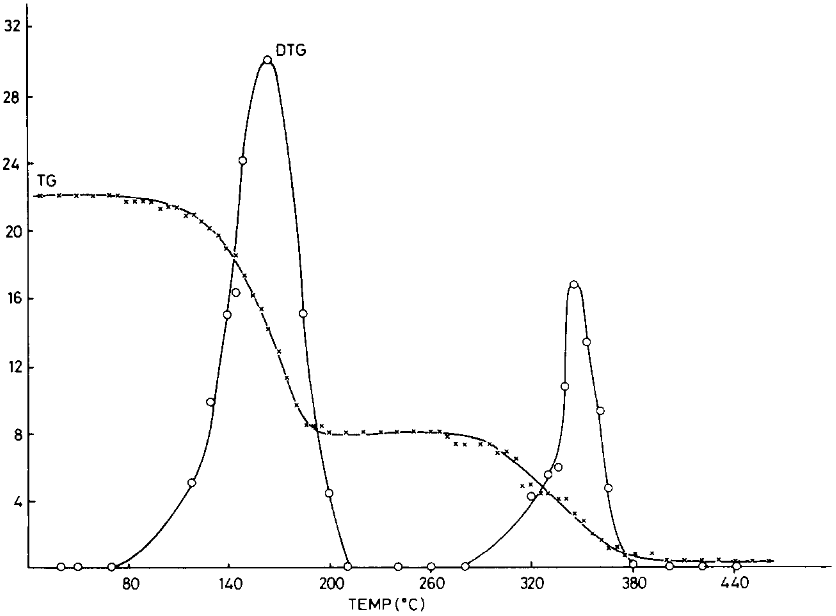

Fig. 1. TG and DTG curves for the thermal analysis of crystalline $MnSO_4 \cdot 4H_2O$.

mass-loss measurements show that in this temperature range three of the total four water molecules are lost from the crystal. The lower the isothermal temperature, the longer the time required for the release of three water

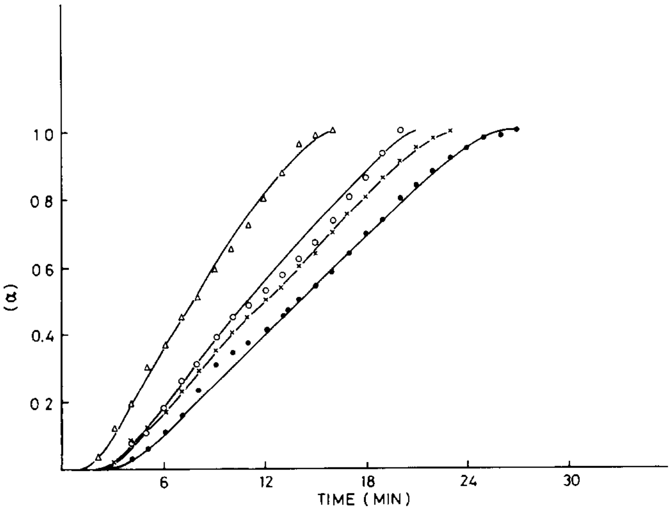

Fig. 2. Plots of fraction reacted vs. time: (●) 160 °C, (×) 170 °C, (○) 180 °C, (△) 190 °C.

TABLE 1

Mechanistic functions $F(\alpha)$ [a]

$F(\alpha)$	Symbol	Rate controlling process
α^2	D_1	One-dimensional diffusion.
$\alpha+(1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion, cylindrical symmetry.
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion, spherical symmetry; Jander function.
$1-2/3\alpha-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion, spherical symmetry; Ginstling–Brounshtein function.
$1-(1-\alpha)^{1/2}$	R_2	Phase boundary reaction, cylindrical symmetry.
$1-(1-\alpha)^{1/3}$	R_3	Phase boundary reaction, spherical symmetry.
$-\ln(1-\alpha)$	F_1	Random nucleation, on nucleus on each particle.
$[-\ln(1-\alpha)]^{2/3}$	$A_{1.5}$	Random nucleation and subsequent growth, Avrami–Erofeev type functions.
$[-\ln(1-\alpha)]^{1/2}$	A_2	
$[-\ln(1-\alpha)]^{2/5}$	$A_{2.5}$	
$[-\ln(1-\alpha)]^{1/3}$	A_3	
$[-\ln(1-\alpha)]^{1/4}$	A_4	

[a] The symbols used are similar to those in ref. 11.

molecules; α vs. t curves in the temperature range 330–360 °C show similar results.

For the calculation of kinetic parameters from isothermal measurements, it was assumed that the equation

$$d\alpha/dt = kF(\alpha) \tag{1}$$

holds for the isothermal dehydration of crystalline $MnSO_4 \cdot 4\ H_2O$. Here, α is the fraction dehydrated at time t, and k is the rate constant. Integration of eqn. (1) gives:

$$F(\alpha) = \int [d\alpha/f(\alpha)] = tZ\exp(-E/RT) \tag{2}$$

The function $F(\alpha)$, which describes the mechanism of isothermal dehydration, can be determined by plotting various theoretical functions against time, t. The correct function should give a straight line plot with slope k. Table 1 gives the different mechanistic functions $F(\alpha)$ used in determining the reaction mechanism.

Typical plots of $F(\alpha)$ vs. t in the temperature ranges 160–190 °C and 330–360 °C are shown in Fig. 3, parts (a) and (b), respectively. It is observed that the $F(\alpha)$ vs. t plot is a straight line for a number of $F(\alpha)$. It is seen from Fig. 3(a) that there are three slope changes in the curve. These three slope changes together with the mass loss measurements suggest that the dehydration of $MnSO_4 \cdot 4H_2O$, with respect to time, takes place in the following fashion:

$$MnSO_4 \cdot 4H_2O \xrightarrow{9\ \text{min}} MnSO_4 \cdot 3H_2O + H_2O \xrightarrow{17\ \text{min}} MnSO_4 \cdot 2H_2O + H_2O$$

$$\xrightarrow{23\ \text{min}} MnSO_4 \cdot H_2O + H_2O\ (T = 170\,°C)$$

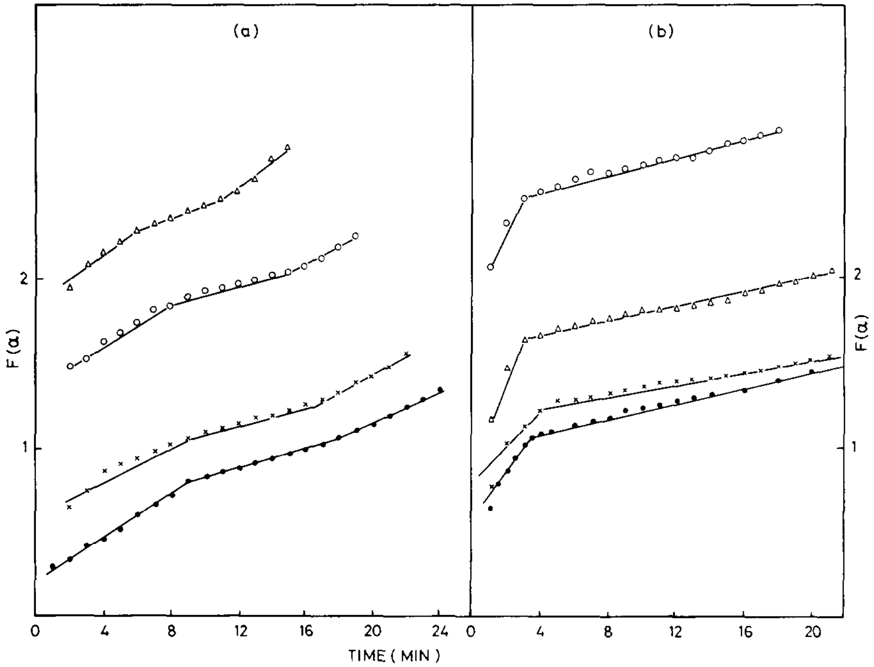

Fig. 3. Plots of $F(\alpha)$ (isothermal) vs. time for a function $F(\alpha) = \{-\log(1-\alpha)\}^{0.25}$ at: (a) 160, 170, 180 and 190°C; (b) 330, 340, 350 and 360°C. (●) 160 and 330°C; (×) 170 and 340°C; (○) 180 and 350°C; (△) 190 and 360°C. The scale marked along the Y-axis is for (●), for other temperatures the scale is changed suitably.

Figure 3(b) shows two slope changes in the curve. Mass loss measurements with time suggest the following dehydration scheme for $MnSO_4 \cdot 4H_2O$:

$$MnSO_4 \cdot 4H_2O \xrightarrow{4\ \text{min}} MnSO_4 \cdot H_2O + 3H_2O \xrightarrow{24\ \text{min}} MnSO_4 + H_2O \ (T = 340°\text{C})$$

A typical plot of $-\log k$ versus $1/T$ for the temperature range 160–190°C is shown for the functions $F(\alpha) = [-\log(1-\alpha)]^{0.25}$ in Fig. 4. Activation energy and frequency factor have been calculated in terms of the Arrhenius equation for different dehydration steps and are summarized in Table 2.

It has been shown by the theoretical analysis of Criado and Morales [5] that, in order to assign the proper form of $F(\alpha)$, both isothermal and dynamic TG studies are necessary. Dharwadkar et al. [6] and Tang and Choudhary [7] support this view. The dehydration study on $Na_2CO_3 \cdot H_2O$ and $K_2CO_3 \cdot 1.5H_2O$ by Deshpande et al. [8,9] shows that in order to determine the proper form of $F(\alpha)$, the consistency of E and Z values obtained from isothermal and dynamic TG studies should be considered.

It is observed that, for the same dehydration step, several $F(\alpha)$ gave straight line plots with respect to time and, therefore, the corresponding $F(\alpha)$, E and Z values could be calculated. To find the exact form of $F(\alpha)$,

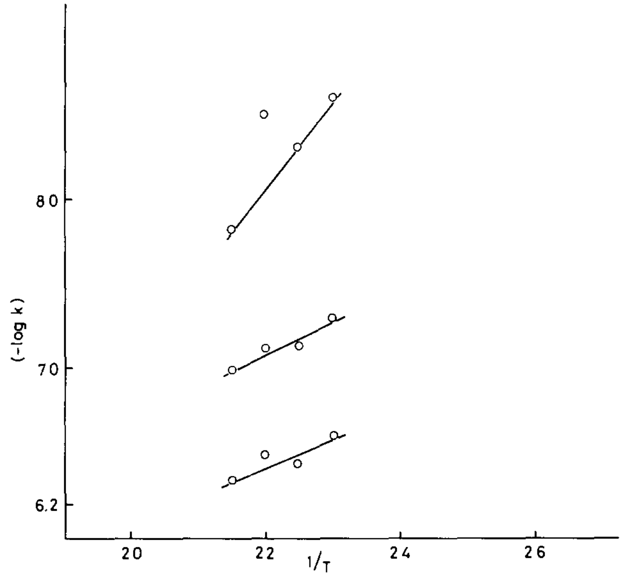

Fig. 4. The Arrhenius plots for the isothermal dehydration of crystalline $MnSO_4 \cdot 4H_2O$ for $F(\alpha) = \{-\log(1-\alpha)\}^{0\,25}$ in the temperature range 160–190°C for the three dehydration steps of 1 mole each shown in isothermal TG. The scale marked along the y-axis is for the first step, for the remaining two steps the scale is changed.

TABLE 2

Functions, $F(\alpha)$, and kinetic parameters for the thermal dehydration of $MnSO_4$ from isothermal TG [a]

$F(\alpha)$	Step	Temp. range			
		160–190°C		330–360°C	
		E	Z	E	Z
$[-\log(1-\alpha)]^{0\,66}$	1	10.86	$(4.88 \pm 1.07)10^2$	7.05	1.67 ± 0.21
	2	7.6	(10.84 ± 2.95)	–	–
	3	3.95	(0.37 ± 0.07)	–	–
$[-\log(1-\alpha)]^{0\,5}$	1	13.83	$(13.31 \pm 3.43)10^3$	3.80	0.09 ± 0.01
	2	9.88	$(10.73 \pm 3.55)10^1$	–	–
	3	5.81	(2.08 ± 0.32)	–	–
$[-\log(1-\alpha)]^{0\,4}$	1	9.88	$(14.10 \pm 3.35)10^1$	5.81	0.39 ± 0.07
	2	9.40	$(5.17 \pm 1.40)10^1$	–	–
	3	6.58	(3.50 ± 0.66)	–	–
$[-\log(1-\alpha)]^{0\,33}$	1	21.95	$(11.50 \pm 3.73)10^7$	6.17	0.45 ± 0.10
	2	12.35	$(12.44 \pm 3.26)10^2$	–	–
	3	10.4	$(23.73 \pm 3.16)10^1$	–	–
$[-\log(1-\alpha)]^{0\,25}$	1	7.90	(13.23 ± 2.43)	7.90	1.52 ± 0.28
	2	7.90	(6.13 ± 1.09)	6.58	0.08 ± 0.009
	3	10.4	$(16.64 \pm 2.22)10^1$	–	–

[a] E in kcal mol^{-1}, Z in s^{-1}.

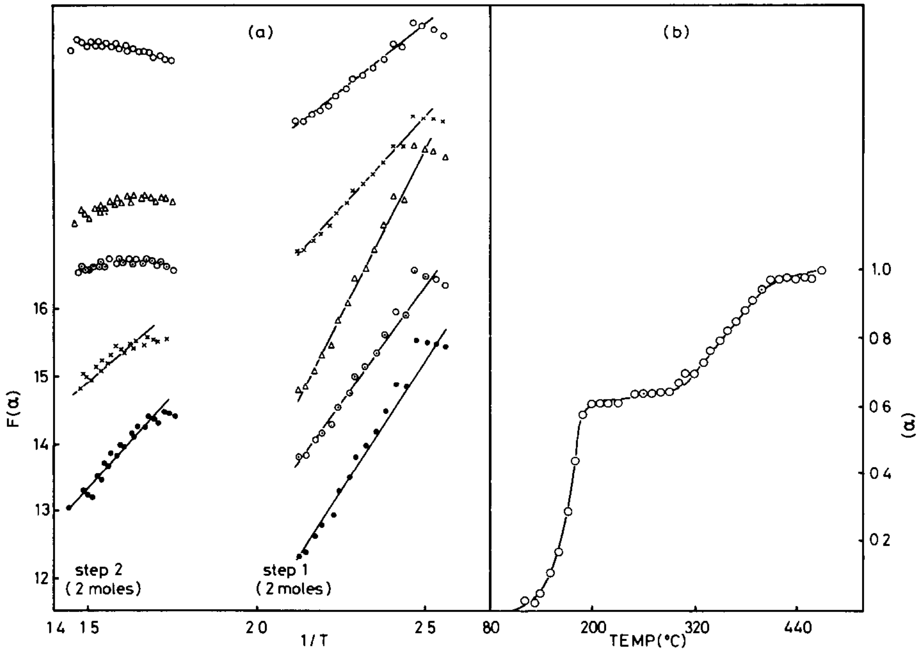

Fig. 5. (a) Plots of $-\ln[F(\alpha)/T^2]$ vs. $1/T$ for the thermal dehydration of crystalline $MnSO_4 \cdot 4H_2O$ (dynamic). (●, ×, △, ⊙, ○) Curves: (●) $n=1$; (×) $n=0.66$; (△) $n=0.5$; (⊙) $n=0.4$; (○) $n=0.25$. The scale marked along the y-axis is for (●), for other functions the scale is changed suitably to draw the remaining curves. (b) Plot of α vs. T for crystalline $MnSO_4 \cdot 4H_2O$.

E and Z values were calculated from dynamic TG measurements by using the Coats and Redfern [10] equation.

$$\ln F(\alpha)/T^2 = \ln ZR/\phi E(1-[2RT/E]) - (E/RT) \qquad (3)$$

where 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.

Figure 5 shows a typical plot of $F(\alpha) = [-\log(1-\alpha)]^n$ (where $n = 1$, 0.66, 0.5, 0.4 and 0.25) versus $1/T$ and α versus temperature (curve A). It is seen from the Figure that the α versus temperature curve (curve b) shows two different regions, each region corresponds to the loss of two water molecules; this confirms the steps given by DTG. It is observed that, for the dehydration of the first two molecules, all the functions, including $[-\log(1-\alpha)]$ give straight line plots. For the next step of the loss of two water molecules, however, only the functions $[-\log(1-\alpha)]$ and $[-\log(1-\alpha)]^{0\,66}$ give straight line plots. It is also seen from Fig. 5 (curve a) that there is a temperature range in between the two dehydration regions where a straight line plot with an opposite slope is observed. The straight line plot, therefore, has no meaning, because in this temperature range there is no loss in mass of the crystal with the change in temperature. Kinetic parameters obtained for the dehydration of the $MnSO_4 \cdot 4H_2O$ crystal for the two dehydration steps using different forms of $F(\alpha)$ are tabulated in Table 3.

It is seen from Table 2 that, in the two temperature ranges 160–190°C and 330–360°C, E and Z values agree for the function $[-\log(1-\alpha)]^{0.25}$ for the first three water molecules giving a dehydration mechanism of random nucleation and subsequent growth. It seems that the dehydration mechanism is followed irrespective of the number of water molecules involved in a particular step. This inference can also be substantiated if α versus time curves for the two temperature ranges are compared. In the temperature range 160–190°C, an α versus time curve is plotted for every step taking $t = 0$ to be when one water molecule is completely removed and the dehydration of the second just started. It is observed that the nature of these curves is exactly similar. In the temperature range 160–190°C, the three dehydrating water molecules show three steps of one mole each, whereas in the temperature range 330–360°C, three water molecules are removed in one step only. The fourth water molecule, which is removed in the temperature range 330–360°C, is also shown by a straight line for $F(\alpha)$ versus time for $F(\alpha) = [-\log(1-\alpha)]^{0\,25}$. The isothermal study, therefore, suggests $F(\alpha)$ is of the form $[-\log(1-\alpha)]^{0\,25}$ for the dehydration of $MnSO_4 \cdot 4H_2O$ in the entire temperature range.

If E and Z values from isothermal and dynamic studies for $F(\alpha) = [-\log(1-\alpha)]^{0\,25}$ are compared, no agreement is observed, but some agreement between E and Z values from these studies is observed for other functions. These functions also give the mechanism of dehydration as random nucleation and subsequent growth in the entire temperature range.

The disagreement between E and Z values from the isothermal and dynamic studies for determining the proper form of $F(\alpha)$ may be due to the following.

(1) In the dynamic study, each step corresponds to two moles of water and in isothermal study, depending upon the temperature range, the steps correspond to 1 mole, 1 mole and 1 mole, or 3 moles and 1 mole.

(2) The difference in time available for dehydration in isothermal and dynamic studies.

(3) The amount of water vapour pressure built up inside the crystal due to the difference in time available for dehydration.

(4) The change in the number of paths available for dehydration.

The literature survey shows that agreement of E and Z values from isothermal and dynamic TG measurements, to suggest proper $F(\alpha)$ and thereby the dehydration mechanism, is obtained only when the number of dehydrating water molecules is two or less than two ($Na_2CO_3 \cdot H_2O$, $CaSO_4 \cdot H_2O$, $BaCl_2 \cdot 2H_2O$, etc.). It is seen from this study that the criteria of agreement between E and Z values from isothermal and dynamic TG measurements to suggest proper $F(\alpha)$, may not be applicable for crystals

TABLE 3

Functions $F(\alpha)$ and kinetic parameters for the thermal dehydration of $MnSO_4 \cdot 4H_2O$ from dynamic TG

$F(\alpha)$	E (kcal mol^{-1})		Z (S^{-1})		Dehydration temperature (°C)	
	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2
$-\log(1-\alpha)$	14.55 ± 1.05	4.83 ± 0.25	$(2.23 \pm 0.65)10^9$	$(2.66 \pm 0.95)10^{12}$	172 ± 4	340 ± 2.5
$[-\log(1-\alpha)]^{0.66}$	9.87 ± 0.42	3.35 ± 0.16	$(2.78 \pm 0.58)10^9$	of the order of 10^{22}		
$[-\log(1-\alpha)]^{0.5}$	7.20 ± 0.95	–	$(4.60 \pm 1.50)10^9$	–		
$[-\log(1-\alpha)]^{0.4}$	5.03 ± 0.41	–	$(2.37 \pm 0.18)10^9$			
$[-\log(1-\alpha)]^{0.33}$	3.94 ± 0.42	–	Of the order of 10^{12}			
$[-\log(1-\alpha)]^{0.25}$	2.84 ± 0.51	–	Of the order of 10^{12}			

having a large number of water molecules in general and the $MnSO_4 \cdot 4H_2O$ crystal in particular. Thus the study shows that the possible mechanism for the dehydration is random nucleation and subsequent growth. The same mechanism is described by different functions in isothermal and dynamic measurements.

CONCLUSION

It is concluded from the DTG study that $MnSO_4 \cdot 4H_2O$ dehydrates in two steps of 2 moles each at mean temperatures of 172 and 340°C, respectively. On the other hand, the isothermal study shows that, in the temperature range 160–190°C, there are three distinct steps of dehydration of 1 mole each. In the temperature range 330–360°C, however, two dehydration steps comprising of 3 moles and 1 mole are observed.

For the $MnSO_4 \cdot 4H_2O$ crystal the general mechanism of dehydration for all the steps is random nucleation and subsequent growth. The proper form of the function $F(\alpha)$ which describes this mechanism is different in the isothermal and dynamic studies.

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