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CHEMISTRY OF BORATE IN SALT LAKE BRINE. XIV. PHASE TRANSITION AND KINETICS OF DEHYDRATION DURING HEATING OF $MgO \cdot 3B_2O_3 \cdot nH_2O$ *

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ABSTRACT

The temperature and enthalpy of dehydration or recrystallization of synthetic $MgO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$) during heating having been determined by DTA, TG, DTG and DSC. The products have been verified by X-ray powder diffraction, infrared spectrograms and chemical analysis and the thermochemical reactions have been given. The phase composition of the recrystallization at high temperature were confirmed as crystal-state $2MgO \cdot 3B_2O_3$ and amorphous B_2O_3 by physical analysis after the phase separated by esterification between B_2O_3 and methol alcohol. Using TG and DTG data, the kinetic parameters have been calculated by computer and the kinetic equations of non-isothermo-dehydration reactions have been given.

INTRODUCTION

All kind of Mg borates, including simple and double salts, hydrates and anhydrates, can be found, some of which can be found in nature as minerals and some synthesized only in the laboratory. So far it is known that $MgO \cdot 3B_2O_3 \cdot nH_2O$ has five different hydrates, i.e. $MgO \cdot 3B_2O_3 \cdot 7\frac{1}{2}H_2O$ (Macallisterite [1]), $MgO \cdot 3B_2O_3 \cdot 5H_2O$ (Aksaite [2]), $MgO \cdot 3B_2O_3 \cdot 6H_2O$ [3], $MgO \cdot 3B_2O_3 \cdot 7H_2O$ [4] and $MgO \cdot 3B_2O_3 \cdot 4H_2O$ [5].

Schwartz [6], Kanteeva and Leonteva [7], and Abdyllaev and Agaev [8] studied the thermal behaviour of Macallisterite and Aksaite during heating, and suggested that the recrystallized products of Macallisterite and Aksaite were crystalline MgB_4O_7 and amorphous B_2O_3. We have also studied the phase transformation of four different hydrated Mg hexaborates at high temperature and indicated that the recrystallized products are the same as crystaline $2MgO \cdot 3B_2O_3$ and the amorphous B_2O_3. At the same time, the thermochemical reaction equations and the kinetic equations of dehydration during heating and phase transition reactions at high temperature have been given.

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EXPERIMENTAL

Syntheses of materials

The $MgO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$) were synthesized from $MgCl_2 \cdot 6H_2O$, H_3BO_3 and MgO, all of which were analytical grade reagents of P.R.C. production. The methods of synthesis were

$MgO \cdot 3B_2O_3 \cdot 5H_2O$. 20.0 g MgO, 186.0 g H_3BO_3, 1000 g $MgCl_2 \cdot 6H_2O$ and 250.0 g H_2O were transferred to a flask fitted with a reflux condenser and heated to boiling point for 10 days. The Mg borate crystallized out, and was then separated by centrifuge at 3000 rev min^{-1}. It was washed thoroughly with distilled water followed in succession by alcohol and ether before drying at 60 °C to constant weight.

$MgO \cdot 3B_2O_3 \cdot 6H_2O$ and $MgO \cdot 3B_2O_3 \cdot 7H_2O$. See ref. 3.

$MgO \cdot 3B_2O_3 \cdot 7\frac{1}{2}H_2O$. 15.7 g MgO and 187.5 g H_3BO_3 were dissolved in 1250 ml water at 60–70 °C, filtered and the filtered liquid transferred to a flask which was placed in a water bath at 10 °C. The contents were stirred with an electromagnetic stirrer for about 10 days. The crystalline solid phase was separated and washed thoroughly with water followed in succession by alcohol and ether before drying in air at room temperature to constant weight.

METHOD

Thermal analysis

DTA investigations were carried out by means of the high-temperature equipment manufactured by Dupont, Model 1090. The samples (15.00 mg of powder crystal) were heated from room temperature to 1100 °C at a heating rate of 10 °C min^{-1}. Measurements were performed in air flowing at a rate of 80 ml min^{-1}.

TG and DTG measurements were carried out in a Perkin-Elmer TGS-2 thermogravimeter. The temperature was calibrated with Perkalloy. The samples (5.00 mg) were heated from room temperature to 700 °C at a rate of 10 °C min^{-1}. Measurements were performed in N_2 flowing at a rate of 40 ml min^{-1} and at a recording rate of 180 mm min^{-1}.

A DSC made by Perkin-Elmer was used to measure the enthalpies of the dehydration reaction while the samples (3.00 mg) were heated from room temperature to 700 °C at a rate of 10 °C min^{-1}. Measurements were performed in N_2 flowing at a rate of 40 ml min^{-1}.

Infrared spectra and X-ray diffraction

Based on the results of thermoanalysis, the samples of $MgO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$) were heated in platinum crucibles in an electric furnace to various temperatures at a heating rate of 10 ° C min^{-1} and were then studied by infrared spectra and X-ray powder diffraction. Infrared spectra of the thermally treated samples were recorded in KBr disks with a Perkin-Elmer 683 Spectrophotometer. X-Ray diffraction spectra were performed on an X-ray diffractometer, Model D/MAX-IIIB, made in Japan.

RESULTS AND DISCUSSION

DTA, TG, DTG and DSC peaks

All the thermal curves of $MgO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$) were quite different. In the DTA curve of $MgO \cdot 3B_2O_3 \cdot 5H_2O$, only one endothermic peak of dehydration appeared at 310 ° C (Fig. 1), in the TG and DTG curves at 304° C (Fig. 2), and in the DSC curve at 287 ° C (Fig. 3). The value of the enthalpy determined by DSC is $\Delta H = +389.30$ kJ mol^{-1}.

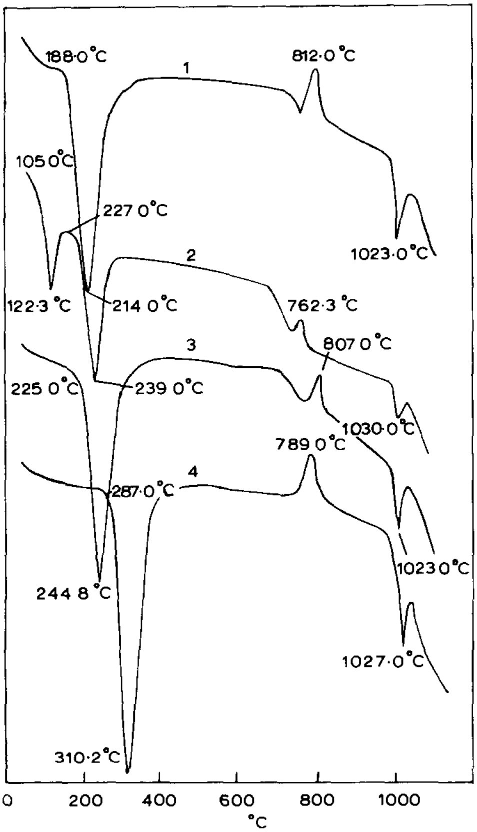

Fig. 1. DTA of $MgO \cdot 3B_2O_3 \cdot nH_2O$. 1, $n = 7\frac{1}{2}$; 2, $n = 7$; 3, $n = 6$; 4, $n = 5$.

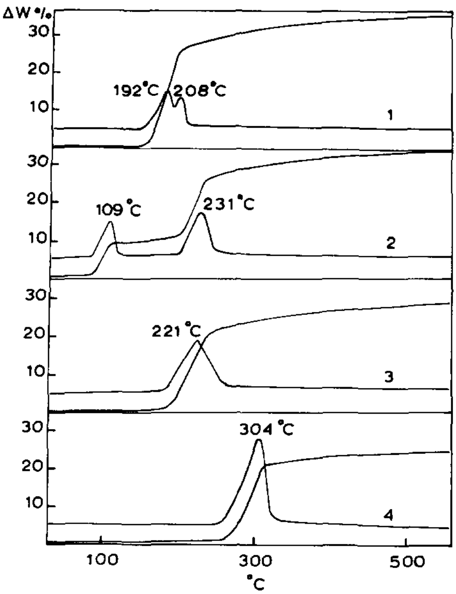

Fig. 2. TG and DTG of $MgO \cdot 3B_2O_3 \cdot nH_2O$. 1, $n = 7\frac{1}{2}$; 2, $n = 7$; 3, $n = 6$; 4, $n = 5$.

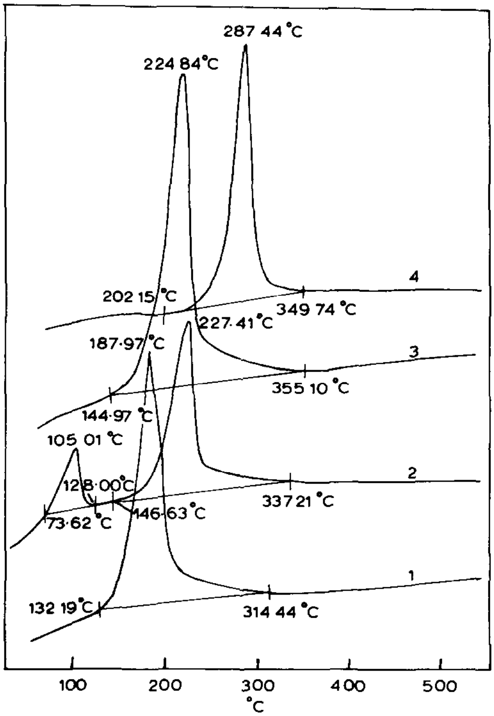

Fig. 3. DSC of $MgO \cdot 3B_2O_3 \cdot nH_2O$. 1, $n = 7\frac{1}{2}$; 2, $n = 7$; 3, $n = 6$; 4, $n = 5$.

There also appeared only one peak in the DTA curve of $MgO \cdot 3B_2O_3 \cdot 6H_2O$ at 244° C (Fig. 1), in the TG and DTG curves at 221° C (Fig. 2) and in the DSC curve at 224° C (Fig. 3). The value of the enthalpy determined by DSC is $\Delta H = +428.65$ kJ mol^{-1}.

There are two separate peaks in the DTA curve of $MgO \cdot 3B_2O_3 \cdot 7H_2O$, one at 122° C and the other at 239° C (Fig. 1). Two peaks appeared in the TG and DTG curves at 109° C and 231° C, respectively (Fig. 2), and in the DSC curve two peaks appeared separately at 105.0° C and 227.4° C (Fig. 3). The value of the enthalpy determined by DSC is $\Delta H_1 = +89.05$ kJ mol^{-1} and $\Delta H_2 = 276.30$ kJ mol^{-1}.

In the DTA curve of $MgO \cdot 3B_2O_3 \cdot 7\frac{1}{2}H_2O$, one peak appears at 214° C (Fig. 1), in DTG curve two peaks appear at 192° C and 208° C (Fig. 2), and in the DSC curve one peak at 188° C (Fig. 3). The enthalpy of dehydration is $\Delta H = +525.46$ kJ mol^{-1}.

In all the DTA curves of $MgO \cdot 3B_2O_3 \cdot nH_2O$ between 700° C and 820° C there appeared one small obvious exothermic peak which is characteristic of recrystallization. The results are shown in Fig. 1. When the samples were heated above 1000° C, they showed an endothermic peak which is named the melting point in the curves of the $MgO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$).

Infrared spectra

The four different compounds in the series $MgO \cdot 3B_2O_3 \cdot nH_2O$ and their products of dehydration and recrystallization isolated at various stages of thermal analysis were investigated by infrared spectroscopy (Fig. 4). In the IR spectra of $MgO \cdot 3B_2O_3 \cdot nH_2O$, most of the absorption bands (from 700 cm^{-1} to 1200 cm^{-1}) which depend only on the structure of the group $B_6O_7(OH)_4^{2-}$ are nearly the same with only slight differences in the intensities. At the different stages of dehydration, the spectra of the products retain almost the same shape and the absorption bands become weaker as the temperature increases. As the temperature rises above 400° C, only a few very wide bands appear in the spectra of the products and the sharp bands disappear completely, indicating that all the dehydrated products become amorphous. When the materials are heated continuously to the temperature at which recrystallization occurs a lot of new sharp bands again appear in the spectra.

X-Ray diffraction data

Each of the synthetic $MgO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$) compounds and the samples heated to different temperatures were examined by X-ray powder diffraction. The four different hydrated Mg hexaborates have their own characteristics of X-ray diffractograms shown in Fig. 5. During dehydration, the X-ray diffraction peak becomes weaker as the temperature rises.

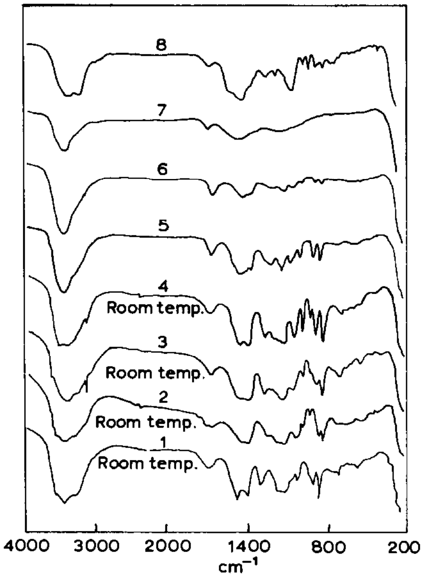

Fig. 4. IR spectra of MgO·3B_2O_3·$n$$H_2O$ and the dehydration and recrystallization products of MgO·3B_2O_3·7H_2O. 1, $n = 7\frac{1}{2}$; 2, $n = 6$; 3, $n = 5$; 4, $n = 7$; 5, 6, dehydration products of MgO·3B_2O_3·7H_2O; 7, dehydration products of MgO·3B_2O_3·$n$$H_2O$; 8, recrystallization products of MgO·3B_2O_3·$n$$H_2O$.

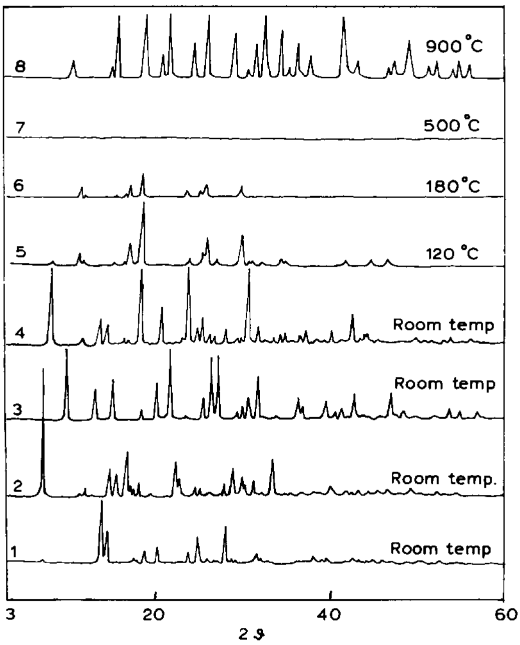

Fig. 5. X-Ray diffractograms of MgO·3B_2O_3·$n$$H_2O$ and the dehydration and recrystallization products of MgO·3B_2O_3·7H_2O. For key, see Fig. 4.

At last, all the samples heated above 400 ° C became amorphous and have no peaks in the diffractograms. When the samples were heated continuously to above 800 ° C, the amorphous products began to transform into the crystalline state. At the same time, there appeared new characteristic peaks in the X-ray diffractograms.

Chemical analysis

The MgO, B_2O_3 and H_2O contents were determined in the synthesized samples of $MgO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$). The $MgO : B_2O_3 : H_2O$ molar ratios shown in Table 1 are in exact agreement with the respective molecular formulae.

The analytical results of all the amorphous materials obtained by heating the synthetic samples to 500 ° C are shown in Table 1 and it can be seen that they have the same molar ratio as the synthesized samples, $MgO : B_2O_3 = 1 : 3$. The statistical chemical formulas are the same as $MgO \cdot 3B_2O_3$. The samples heated above 800 ° C recrystallized and the products were allowed to react with sufficient methyl alcohol at the boiling point. After the esterification reactions were completed, the residual products were analyzed and the results showed that the composition was much different from that of the amorphous products of dehydration. The composition of the recrystallized products can be expressed as $2MgO \cdot 3B_2O_3$, which is the same as the results for dehydrated and recrystallized inderite.

Interpretation

Dehydration reactions are associated with weight loss. The results obtained from TG, DTG, IR spectrographs and X-ray diffractograms can give information about the different reactions occurring in connection with the various DTA peaks. The DSC thermographs showed that every dehydration reaction had to be accompanied by an endothermal effect, and all the recrystallization reactions with an exothermal effect.

In the DTA, TG, DTG and DSC thermograms of $MgO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$), one or two dehydration processes occur. The IR spectra and X-ray diffraction analysis showed that no new characteristic structural peaks appeared, which meant that the crystalline structure did not change during dehydration, except for the X-ray diffractograms of the first dehydrated products of $MgO \cdot 3B_2O_3 \cdot 7H_2O$ (Fig. 5) and $MgO \cdot 3B_2O_3 \cdot 7\frac{1}{2}H_2O$.

As the dehydration reactions were completed, all of the characteristic structural peaks disappeared not only in the IR spectragraph but also in the X-ray powder diffractograms. This means that, at above 500 ° C, the crystalline states of the different hydrated Mg hexaborates have been transformed into the amorphous $MgO \cdot 3B_2O_3$.

TABLE 1

Analytical results of $MgO\cdot 3B_2O_3\cdot nH_2O$ and their dehydrated and recrystallized products

Sample	Condition	Analytical results						$MgO:B_2O_3:H_2O$		
		MgO		B_2O_3		H_2O				
		(%)	(m)	(%)	(m)	(%)	(m)	(m)	(m)	(m)
$MgO\cdot 3B_2O_3\cdot 5H_2O$	Synthetic	11.89	0.295	61.35	0.881	26.55	1.474	1.00	2.99	5.00
	Dehydrated product (500 °C)	16.22	0.402	83.78	1.203			1.00	2.99	
	Recrystallized product (esterification)	27.77	0.689	72.23	1.037			2.00	3.01	
$MgO\cdot 3B_2O_3\cdot 6H_2O$	Synthetic	11.27	0.280	58.20	0.836	30.51	1.693	1.00	2.99	6.05
	Dehydrated product (500 °C)	16.13	0.400	83.87	1.205			1.00	3.01	
	Recrystallized product (esterification)	27.67	0.686	72.33	1.039			2.00	3.03	
$MgO\cdot 3B_2O_3\cdot 7H_2O$	Synthetic	10.73	0.266	54.95	0.789	33.67	1.869	1.00	2.97	7.02
	Dehydrated product (500 °C)	16.09	0.399	83.91	1.205			1.00	3.02	
	Recrystallized product (esterification)	27.64	0.686	72.36	1.039			2.00	3.03	
$MgO\cdot 3B_2O_3\cdot 7\frac{1}{2}H_2O$	Synthetic	10.48	0.260	54.22	0.779	35.21	1.954	1.00	3.00	7.52
	Dehydrated product (500 °C)	16.41	0.407	83.58	1.200			1.00	2.95	
	Recrystallized product (esterification)	27.77	0.689	72.23	1.037			2.00	3.01	

When the samples were heated continuously to above 800 °C, in every DTA curve there appeared only one clear small characteristic peak which was accompanied by an exothermal effect. The results obtained from the IR spectrographs and the X-ray diffractograms in which there appeared new characteristic peaks, can give information about reactions which occur in connection with the DTA exothermal peak (Fig. 1).

In order to determine how many phases existed in the system, we succeeded in separating products of the exothermal reaction at high temperature by means of the reactions between B_2O_3 and methyl alcohol

$$B_2O_3 + 3\ CH_3OH \rightarrow B(OCH_3)_3 + B(OH)_3$$

$$B(OH)_3 + 3\ CH_3OH \rightarrow B(OCH_3)_3 + 3\ H_2O$$

In this way, the composition of the recrystallized phase of the four series compounds have been determined. From the analytical results of the samples taken from the products obtained before and after the esterification, the conclusion was reached that the products of the recrystallization at high temperature have two phases; one is the amorphous B_2O_3 and the other is the crystalline $2MgO \cdot 3B_2O_3$, not $MgO \cdot 2B_2O_3$ as reported in the literature [6–8].

The following reactions may occur in the course of the thermal analysis of $MgO \cdot 3B_2O_3 \cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$).

(1) Dehydration

$n = 5$

$$\underset{\text{crystal}}{MgO \cdot 3B_2O_3 \cdot 5H_2O} \xrightarrow{304\,^\circ C} \underset{\text{amorphous}}{MgO \cdot 3B_2O_3} + \underset{\text{gas}}{5\ H_2O}$$

$\Delta H = +389.30\ \text{kJ mol}^{-1}$

$n = 6$

$$\underset{\text{crystal}}{MgO \cdot 3B_2O_3 \cdot 6H_2O} \xrightarrow{221\,^\circ C} \underset{\text{amorphous}}{MgO \cdot 3B_2O_3} + \underset{\text{gas}}{6\ H_2O}$$

$\Delta H = +428.65\ \text{kJ mol}^{-1}$

$n = 7$

$$\underset{\text{crystal}}{MgO \cdot 3B_2O_3 \cdot 7H_2O} \xrightarrow{109\,^\circ C} \underset{\text{amorphous}}{MgO \cdot 3B_2O_3 \cdot 5H_2O} + \underset{\text{gas}}{2\ H_2O}$$

$\Delta H_1 = +89.05\ \text{kJ mol}^{-1}$

$$\underset{\text{crystal}}{MgO \cdot 3B_2O_3 \cdot 5H_2O} \xrightarrow{231\,^\circ C} \underset{\text{amorphous}}{MgO \cdot 3B_2O_3} + \underset{\text{gas}}{5\ H_2O}$$

$\Delta H_2 = +276.30\ \text{kJ mol}^{-1}$

$$\Delta H = \Delta H_1 + \Delta H_2 = +365.35\ \text{kJ mol}^{-1}$$

$n = 7\frac{1}{2}$

$$\underset{\text{crystal}}{MgO\cdot 3B_2O_3\cdot 7\tfrac{1}{2}H_2O} \xrightarrow{192^\circ C} \underset{\text{amorphous}}{MgO\cdot 3B_2O_3\cdot 4H_2O} + \underset{\text{gas}}{3.5\ H_2O}$$

$$\underset{\text{crystal}}{MgO\cdot 3B_2O_3\cdot 4H_2O} \xrightarrow{208^\circ C} \underset{\text{amorphous}}{MgO\cdot 3B_2O_3} + \underset{\text{gas}}{4\ H_2O}$$

$$\Delta H = \Delta H_1 + \Delta H_2 = +525.46\ \text{kJ mol}^{-1}$$

(2) Recrystallization

$$\underset{\text{amorphous}}{2\ (MgO\cdot 3B_2O_3)} \rightarrow \underset{\text{crystal}}{2MgO\cdot 3B_2O_3} + \underset{\text{amorphous}}{3\ B_2O_3}$$

(3) Liquefaction

$$\underset{\text{crystal}}{2\ MgO\cdot 3B_2O_3} + \underset{\text{amorphous}}{3\ B_2O_3} \rightarrow \underset{\text{liquid}}{MgO\cdot 3B_2O_3}$$

Kinetic equations of dehydration

All the TG and DTG peaks of the $MgO\cdot 3B_2O_3\cdot nH_2O$ ($n = 5, 6, 7, 7\frac{1}{2}$) were analyzed by assuming the validity of the rate equation

$$\frac{d\alpha}{dt} = K(1-\alpha)^n$$

In this equation, α is the fraction of the sample which has been decomposed, n is the apparent reaction order, and the rate constant K is given by the Arrhenius equation

$$K = A\ \exp\left(-\frac{E}{RT}\right)$$

where E is the activation energy, A the frequency factor, R the gas constant and T the temperature (in K). The parameters E, n and A were calculated using the following two methods.

(a) According to Freeman and Carrol [9], a plot of $\ln(d\alpha/dT)/\ln(1-\alpha)$ against $(1/T)/\ln(1-\alpha)$ should give a straight line with a slope of $-E/R$ and an intercept of n at the y axis. A total of 11–19 data points were taken for each peak. The results of kinetic parameters calculated by the Freeman–Carrol method are shown in Table 2.

(b) Coats and Redfern [10] reported the integral equation

$$\frac{(1-\alpha)-1}{1-n} = \frac{AEP(x)}{\beta R} \qquad (n \neq 1)$$

$$\ln(1-\alpha) = \frac{AEP(x)}{R} \qquad (n \neq 1)$$

TABLE 2

Kinetic parameters calculated by the Freeman–Carrol and Coats–Redfern methods for the dehydration of $MgO \cdot 3B_2O_3 \cdot nH_2O$

Sample	Calculated kinetic parameters					
	Freeman–Carrol			Coats–Redfern		
	E (kJ mol^{-1})	n	A (s^{-1})	E (kJ mol^{-1})	n	A (s^{-1})
$MgO \cdot 3B_2O_3 \cdot 5H_2O$	172.43	0.92	3.25×10^{17}	162.00	1.00	3.23×10^{14}
$MgO \cdot 3B_2O_3 \cdot 6H_2O$	127.75	2.00	2.34×10^{15}	127.91	2.00	2.02×10^{13}
$MgO \cdot 3B_2O_3 \cdot 7H_2O$ (1)	124.66	0.96	8.34×10^{17}	129.76	0.90	8.56×10^{17}
$MgO \cdot 3B_2O_3 \cdot 7H_2O$ (2)	171.61	2.15	6.74×10^{19}	182.02	2.20	1.16×10^{19}
$MgO \cdot 3B_2O_3 \cdot 7\frac{1}{2}H_2O$ (1)	150.96	0.64	7.38×10^{18}	145.95	0.70	3.44×10^{17}
$MgO \cdot 3B_2O_3 \cdot 7\frac{1}{2}H_2O$ (2)				223.68	1.00	6.63×10^{23}

where

$$P(x) = \frac{1}{x}\left(1 + \frac{2}{x} + \frac{3}{x} + \dots\right)$$

It is considered that, in general, $E/RT \gg 1$ if only the first two items in the series are taken. Replacing this in the integral equation gives

$$Y = \frac{E}{R}X + \ln\frac{AR}{E}$$

where

$$X = \frac{1}{x};$$

$$Y = \ln\frac{1-(1-\alpha)}{(1-n)T} \quad (n \neq 1)$$

$$Y = \ln\frac{-\ln(1-\alpha)}{T} \quad (n = 1)$$

A plot of X against Y should give a straight line with a slope of $-E/R$ and an intercept of $\ln(AR/\beta E)$ on the Y axis. The results of kinetic parameters can be calculated by computer and are shown in Table 2. It is emphasized that taking the initial and final values from TG curve is the key to the calculation of the kinetic parameters.

Kinetic parameters during the dehydration of the $MgO \cdot 3B_2O_3 \cdot nH_2O$ have been calculated and the corresponding kinetic equations are

$n = 5$

$$\frac{d\alpha}{dt} = 3.25 \times 10^{17} \exp\left(-\frac{172426}{RT}\right)(1-\alpha)^{0.92}$$

$n = 6$

$$\frac{d\alpha}{dt} = 2.34 \times 10^{15} \exp\left(-\frac{127751}{RT}\right)(1-\alpha)^{2.00}$$

$n = 7$

The first dehydration step

$$\frac{d\alpha}{dt} = 8.34 \times 10^{17} \exp\left(-\frac{124662}{RT}\right)(1-\alpha)^{0.96}$$

The second dehydration step

$$\frac{d\alpha}{dt} = 6.74 \times 10^{19} \exp\left(-\frac{171605}{RT}\right)(1-\alpha)^{2.15}$$

$n = 7\frac{1}{2}$

The first dehydration step

$$\frac{d\alpha}{dt} = 7.38 \times 10^{18} \exp\left(-\frac{150961}{RT}\right)(1-\alpha)^{0.64}$$

The second dehydration step

$$\frac{d\alpha}{dt} = 6.63 \times 10^{23} \exp\left(-\frac{223680}{RT}\right)(1-\alpha)^{1.00}$$

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