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Dehydration of $NiCl_2 \cdot 6H_2O$

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Abstract

Powdered samples of nickel chloride hexahydrate prepared by grinding small crystallites grown by slow evaporation of an aqueous solution have been studied by dynamic and isothermal TG measurements. It is observed from dynamic TG that hexahydrated nickel chloride dehydrates in two steps releasing 5 moles H_2O and 1 mole H_2O at mean temperatures of 224 and 291°C, respectively. Isothermal TG measurements, dependent upon temperature show different dehydration pattern with respect to time. In the temperature range 240–300°C dehydration pattern similar to dynamic TG has been observed. From dynamic and isothermal measurements the kinetic parameters E and Z are calculated. It is observed that the general mechanism of dehydration in these samples for both steps is random nucleation and subsequent growth. The same mechanism is described by different functions in isothermal and dynamic studies. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermal dehydration; $NiCl_2 \cdot 6H_2O$

1. Introduction

Dehydration process in many metal hydrates has been studied in this laboratory [1–8]. It has been observed that the dehydration steps given by the dynamic TG study are different from those given by the isothermal TG studies. Dehydration steps given by isothermal method are temperature dependent. If the salt is studied at temperatures near its final dehydration temperature, it gives only two dehydration steps. This fact has also been stressed by Ben Dor and Mangalith [9]. They had studied many polyhydrated metal sulphates and reported that all but one of the molecules are evolved at relatively low temperatures (beginning at 60°C) and then after a significant rise in temperature, the last molecule is evolved.

Kinetics of dehydration of $NiCl_2 \cdot 6H_2O$ has been studied by Mishra et al. [10] by isothermal and dynamic methods. They had observed that the initial stages of dehydration followed first-order nucleation and growth product from molten phase (140°C). Activation energy values derived from isothermal and non-isothermal methods agree well for major regions of dehydration. The survey of the literature indicates that very little work has been carried out on the kinetics of various dehydration steps in $NiCl_2 \cdot 6H_2O$. This paper is an attempt to study the mechanism of dehydration in $NiCl_2 \cdot 6H_2O$ using isothermal and dynamic TG techniques.

2. Experimental

AR grade hexahydrated nickel chloride was procured. Slow evaporation of its aqueous solution could

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not give good crystals. Therefore TG study was carried out on powdered samples. The TG study was carried out using TG assembly fabricated in the laboratory, details of which are given elsewhere [6].

Measurement of mass loss was carried out in air in the temperature range 30–400°C. The powder was heated a the rate of 5°C/min. The value of $\Delta m/\Delta t$, i.e. rate of change of mass (mg/min) was calculated at different temperatures. Curves of change in mass versus temperature [TG] and rate of change of mass versus temperature [DTG] were plotted. Also α, the fraction dehydrated at temperature T (°C) was plotted against temperature. Isothermal TG measurements were carried out by maintaining the temperature constant within ±1°C; Measurements of loss in mass were made in two temperature ranges: (i) 170–200°C and (ii) 240–270°C at an interval of 10°C. The loss in mass versus time as well as α, the fraction dehydrated at time t were plotted against time.

3. Results and discussion

Fig. 1 shows representative curves of TG and DTG for the sequence of dehydration steps in $NiCl_2{\cdot}6H_2O$ powdered sample. It is observed that two DTG maxima occur at mean temperatures of 224 and 291°C. The mass loss measurements suggest the sequence of dehydration as 5 moles and 1 mole at these mean temperatures. For a sample mass of 2417 mg, the observed loss in mass corresponds to liberation of six water molecules.

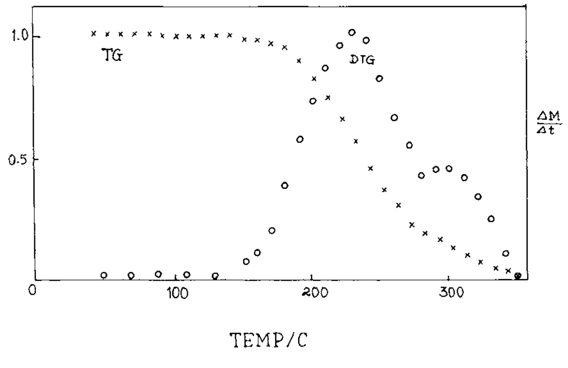


Fig. 1. TG and DTG curves for the thermal dehydration of $NiCl_2{\cdot}6H_2O$.

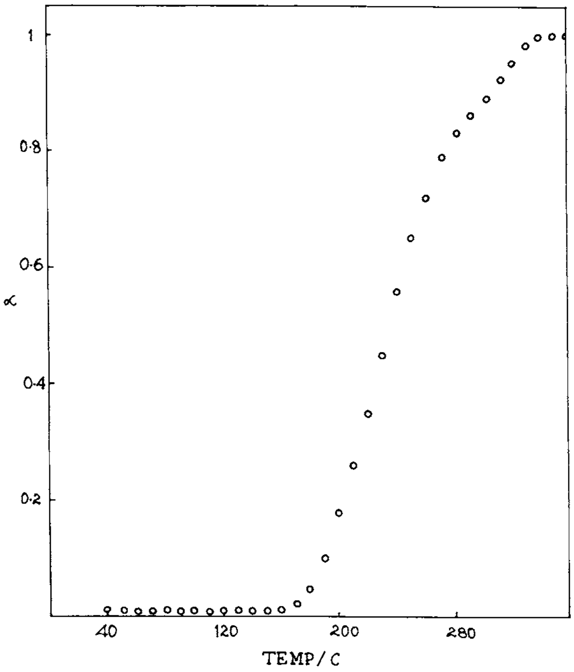


Fig. 2. Plot of α vs. T for $NiCl_2{\cdot}6H_2O$.

The dynamic TG measurements show the following scheme of dehydration in powdered $NiCl_2{\cdot}6H_2O$ samples with respect to temperatures.

$$NiCl_2 \cdot 6H_2O \xrightarrow{224^\circ C} NiCl_2 \cdot 1H_2O + 5H_2O$$

$$NiCl_2 \cdot H_2O \xrightarrow{291^\circ C} NiCl_2 + H_2O$$

From the mass loss measurements one can calculate α the fraction dehydrated at a particular temperature T (°C). Fig. 2 shows α versus T temperature plot for a powdered sample of mass 2300 mg. This curve shows 2 regions with changing slopes, indicating two dehydration steps. Using Coats and Redfern equation (Eq. (1)) [11],

$$\ln\left[\frac{f(\alpha)}{T^2}\right] = \ln\left(\frac{ZR}{\phi E}\right)\left[1 - \left(\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (1)$$

where T is the absolute temperature, Z the frequency factor, R the gas constant, ϕ the linear heating rate, E the activation energy, the activation energy E and frequency factor Z can be calculated.

Fig. 3 shows the typical plot of $-\log[f(\alpha)/T^2]$ versus $1/T$, where $f(\alpha) = -\log(1-\alpha)^n$ and $n = 1$, 0.66, 0.5, 0.4, 0.33 and 0.25.

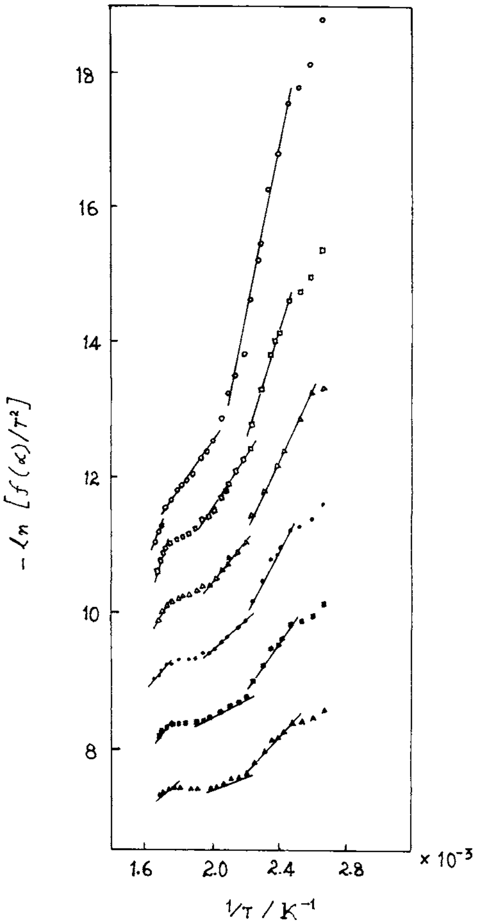


Fig. 3. Plots of $-\ln(f(\alpha)/T^2$ vs. $1/T$ for the thermal dehydration of $NiCl_2 \cdot 6H_2O$ (dynamic): (▲), $n = 0.25$; (■), $n = 0.33$; (●), $n = 0.4$; (△), $n = 0.5$; (□), $n = 0.66$; (○), $n = 1$. The scale marked along the y-axis is for $n = 1$. For other functions, the scale was altered as appropriate for drawing the remaining curves.

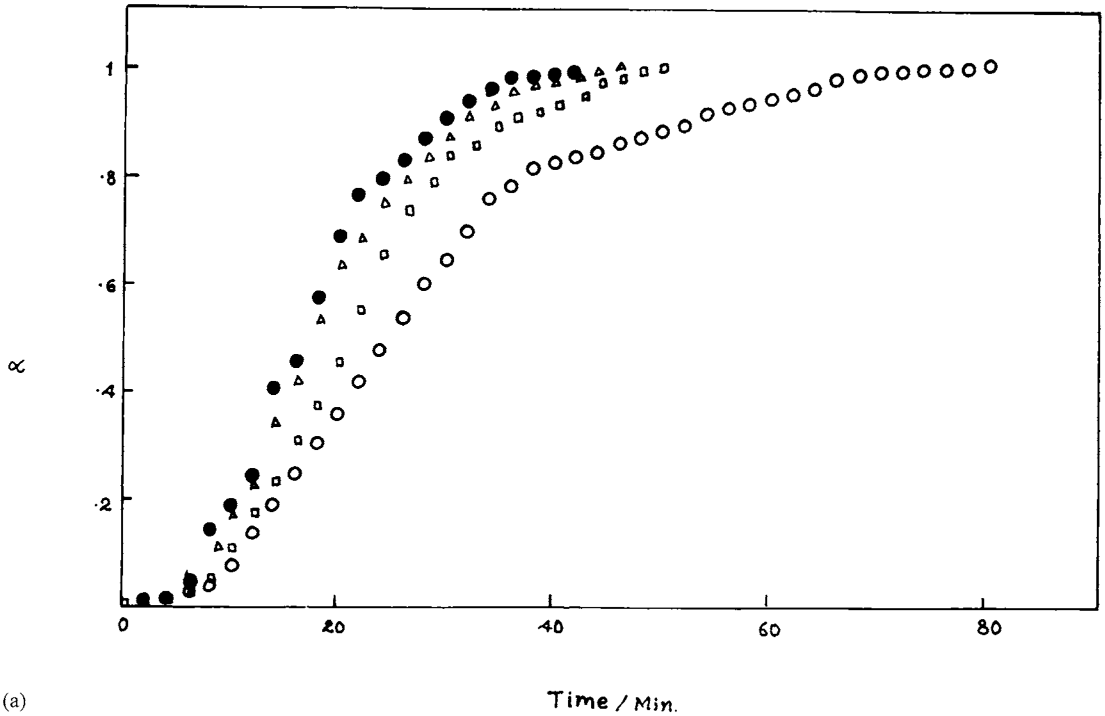
It can be seen from the figure that all the functions give linear plots and there are three slope changes. The mass loss measurements indicate that the first linear part is for the loss of 1 mole of H_2O. The second and the third linear part indicate loss of 4 moles and 1 mole of H_2O respectively. This dehydration scheme is different from that given by the DTG. However, linearity in $-\log[f(\alpha)/T^2]$ versus $1/T$ plots generally suggests the mechanism of dehydration rather than suggesting dehydration steps. A change in slope, therefore, indicates a change in mechanism of dehydration rather than dehydration step. For calculation of E and Z, therefore, the second and the third slopes are considered. The activation energy and frequency factor were calculated from these plots are given in Table 1. It has been pointed out by Criado and Morales [12] from their theoretical analysis that the linearity of $-\ln[f(\alpha)/T^2]$ versus $1/T$ in a dynamic TG study is a necessary but not a sufficient criterion for assigning $f(\alpha)$. They have reiterated the necessity of recording atleast 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 Dharwadkar et al. [13].

The isothermal TG measurements were carried out in two temperature ranges (i) 170–200°C and (ii) 240–270°C at an interval of 10°C.

Fig. 4 (curves a and b, respectively) shows a representative plot of α versus time. It can be seen from Fig. 4(a) that for the loss of five water molecules the time required at 170°C is 78 min, 180°C is 38 min, 190°C is 34 min and 200°C is 30 min. The higher the isothermal temperature the shorter is the time required for the loss of five water molecules.

Table 1
Functions $f(\alpha)$ and kinetic parameters for the thermal dehydration of $NiCl_2 \cdot 6H_2O$ from dynamic TG

$f(\alpha)$	E (kcal mol^{-1})		Z (s^{-1})	
	Step 1	Step 2	Step 1	Step 2
$[-\log(1-\alpha)]$	7.80	13.97	5.77×10^{12}	9.04×10^{13}
$[-\log(1-\alpha)]^{0.66}$	10.04	8.17	6.04×10^{16}	8.96×10^{11}
$[-\log(1-\alpha)]^{0.5}$	4.99	5.99	1.44×10^{11}	8.12×10^{10}
$[-\log(1-\alpha)]^{0.4}$	4.18	4.50	1.35×10^{10}	1.27×10^{9}
$[-\log(1-\alpha)]^{0.33}$	3.22	4.60	5.93×10^{9}	8.70×10^{9}
$[-\log(1-\alpha)]^{0.25}$	2.37	3.47	5.67×10^{9}	6.92×10^{9}



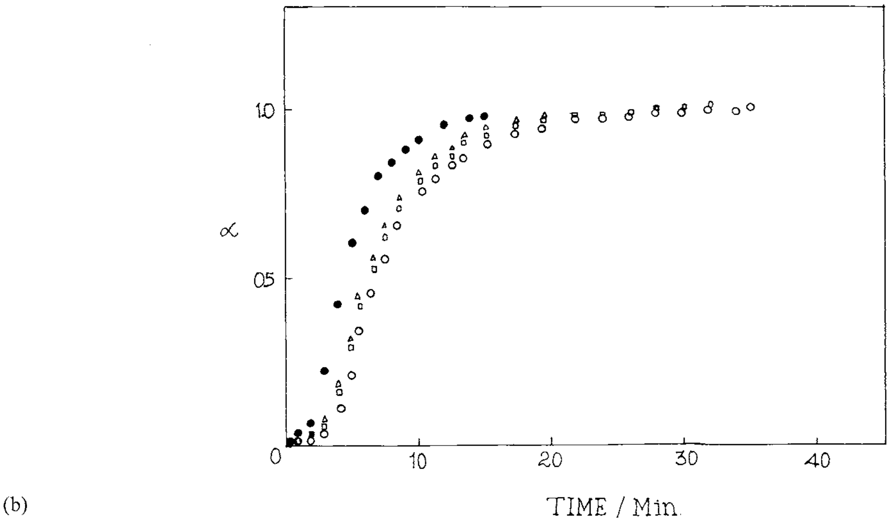


Fig. 4. (a) Plots of fraction reacted α vs. time *t*: (○), 170°C; (□), 180°C; (△), 190°C; (●), 200°C. (b) Plots of fraction reacted α vs. time *t*: (○), 240°C; (□) 250°C; (△), 260°C; (●), 270°C.

Fig. 4(b) shows the plot of α versus time in the temperature range 240–270°C. It can be seen from the figure that five water molecules are lost at a very rapid rate, the sixth water molecule is lost steadily. At lower temperatures, the time required for complete dehydration is greater than that at higher temperatures.

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

$$\frac{d(\alpha)}{dt} = kF(\alpha) \tag{2}$$

holds for the thermal dehydration $NiCl_2 \cdot 6H_2O$. Here α is the fraction of reactant dehydrated at time t and k is the rate constant. The integration of this Eq. (2) gives

$$F(\alpha) = \int \left(\frac{d\alpha}{F(\alpha)}\right) = tZ\exp\left(\frac{-E}{RT}\right)$$

The function $F(\alpha)$ which describes the mechanism of isothermal dehydration can be determined by plotting various theoretical functions against t; the correct function should give a straight line with slope k. The functions used in the study are $[-\log(1-\alpha)]$, $[-\log(1-\alpha)]^{0.66}$, $[-\log(1-\alpha)]^{0.5}$, $[-\log(1-\alpha)]^{0.4}$, $[-\log(1-\alpha)]^{0.33}$, $[-\log(1-\alpha)]^{0.25}$.

Typical plots of $F(\alpha)$, versus time for $F(\alpha) = [-\log(1-\alpha)]^{0.4}$ in the temperature ranges 170–200°C and 240–270°C are shown in Fig. 5(a)

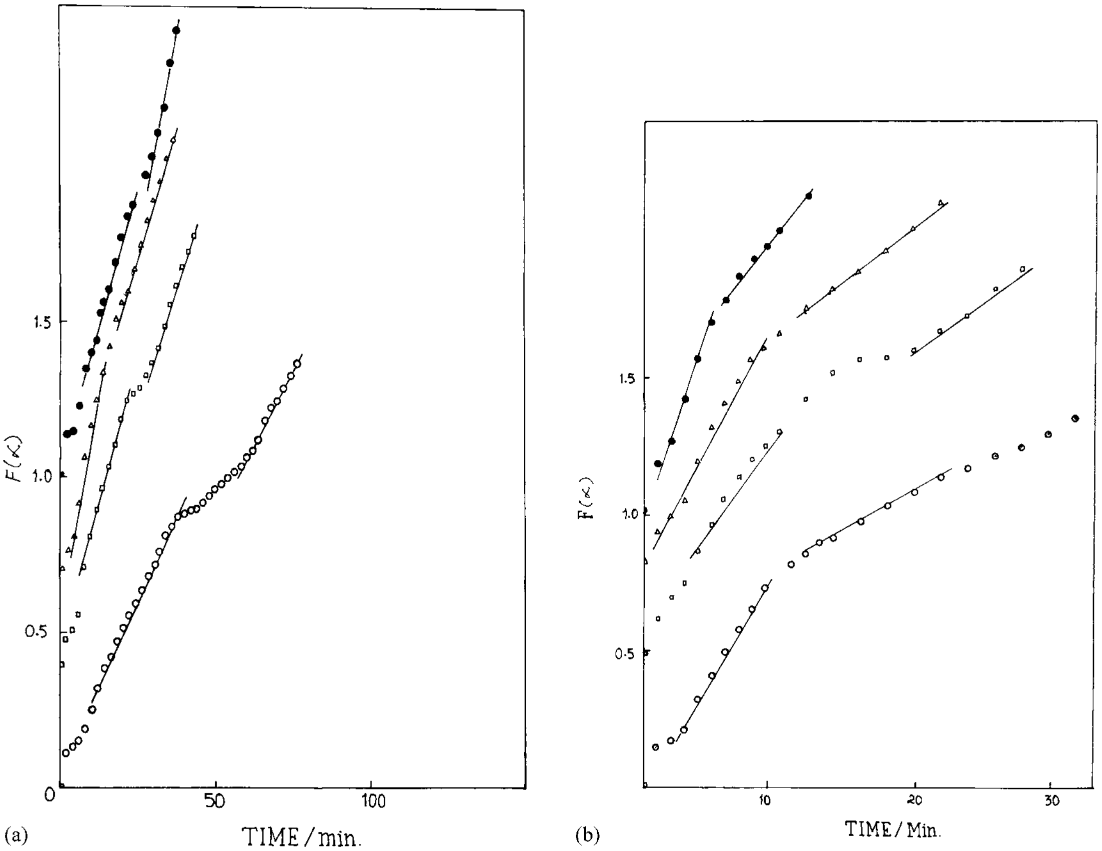


Fig. 5. (a) Plots of $F(\alpha)$ (isothermal) vs. time t for a function $F(\alpha) = [-\log(1-\alpha)]^{0.4}$ at temperatures (○), 170°C; (□), 180°C; (△), 190°C; (●), 200°C. For other functions the scale was altered as appropriate for drawing the remaining curves. (b) Plots of $F(\alpha)$ (isothermal) vs. time t for a function $F(\alpha) = [-\log(1-\alpha)]^{0.4}$ at temperatures (○), 240°C; (□), 250°C; (△), 260°C; (●), 270°C. For other functions the scale was altered as appropriate for drawing the remaining curves.

and (b), respectively. It is observed that all the functions gives straight line plots. In the temperature range 170–200°C (Fig. 5(a)) there are two linear regions. These two regions correspond to the total loss of five water molecules and the two regions indicate dehydration of 4 moles and 1 mole respectively. In the temperature range 240–270°C (Fig. 5(b)) there are again two linear regions. The first region indicates the loss of five water moles and second region indicates the loss of remaining water mole. Thus if the dehydration in the temperature range 170–200°C is considered then $NiCl_2{\cdot}6H_2O$ dehydrates with respect to

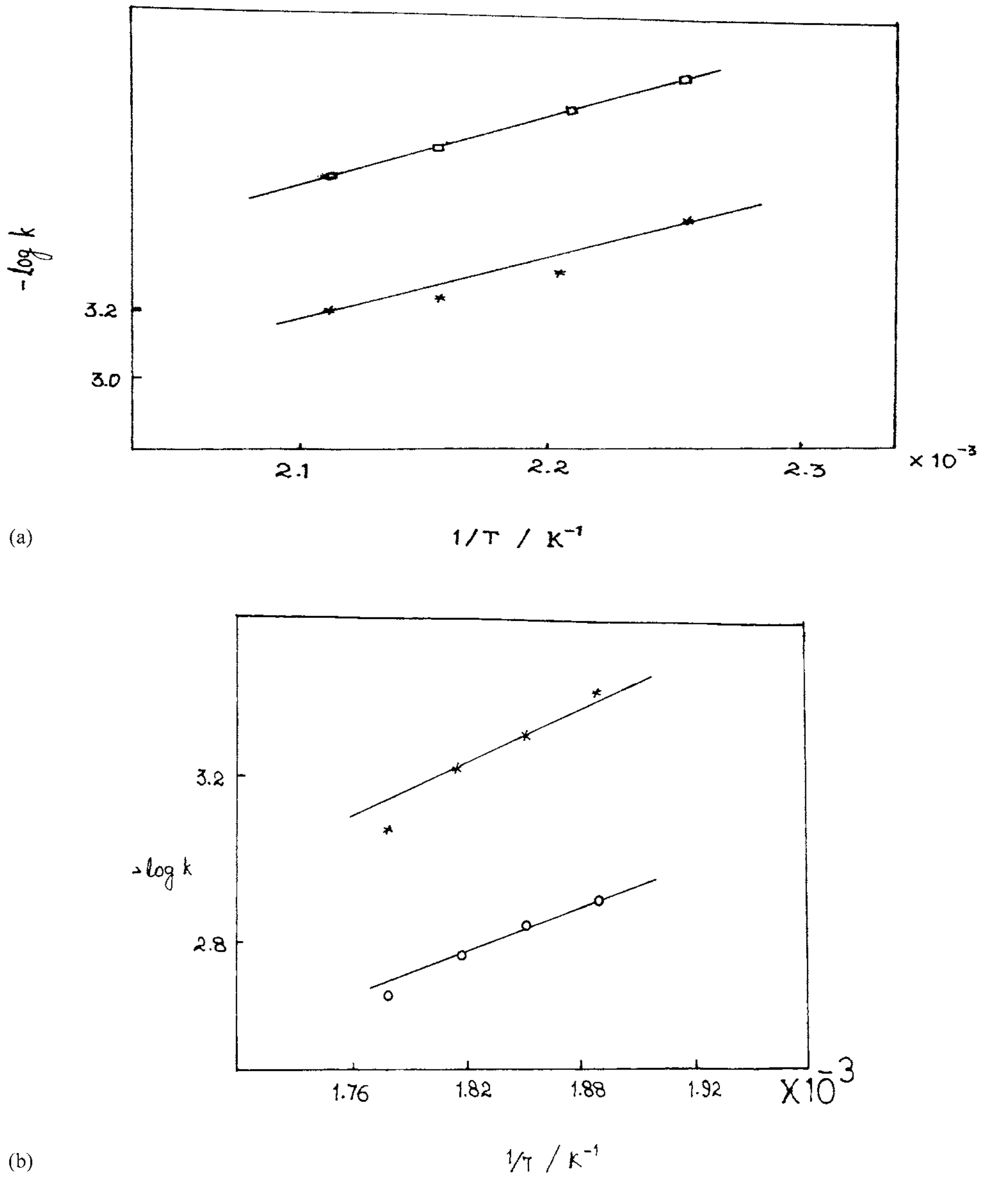


Fig. 6. (a) Arrhenius plots for the isothermal dehydration of $NiCl_2{\cdot}6H_2O$ for $F(\alpha) = [-\log(1-\alpha)]^{0.4}$ in the temperature range 170–200°C. The scale marked along the ordinate is for the first step. The scale for the second step was altered. (○), first step; (*), second step. (b) Arrhenius plots for the isothermal dehydration of $NiCl_2{\cdot}6H_2O$ for $F(\alpha) = [-\log(1-\alpha)]^{0.25}$ in the temperature range 240–270°C. The scale marked along the ordinate is for the first step. The scale for the second step was altered. (○), first step; (*), second step.

Table 2
Functions $F(\alpha)$ and kinetic parameters for the thermal dehydration of $NiCl_2{\cdot}6H_2O$ from isothermal TG

$F(\alpha)$	Step	Temperature range: 160–230°C		Temperature range: 240–300°C	
		E (kcal mol^{-1})	Z (s^{-1})	E (kcal mol^{-1})	Z (s^{-1})
$[-\log(1-\alpha)]$	1	8.34	6.47	7.20	1.66
	2	12.59	1.41×10^{3}	7.33	3.69
$(-\log(1-\alpha)]^{0.66}$	1	8.11	4.65	4.70	0.15
	2	19.57	2.17×10^{6}	17.69	2.88×10^{4}
$[-\log(1-\alpha)]^{0.5}$	1	8.72	9.17	7.44	2.07
	2	25.74	1.84×10^{9}	10.02	2.16×10^{1}
$[-\log(1-\alpha)]^{0.4}$	1	6.63	0.89	6.29	0.67
	2	19.90	1.69×10^{6}	11.93	6.65×10^{1}
$[-\log(1-\alpha)]^{0.33}$	1	868	7.23	7.72	2.52
	2	17.06	4.23×10^{4}	9.80	7.26
$[-\log(1-\alpha)]^{0.25}$	1	9.80	2.04×10^{1}	5.13	0.21
	2	11.37	7.65×10^{1}	18.20	1.51×10^{4}

time in the following fashion.

$$NiCl_2 \cdot 6H_2O \overset{38\,\text{min}}{\rightarrow} NiCl_2 \cdot 2H_2O + 4H_2O \overset{78\,\text{min}}{\rightarrow} NiCl_2H_2O + H_2O, \quad T = 170^{\circ}C$$

In the temperature range 240–270°C the mass loss measurements with time suggest the dehydration scheme as

$$NiCl_2 \cdot 6H_2O \overset{7\,\text{min}}{\rightarrow} NiCl_2 \cdot H_2O + 5H_2O \overset{12\,\text{min}}{\rightarrow} NiCl_2 + H_2O, \quad T = 270^{\circ}C$$

Typical plots of $-\log k$ versus $1/T$, $F(\alpha) = [-\log(1-\alpha)]^{0.4}$ in the two temperature ranges are shown in Fig. 6(a) and (b). The activation energy E and frequency factor Z are calculated in terms of Arrhenius equation for the different dehydration steps and are tabulated in Table 2. Correlation factors for different functions in dynamic and static studies are given in Table 3. Table 4 lists comparison of functions, E values and correlation factors from the dynamic TG measurements and static TG measurements in the temperature range 240–270°C.

A number of workers have suggested that correct dehydration mechanism, activation energy and frequency factor can be obtained by comparing information from both dynamic and static methods. If the data from Table 1 for dynamic TG and that for the temperature range 240–270°C from Table 2 along with correlation factor given in Table 3 are compared, it is observed that there is a good agreement of E values. The Z values differ greatly. Lack of very good agreement in E and Z from the dynamic and static measurements may be due to following factors.

Table 3
Correlation coefficient from dynamic study

$f(\alpha)$	Step 1	Step 2
$[-\log(1-\alpha)]$	0.9914	0.9708
$[-\log(1-\alpha)]^{0.66}$	0.9894	0.9654
$[-\log(1-\alpha)]^{0.5}$	0.9868	0.9588
$[-\log(1-\alpha)]^{0.4}$	0.9831	0.9499
$[-\log(1-\alpha)]^{0.33}$	0.9774	0.9367
$[-\log(1-\alpha)]^{0.25}$	0.9572	0.8945
Static temperature range 170–200°C		
$[-\log(1-\alpha)]$	0.8686	0.7082
$[-\log(1-\alpha)]^{0.66}$	0.8820	0.7132
$[-\log(1-\alpha)]^{0.5}$	0.9327	0.6641
$[-\log(1-\alpha)]^{0.4}$	0.9195	0.7032
$[-\log(1-\alpha)]^{0.33}$	0.9420	0.5369
$[-\log(1-\alpha)]^{0.25}$	0.7031	0.6148
Temperature range 240–270°C		
$[-\log(1-\alpha)]$	0.8820	0.2497
$[-\log(1-\alpha)]^{0.66}$	0.5576	0.6986
$[-\log(1-\alpha)]^{0.5}$	0.9046	0.6042
$[-\log(1-\alpha)]^{0.4}$	0.8811	0.6390
$[-\log(1-\alpha)]^{0.33}$	0.8640	0.8049
$[-\log(1-\alpha)]^{0.25}$	0.7901	0.7793

Table 4
Functions $f(\alpha)$, E values and correlation factors for dynamic and static TG

$f(\alpha)$	Dynamic			Isothermal (240–270°C)		
	Step	E (kcal)	Crrelation factor	Step	E (kcal)	Correlation factor
$[-\log(1-\alpha)]$	1	7.80	0.9914	1	7.20	0.8820
	2	13.97	0.9708	2	7.33	0.9497
$[-\log(1-\alpha)]^{0.66}$	1	10.04	0.9894	1	4.70	0.9576
	2	8.17	0.9654	2	17.69	0.8986
$[-\log(1-\alpha)]^{0.5}$	1	4.99	0.9868	1	7.44	0.9046
	2	5.99	0.9588	2	10.02	0.9042
$[-\log(1-\alpha)]^{0.4}$	1	4.18	0.9831	1	6.29	0.8811
	2	4.5	0.9499	2	11.93	0.9390
$[-\log(1-\alpha)]^{0.33}$	1	3.22	0.9774	1	7.72	0.8640
	2	4.60	0.9367	2	9.80	0.8049
$[-\log(1-\alpha)]^{0.25}$	1	2.37	0.9572	1	5.13	0.7901
	2	3.47	0.8945	2	18.20	0.7793

1. Dehydration steps being different in the two measurements.
2. The difference in time available in the two measurements.
3. The amount of water vapour pressure build up inside the specimen owing to the difference of time available for dehydration.
4. Change in number of paths available for dehydration.

Though no exact values of E and Z can be recommended, the measurements suggest that the possible form of $f(\alpha)$ for dehydration is $-\log(1-\alpha)$ for dynamic TG and $F(\alpha) = [-\log(1-\alpha)]^{0.4}$ for static TG and E values are of the order of 7.5 kcal mol^{-1} and 13 kcal mol^{-1} for the two dehydration steps (see Table 4).

The possible mechanism of dehydration is random nucleation and subsequent growth. The same mechanism is described by different functions in isothermal and dynamic measurements.

4. Conclusions

The dynamic TG study gave the dehydration scheme as 5 moles and 1 mole at temperatures 224 and 291°C whereas the isothermal TG study gave a different dehydration scheme dependent on temperatures. In the temperature range 170–200°C five water molecules come out of the sample in the steps of 4 moles and 1 mole and in the temperature range 240–270°C, two dehydration steps comprising of 5 moles and 1 mole were observed.

The mechanism of dehydration for $NiCl_2{\cdot}6H_2O$ powdered sample for all steps is random nucleation and subsequent growth.

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