

# Synthesis and Thermodynamic Properties of $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$

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A new magnesium borate  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  was synthesized by the method of phase transformation of double salt and characterized by XRD, IR spectra and TG. The structural formula of this compound was  $\text{Mg}[\text{B}_2\text{O}(\text{OH})_6] \cdot \text{H}_2\text{O}$ . The enthalpy of solution of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  in HCl ( $1.0492 \text{ mol} \cdot \text{L}^{-1}$ ) was determined. With the incorporation of the standard molar enthalpies of formation of  $\text{MgO}(s)$ ,  $\text{H}_3\text{BO}_3(s)$ , and  $\text{H}_2\text{O}(l)$ , the standard molar enthalpy of formation of  $-(3135.31 \pm 1.68) \text{ kJ} \cdot \text{mol}^{-1}$  of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  was obtained. Thermodynamic properties of this compound were also calculated by group contribution method.

**Keywords**  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , synthesis, thermodynamic properties, solution calorimetry

## Introduction

There are many kinds of magnesium borates, both natural and synthetic. A borate double salt ( $2\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot \text{MgCl}_2 \cdot 14\text{H}_2\text{O}$ ) named chloropinnoite was obtained from the natural concentrated salt lake brine.<sup>1</sup> In order to find the forming relation between the double salt and magnesium-borate minerals in the salt lakes, the kinetic process of dissolution and transformation of chloropinnoite in water at 20—60 °C was studied.<sup>2,3</sup> These experimental results showed that chloropinnoite dissolved incongruently in water.  $\text{MgCl}_2$  was removed first, then the amorphous midproduct ( $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ ) was formed, and finally, this midproduct was transformed into  $2\text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 15\text{H}_2\text{O}$  or  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  depending on the temperature. Regrettly, the pH value of solution in dissolution process was so great that hydrolysis reaction of  $\text{Mg}^{2+}$  might occur, which led to the midproduct contain-

ing  $\text{Mg}(\text{OH})_2$ . Recently, we obtained this pure magnesium borate when investigating the phase transformation of  $2\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot \text{MgCl}_2 \cdot 14\text{H}_2\text{O}$  in the aqueous solution of boric acid at 0 °C. It is the lower temperature of 0 °C that retards the hydrolysis reaction of  $\text{Mg}^{2+}$ .

Thermodynamic properties play very important roles in scientific research and industrial applications. Li *et al.* have reported the standard molar enthalpy of formation of nine hydrated magnesium borates.<sup>4,5</sup> As part of the continuing study of the thermochemistry of hydrated borates, in this paper we report the synthesis and the thermodynamic properties of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ .

## Experimental

### Reagents and instruments

$\text{H}_3\text{BO}_3$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$  and HCl were of analytical grade, and KCl was spectral purity. X-Ray powder diffraction meter (Rigaku D/MAX-IIIc), Bruker Equinox 55 spectrometer (with KBr pellet), Perkin-Elmer TGA7 thermograph analyzer (at a heating rate of 10 °C/min in flowing  $\text{N}_2$ ), and RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) were used.

### Synthesis of $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$

$2\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot \text{MgCl}_2 \cdot 14\text{H}_2\text{O}$  (1.86 g, synthesized by modification of the reported method<sup>6</sup>),  $\text{H}_3\text{BO}_3$  (0.11 g) and  $\text{H}_2\text{O}$  (40 mL) were transferred to a flask with a

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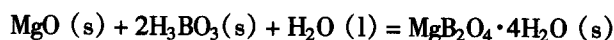
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stirrer, which was set in a constant temperature water bath at 0 °C. After the reaction mixture was stirred for 24 h, the solid in solution was separated, washed thoroughly with alcohol and then ether. Finally, the obtained solid was dried in a vacuum dryer to a constant weight at room temperature, and identified by chemical analysis (determined by EDTA titration for  $\text{Mg}^{2+}$ , by NaOH standard solution in the presence of mannitol for  $\text{B}_2\text{O}_3$ , and by difference for  $\text{H}_2\text{O}$ ), X-ray powder diffraction analysis, FT-IR spectroscopy and TG.

#### Method of calorimetric experiment

$\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  can be regarded as the product of the following reaction:



The standard molar enthalpy of formation of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of  $\text{MgO (s)}$ ,  $\text{H}_3\text{BO}_3(\text{s})$ , and  $\text{H}_2\text{O (l)}$ . The  $\text{H}_3\text{BO}_3$  and  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  were dissolved in approximately  $\text{HCl (1 mol} \cdot \text{L}^{-1})$  respectively, and then the calculated amount of  $\text{MgO}$  was dissolved in aqueous (hydrochloric acid + boric acid) which consisted of approximately  $\text{HCl (1 mol} \cdot \text{L}^{-1})$  and the calculated amount of  $\text{H}_3\text{BO}_3$ . The  $\text{HCl}$  solvent was prepared from analytical grade hydrochloric acid and deionized water, whose concentration ( $1.0492 \text{ mol} \cdot \text{L}^{-1}$ ) was determined by titration with standard sodium carbonate and its density ( $1.022 \text{ g} \cdot \text{cm}^{-3}$ ) was taken from chemical handbook.

A RD496-III heat conduction microcalorimeter, which is a totally automatic instrument utilizing computer control, was used and has been described in detail previously.<sup>7</sup> The temperature of the calorimetric experiment was 298.15 K. An additional double-layer glass tube, which was put in the 15 mL of stainless steel sample cell and reference cell for the microcalorimeter, was used because of the corrosion by  $\text{HCl (aq.)}$  of the stainless steel sample and reference cell. The device of double-layer glass tube used for calorimetry is referred to the method of literature.<sup>8</sup> The lining containing  $\text{HCl (aq.)}$  of double-layer glass tube was broken by a rod after thermal equilibration for at least 3 h, and the  $\text{HCl (aq.)}$  was mixed with solid sample in the outer glass tube, then the thermal effect was recorded automatically on an computer. Total

time required for the complete reaction was about 0.5 h. There were no solid residues observed after the reactions in each calorimetric experiment.

#### Results and discussion

Anal. calcd for  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ :  $\text{MgO}$  22.16,  $\text{B}_2\text{O}_3$  38.26,  $\text{H}_2\text{O}$  39.58; found  $\text{MgO}$  22.05,  $\text{B}_2\text{O}_3$  38.14,  $\text{H}_2\text{O}$  39.81; mole ratio of  $\text{MgO} : \text{B}_2\text{O}_3 : \text{H}_2\text{O}$  is 1.00:1.00:4.04. XRD spectra of synthetic sample had no diffraction peaks which showed that it was amorphous. So the FT-IR spectra of this sample exhibited the following tiny absorptions: the band at  $3425 \text{ cm}^{-1}$  is the stretching of  $\text{O-H}$ , the band at  $1648 \text{ cm}^{-1}$  is assigned to the  $\text{H-O-H}$  bending mode, the band at  $1408 \text{ cm}^{-1}$  is the in-plane bending of  $\text{B-O-H}$ , and the bands at 804 and  $1005 \text{ cm}^{-1}$  are assigned as the symmetric and asymmetric stretching of  $\text{B(4)-O}$ , respectively. It can be seen that the vibration frequencies of FT-IR has not any of characteristic absorption of  $\text{B(3)-O}$ . TG curve indicates that the total loss is 39.43% from 60 to 750 °C, which corresponds to the loss of 4 water molecules and can be compared with calculated value of 39.58%. Therefore, the structural formula of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  can be written as  $\text{Mg}[\text{B}_2\text{O}(\text{OH})_6] \cdot \text{H}_2\text{O}$  in combination with the results of thermal analysis<sup>1</sup> and vibrational spectroscopy<sup>9</sup> of  $2\text{MgO} \cdot 2\text{B}_2\text{O}_3 \cdot \text{MgCl}_2 \cdot 14\text{H}_2\text{O}$ . And the synthetic sample is suitable for the following calorimetric experiments.

To check the performance of RD496-III heat conduction microcalorimeter, calorimetric measurements on the enthalpy of solution of  $\text{KCl}$  in deionized water were made, and the results are listed in Table 1. The experimental value ( $17.23 \pm 0.04$ )  $\text{kJ} \cdot \text{mol}^{-1}$  of  $\Delta_{\text{sol}}H_{\text{m}}$  is in excellent agreement with that of  $17.234 \text{ kJ} \cdot \text{mol}^{-1}$  reported in the literature.<sup>10</sup> This shows that the device for measur-

**Table 1** Enthalpy of solution in water of  $\text{KCl}$  at 298.15 K<sup>a</sup>

No.	<i>m</i> (mg)	$\Delta_{\text{sol}}H_{\text{m}}$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )
1	8.01	17.23
2	8.19	17.15
3	12.02	17.29
4	13.16	17.25
5	15.00	17.27
6	15.02	17.24
7	15.04	17.21
Mean		$17.23 \pm 0.04^b$

<sup>a</sup> In each experiment, 8.00 mL of  $\text{H}_2\text{O}$  was used. <sup>b</sup> Uncertainty is twice the standard deviation of the mean.

ing the enthalpy of solution used in this work is reliable.

The results of the calorimetric measurements are given in Table 2, in which  $m$  is the mass of sample,  $\Delta_{\text{sol}}H_m$  is the molar enthalpy of solution of solute, and the uncertainty is twice the standard deviation of the mean. The molar mass of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  is  $181.9 \text{ g} \cdot \text{mol}^{-1}$ .

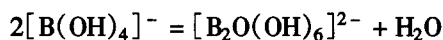
**Table 2** Molar enthalpies of solution of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  in  $1.0492 \text{ mol} \cdot \text{L}^{-1}$  HCl at  $298.15 \text{ K}^a$

No.	$m$ (mg)	$\Delta_{\text{sol}}H_m$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )
1	4.07	-44.23
2	4.10	-44.26
3	4.08	-44.31
4	4.19	-44.27
5	4.00	-44.35
Mean		$-44.28 \pm 0.04^b$

<sup>a</sup> In each experiment,  $2.00 \text{ mL}$  of HCl (aq.) was used. <sup>b</sup> Uncertainty is twice the standard deviation of the mean.

Table 3 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ . The molar enthalpies of solutions of  $\text{H}_3\text{BO}_3(\text{s})$  of  $(21.83 \pm 0.08) \text{ kJ} \cdot \text{mol}^{-1}$  in approximately  $1 \text{ mol} \cdot \text{L}^{-1}$  HCl (aq.), and of  $\text{MgO}(\text{s})$  of  $(-146.20 \pm 0.36) \text{ kJ} \cdot \text{mol}^{-1}$  in the mixture of HCl and  $\text{H}_3\text{BO}_3$  were taken from previous work.<sup>4</sup> The standard molar enthalpies of formation of  $\text{H}_2\text{O}(\text{l})$ ,  $\text{MgO}(\text{s})$  and  $\text{H}_3\text{BO}_3(\text{s})$  were taken from the CODATA key values,<sup>11</sup> namely  $(-285.830 \pm 0.040)$ ,  $(-601.60 \pm 0.30)$ , and  $(-1094.8 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively. The enthalpy of dilution of HCl (aq.) was calculated from the NBS tables.<sup>12</sup> From these data, the standard molar enthalpy of formation of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  was calculated to be  $(-3135.31 \pm 1.68) \text{ kJ} \cdot \text{mol}^{-1}$ . For comparison, the  $\Delta_f H_m^0$  of  $-3132.95 \text{ kJ} \cdot \text{mol}^{-1}$  of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  was

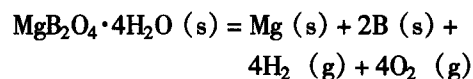
calculated using the group contribution method for the calculation of thermodynamic properties of hydrated borates,<sup>13</sup> and the  $\Delta_f H_m^0$  of  $-2375.68 \text{ kJ} \cdot \text{mol}^{-1}$  of  $[\text{B}_2\text{O}(\text{OH})_6]^{2-}$  taken from the referring literature.<sup>14</sup> The calculated value is close to the experimental result. The relative error is  $-0.08\%$ . This result shows that the proposed structural formula of this compound,  $\text{Mg}[\text{B}_2\text{O}(\text{OH})_6] \cdot \text{H}_2\text{O}$ , is correct in turn. So we also used a group contribution method to calculate  $\Delta_f G_m^0$  of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  to be  $-2774.54 \text{ kJ} \cdot \text{mol}^{-1}$ , and the  $\Delta_f G_m^0$  of  $-2082.46 \text{ kJ} \cdot \text{mol}^{-1}$  of  $[\text{B}_2\text{O}(\text{OH})_6]^{2-}$  was calculated from the  $\Delta_f G_m^0$  of  $[\text{B}(\text{OH})_4]^-$  according to the following equation:



Combining  $\Delta_f H_m^0$  of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , the standard molar entropy of formation of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , has been calculated at  $-1210.03 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  according to following equation:

$$\Delta_f S_m^0 = (\Delta_f H_m^0 - \Delta_f G_m^0) / T$$

Finally, the standard molar entropy,  $S_m^0$ , of  $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  to be  $176.90 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  according to following reaction:



The standard molar entropies of the elements were taken from CODATA key values to be  $32.67$ ,  $5.90$ ,  $130.571$  and  $205.043 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  for  $\text{Mg}(\text{s})$ ,  $\text{B}(\text{s})$ ,  $\text{H}_2(\text{g})$ , and  $\text{O}_2(\text{g})$ , respectively.

**Table 3** Thermochemical cycle and results for the derivation of  $\Delta_f H_m^0$  ( $\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ ,  $298.15 \text{ K}$ )

No.	Reaction	$\Delta_f H_m^0$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )
1	$2\text{H}_3\text{BO}_3(\text{s}) + 95.425 (\text{HCl} \cdot 52.088\text{H}_2\text{O}) = 2\text{H}_3\text{BO}_3(\text{aq.}) + 95.425 (\text{HCl} \cdot 52.088\text{H}_2\text{O})$	$43.66 \pm 0.16$
2	$\text{MgO}(\text{s}) + 2\text{H}_3\text{BO}_3(\text{aq.}) + 95.425 (\text{HCl} \cdot 52.088\text{H}_2\text{O}) = \text{MgCl}_2(\text{aq.}) + 2\text{H}_3\text{BO}_3(\text{aq.}) + 93.425 (\text{HCl} \cdot 53.213 \text{H}_2\text{O})$	$-146.20 \pm 0.36$
3	$\text{MgCl}_2(\text{aq.}) + 2\text{H}_3\text{BO}_3(\text{aq.}) + 93.425 (\text{HCl} \cdot 53.213\text{H}_2\text{O}) = \text{MgB}_2\text{O}_4 \cdot 4\text{H}_2\text{O}(\text{s}) + 95.425 (\text{HCl} \cdot 52.077\text{H}_2\text{O})$	$44.28 \pm 0.04$
4	$95.425 (\text{HCl} \cdot 52.077\text{H}_2\text{O}) + \text{H}_2\text{O}(\text{l}) = 95.425 (\text{HCl} \cdot 52.088\text{H}_2\text{O})$	$-0.02 \pm 0.01$
5	$\text{MgO}(\text{s}) + 2\text{H}_3\text{BO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) = \text{MgB}_2\text{O}_4 \cdot 4\text{H}_2\text{O}(\text{s})$	$-58.28 \pm 0.40$

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