



# Synthesis and thermochemistry of two zinc borates, $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$ and $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$

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## ABSTRACT

Two pure zinc borates,  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  and  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$  have been synthesized and characterized by XRD, FT-IR, DTA-TG techniques and chemical analysis. The molar enthalpies of solution of  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}(\text{s})$  and  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}(\text{s})$  in  $1\text{ mol dm}^{-3}\text{ HCl}(\text{aq})$  were measured to be  $15.42 \pm 0.03\text{ kJ mol}^{-1}$  and  $57.78 \pm 0.11\text{ kJ mol}^{-1}$ , respectively. The molar enthalpy of solution of  $\text{ZnO}(\text{s})$  in  $(\text{HCl} + \text{H}_3\text{BO}_3)(\text{aq})$  was determined to be  $-80.01 \pm 0.15\text{ kJ mol}^{-1}$ . With incorporation of the previously determined enthalpy of solution of  $\text{H}_3\text{BO}_3(\text{s})$  in  $1\text{ mol dm}^{-3}\text{ HCl}(\text{aq})$ , and the standard molar enthalpies of formation for  $\text{ZnO}(\text{s})$ ,  $\text{H}_3\text{BO}_3(\text{s})$ , and  $\text{H}_2\text{O}(\text{l})$ , the standard molar enthalpies of formation of  $-6738.1 \pm 4.8\text{ kJ mol}^{-1}$  for  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  and  $-11,786.4 \pm 8.0\text{ kJ mol}^{-1}$  for  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$  were obtained.

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## 1. Introduction

There are many kinds of zinc borates [1] found in nature as well as synthesized in the laboratory. Some of these borates have useful properties. For example, zinc borates with different chemical formula such as  $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot n\text{H}_2\text{O}$  ( $n = 3, 7$ ),  $4\text{ZnO}\cdot \text{B}_2\text{O}_3\cdot \text{H}_2\text{O}$ , and  $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3$  are the fire retardant materials used in plastics [2].

Thermodynamic properties play very important roles in scientific research and industrial applications. As for the thermochemistry of borates, the standard molar enthalpies of formation of many alkaline, and alkaline-earth metal borates have been measured [3–11]. However, studies of the thermochemistry of the transition metal borates, such as zinc borates, are not reported in the literature. This paper reports the determination of standard molar enthalpies of formation of two zinc borates,  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  and  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$ , by using a heat conduction microcalorimeter.

## 2. Experimental

### 2.1. Synthesis and characterization of samples

All reagents used in the synthesis were of analytic grade (made in Xi'an Chemical Factory, China).

$\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  was prepared by the following procedure: 6.671 g of  $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ , 0.203 g of ZnO are added to a solution of 5.032 g of  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$  in 77.5 ml of distilled water. The mixture

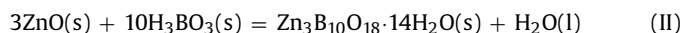
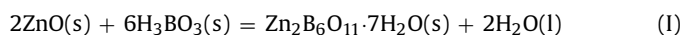
was put into the flask and was refluxed at the boiling point. After 11 h, the mixture was stored at room temperature for several days. The solids were separated and washed thoroughly with distilled water, and then with alcohol and ether, and finally dried at room temperature to a constant mass.

$\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$  was prepared by the following procedure: 3.048 g of  $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$  is added to a solution of 4.945 g of  $\text{H}_3\text{BO}_3$  in 50 ml of distilled water. A solution of 2.304 g of  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$  in 10 ml of distilled water was added and the solution was left in a closed beaker. The mixture was stirred for 1 h at room temperature. After several days, the resulting white precipitate was filtered, then washed with absolute alcohol and absolute ether, and finally, dried at room temperature to constant mass.

The two synthetic samples were characterized by X-ray powder diffraction (XRD, Rigaku D/MAX-IIIIC with Cu target at  $8^\circ\text{ min}^{-1}$ ), FT-IR spectroscopy (Nicolet NEXUS 670 FT-IR spectrometer with KBr pellets at room temperature), and TG-DTA (TA-SDT Q600 simultaneous thermal analyzer at a heating rate of  $10\text{ K min}^{-1}$  in flowing  $\text{N}_2$ ). The chemical compositions of the samples were determined by EDTA titration for  $\text{Zn}^{2+}$ , by NaOH standard solution in the presence of mannitol for  $\text{B}_2\text{O}_3$ , and by the mass loss in the TG curve for  $\text{H}_2\text{O}$ .

### 2.2. Calorimetric experiment

$\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  and  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$  can be regarded as the products of the following reactions (I) and (II), respectively:



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The 1 mol dm<sup>-3</sup> HCl(aq) solvent can rapidly dissolve all components of reactions (I) and (II). The solution was prepared from analytical grade hydrochloric acid and deionized water, and its concentration, 1.0004 mol dm<sup>-3</sup>, was determined by titration with standard sodium carbonate.

The thermochemical cycles used are given in Tables 4 and 5. The molar enthalpies of solution of H<sub>3</sub>BO<sub>3</sub>(s), Zn<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·7H<sub>2</sub>O(s) and Zn<sub>3</sub>B<sub>10</sub>O<sub>18</sub>·14H<sub>2</sub>O(s) in 1 mol dm<sup>-3</sup> HCl(aq) were measured, respectively. The calculated amount of ZnO(s) was dissolved in (hydrochloric acid + boric acid) aqueous solution which consisted of 1 mol dm<sup>-3</sup> HCl(aq) and the calculated amount of H<sub>3</sub>BO<sub>3</sub>(s). In all these determinations, strict control of the stoichiometry in each step of the calorimetric cycle must be observed, with the objective that the dissolution of the reactants give the same composition as those of the products in reactions (I) and (II). Applying Hess's law, the enthalpy of reaction (5) can be calculated according to the following expression:

$$\Delta_r H_m^\circ(5) = \Delta_r H_m^\circ(1) + \Delta_r H_m^\circ(2) - \Delta_r H_m^\circ(3) - \Delta_r H_m^\circ(4) \quad (4)$$

The standard molar enthalpies of formation of Zn<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·7H<sub>2</sub>O and Zn<sub>3</sub>B<sub>10</sub>O<sub>18</sub>·14H<sub>2</sub>O can be obtained from the value of  $\Delta_r H_m^\circ(5)$  in combination with the molar enthalpies of formation of H<sub>3</sub>BO<sub>3</sub>(s), ZnO(s), and H<sub>2</sub>O(l).

All the enthalpies of solution were measured with an RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which is a totally automatic instrument by using a computerized control that has been described in detail previously [9,12]. Total time required for the complete dissolution reaction was about 0.5 h. There were no solid residues observed after the reactions in each calorimetric experiment.

To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction  $\geq 0.9999$ ) in deionized water was determined to be  $17.563 \pm 0.099$  kJ mol<sup>-1</sup>, which was in agreement

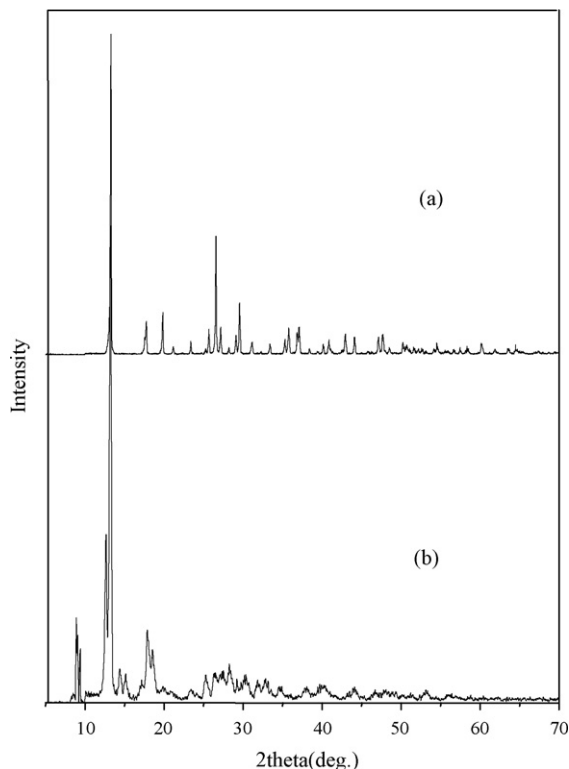


Fig. 1. X-ray powder diffraction patterns of samples. (a) Zn<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·7H<sub>2</sub>O and (b) Zn<sub>3</sub>B<sub>10</sub>O<sub>18</sub>·14H<sub>2</sub>O.

Table 1  
XRD data of synthetic samples and corresponding JCPDS cards values<sup>a</sup>.

Measured values			JCPDS cards values		
2θ (°)	d (Å)	I/I <sub>0</sub>	2θ (°)	d (Å)	I/I <sub>0</sub>
Zn <sub>2</sub> B <sub>6</sub> O <sub>11</sub> ·7H <sub>2</sub> O					
13.280	6.6617	100	13.207	6.6984	100
17.779	4.9847	10.3	17.687	5.0106	31
19.875	4.4635	13.0	19.824	4.4750	25
23.422	3.7950	3.9	389	3.8003	7
25.704	3.4630	7.7	25.590	3.4782	34
26.600	3.3483	36.6	593	3.3492	47
27.217	3.2738	8.3	27.092	3.2887	37
29.141	3.0618	5.7	29.145	3.0615	13
29.617	3.0138	15.8	29.519	3.0235	61
31.218	2.8627	3.6	31.237	2.8611	9
33.443	2.6772	3.1	33.466	2.6754	9
35.361	2.5362	4.6	35.391	2.5342	14
35.841	2.5034	7.9	35.813	2.5053	30
36.918	2.4328	6.6	36.936	2.4317	17
37.156	2.4178	8.3	37.136	2.4190	43
43.019	2.1008	6.2	43.064	2.0987	25
44.176	2.0484	5.2	44.240	2.0457	12
47.759	1.9028	5.8	47.830	1.9001	23
Zn <sub>3</sub> B <sub>10</sub> O <sub>18</sub> ·14H <sub>2</sub> O					
9.378	9.4226	10.5	10.813	9.5000	39
13.220	6.6918	100	15.218	6.7600	54
14.401	6.1455	5.1	16.415	.2700	23
15.160	5.8395	5.1	17.603	5.8500	25
18.541	4.7816	8.2	21.632	4.7700	31
23.420	3.7953	1.9	27.248	3.8000	39
25.280	3.5200	4.7	29.635	3.5000	21
26.380	3.3757	4.9	30.806	3.3700	22
28.280	3.1531	4.2	33.017	3.1500	23
30.400	2.9379	4.5	35.576	2.9300	100
31.877	2.8050	2.7	37.287	2.8000	26
32.840	2.7249	2.8	38.872	2.6900	54
38.138	2.3577	1.7	44.380	2.3700	62
34.900	2.5687	1.9	40.600	2.5800	57
53.218	1.7198	1.6	62.719	1.7200	85

<sup>a</sup> Data in JCPDS card (File No. 32–1461) obtained with Co target, and the others data obtained with Cu target.

with that of  $17.524 \pm 0.028$  kJ mol<sup>-1</sup> reported in the literature [13].

### 3. Results and discussion

#### 3.1. Chemical analysis of synthetic samples

The chemical analytical data of synthetic samples are (calcd./found, %), ZnO (32.70/32.37), B<sub>2</sub>O<sub>3</sub> (41.96/41.76), H<sub>2</sub>O (25.34/25.96) for sample of Zn<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·7H<sub>2</sub>O and ZnO (28.91/29.35), B<sub>2</sub>O<sub>3</sub> (41.22/41.67), H<sub>2</sub>O (29.87/31.53) for sample of Zn<sub>3</sub>B<sub>10</sub>O<sub>18</sub>·14H<sub>2</sub>O, which are consistent with the theoretical values.

#### 3.2. X-ray powder diffraction

The XRD patterns of synthetic samples are given in Fig. 1. The data of XRD patterns of the synthetic samples and corresponding data in JCPDS cards are listed in Table 1. The main characteristic *d* values for samples of Zn<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·7H<sub>2</sub>O and Zn<sub>3</sub>B<sub>10</sub>O<sub>18</sub>·14H<sub>2</sub>O agree with those of JCPDS cards (File Nos. 72–1789 and 32–1461) and shows absence of other crystalline forms in the synthetic samples, respectively. It is worth noting that the determined XRD data obtained with Cu target for Zn<sub>3</sub>B<sub>10</sub>O<sub>18</sub>·14H<sub>2</sub>O and corresponding XRD data in JCPDS card (File No. 32–1461) obtained with Co target, which leads to the different 2θ values between them.

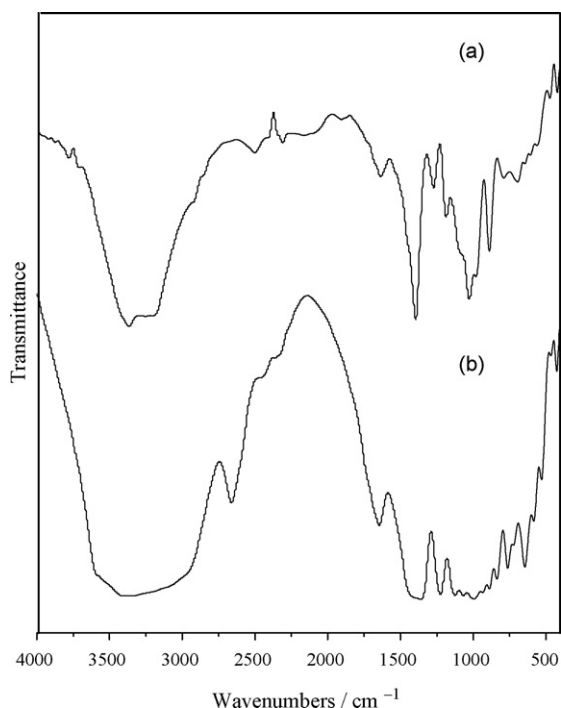


Fig. 2. FT-IR spectra of samples. (a)  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  and (b)  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$ .

### 3.3. FT-IR spectra

The FT-IR spectra (Fig. 2) of samples exhibited the following absorption bands and they were assigned referring to the literature [14].

For sample of  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$ : the band at  $3374\text{ cm}^{-1}$  is the stretching of O–H. The band at  $2510\text{ cm}^{-1}$  is the O–H stretching because of hydrogen bond. The band at  $1644\text{ cm}^{-1}$  is assigned to the H–O–H bending mode, which shows the compound containing the crystalline water. The bands at  $1181\text{ cm}^{-1}$  and  $1274\text{ cm}^{-1}$  might be the in-plane bending of B–O–H. The band at  $1391\text{ cm}^{-1}$  is the asymmetric stretching of B(3)–O. The bands at  $1022\text{ cm}^{-1}$  and  $883\text{ cm}^{-1}$  are the asymmetric and symmetric stretching of B(4)–O. The band at  $685\text{ cm}^{-1}$  is the out-of-plane bending mode of B(3)–O. The band at  $433\text{ cm}^{-1}$  is the bending of B(4)–O.

For sample of  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$ : the band at  $3355\text{ cm}^{-1}$  is the stretching of O–H. The band at  $2662\text{ cm}^{-1}$  is the O–H stretching because of hydrogen bond. The band at  $1645\text{ cm}^{-1}$  is the H–O–H bending mode, which shows that the compound contains crystalline water. The band at  $1224\text{ cm}^{-1}$  might be the in-plane bending of B–O–H. The peaks at  $1122\text{ cm}^{-1}$ ,  $831\text{ cm}^{-1}$  and  $762\text{ cm}^{-1}$  might be the asymmetric and symmetric stretching of B(4)–O. The band at  $1358\text{ cm}^{-1}$  is the asymmetric stretching of B(3)–O. The peak at  $644\text{ cm}^{-1}$  is the out-of-plane bending of B(3)–O. The peaks at  $530\text{ cm}^{-1}$  and  $590\text{ cm}^{-1}$  are the bending of B(3)–O. The peak at  $432\text{ cm}^{-1}$  is the bending of B(4)–O.

### 3.4. Thermal analysis

The simultaneous TG–DTA curves of sample of  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  (Fig. 3) indicate that the total mass loss is 25.96% from 423 K to 1023 K, which corresponds to the loss of seven water molecules and agrees with the calculated value of 25.34%. In the DTA curve, the endothermic peak appearing at 476 K is related to the elimination of crystalline water. The formed amorphous phase of  $\text{Zn}_2\text{B}_6\text{O}_{11}$  recrystallizes as shown by the exothermic peak at 953 K.

The simultaneous TG–DTA curves of sample of  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$  (Fig. 4) indicate that the total mass loss is 31.53% from 356 K to 973 K, which corresponds to the loss of 14 water molecules and is near to the calculated value of 29.87%. This error might be resulted from the existence of moisture on the surface of this sample. In the DTA curve, the endothermic peak appearing at 420 K is related to the elimination of crystalline water. The formed amorphous phase of  $\text{Zn}_3\text{B}_{10}\text{O}_{18}$  recrystallizes as shown by the exothermic peak at 970 K.

All of above results indicate that the synthetic samples are pure and suitable for the calorimetric experiments.

### 3.5. Results of calorimetric experiment

The molar enthalpies of solution of  $\text{ZnO}(\text{s})$  in  $(\text{HCl} + \text{H}_3\text{BO}_3)(\text{aq})$  at 298.15 K are listed in Table 2. The molar enthalpies of solution of  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  and  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$  in  $\text{HCl}(\text{aq})$  at 298.15 K are listed in Table 3, 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 estimated as twice the standard deviation of the mean with  $n = 5$ .

Tables 4 and 5 give the thermochemical cycles used for the derivation of the standard molar enthalpy of formation of

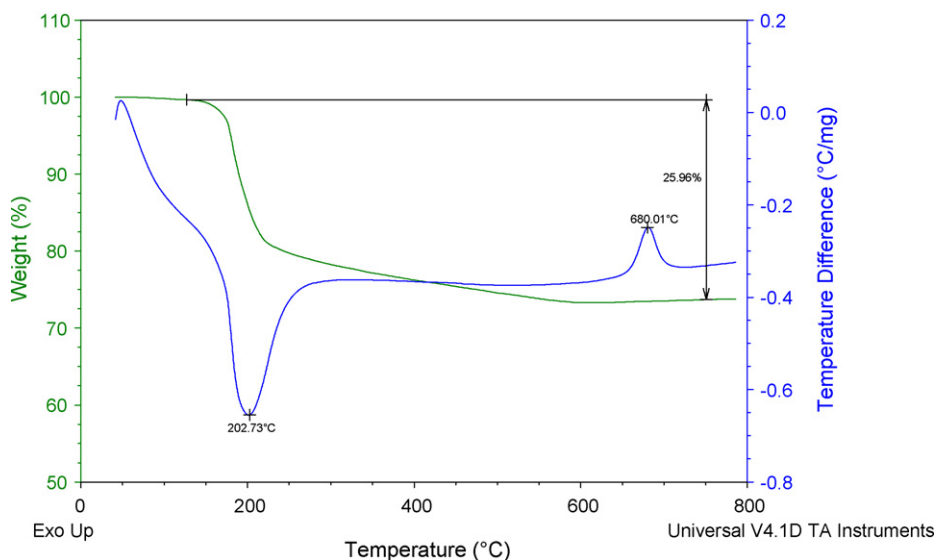


Fig. 3. Simultaneous TG–DTA curves of sample  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$ .

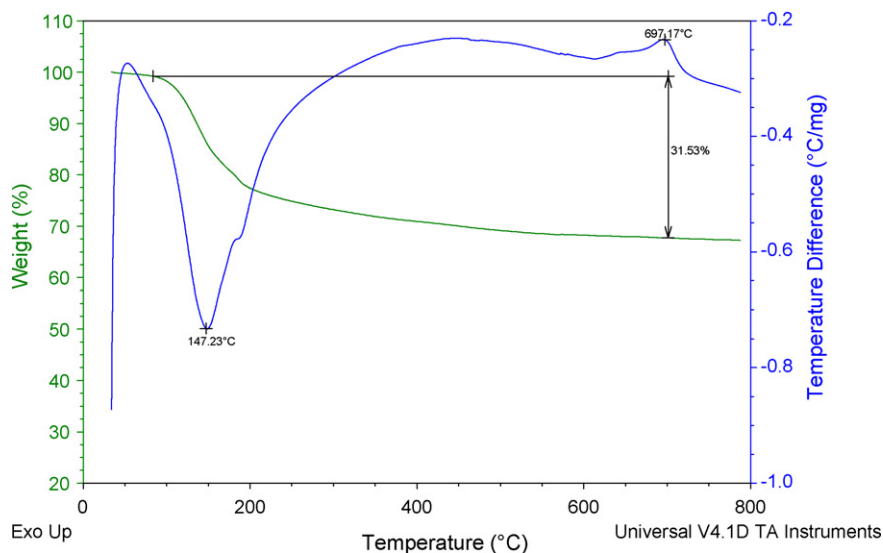


Fig. 4. Simultaneous TG–DTA curves of sample  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$ .

**Table 2**

The molar enthalpies of solution of  $\text{ZnO}(\text{s})$  in the mixed solvent that consisted of  $1 \text{ mol dm}^{-3} \text{ HCl}(\text{aq})$  and calculated amount of  $\text{H}_3\text{BO}_3$  at  $298.15 \text{ K}^{\text{a}}$ .

No.	$m$ (mg)	$\Delta_r H$ (mJ)	$\Delta_{\text{sol}} H_{\text{m}}$ ( $\text{kJ mol}^{-1}$ )
1	2.29	−2253.758	−80.10
2	2.34	−2303.145	−80.10
3	2.24	−2305.434	−80.12
4	2.23	−2184.547	−79.72
5	2.23	−2194.896	−79.99
Mean			$-80.01 \pm 0.15^{\text{b}}$

<sup>a</sup> In each experiment,  $2.00 \text{ cm}^3$  of  $\text{HCl}(\text{aq})$  was used.

<sup>b</sup> Uncertainty is estimated as twice the standard deviation of the mean.

$\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  and  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$ . The molar enthalpy of solution of  $\text{H}_3\text{BO}_3(\text{s})$  of  $21.84 \pm 0.05 \text{ kJ mol}^{-1}$  in  $1 \text{ mol dm}^{-3} \text{ HCl}(\text{aq})$  was taken from our previous work [11]. The enthalpy of dilution of  $\text{HCl}(\text{aq})$  was calculated from NBS tables [15]. The enthalpies change of  $-44.36 \pm 0.43 \text{ kJ mol}^{-1}$  for the formation of  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  and  $-79.39 \pm 0.68 \text{ kJ mol}^{-1}$  for the formation of  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$  from the reagents in the solid phase (reactions (I) and (II)) were calculated on the basis of the thermochemical cycles. The standard

**Table 4**

Thermochemical cycle and results for the derivation of  $\Delta_f H_{\text{m}}^{\circ}$  ( $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$ ,  $298.15 \text{ K}$ )<sup>a</sup>.

No.	Reaction	$\Delta_r H^{\circ}$ ( $\text{kJ mol}^{-1}$ )	Ref.
1	$6\text{H}_3\text{BO}_3(\text{s}) + 140.062(\text{HCl}\cdot 54.561\text{H}_2\text{O}) = 6\text{H}_3\text{BO}_3(\text{aq}) + 140.062(\text{HCl}\cdot 54.561\text{H}_2\text{O})$	$131.04 \pm 0.30$	[11]
2	$2\text{ZnO}(\text{s}) + 6\text{H}_3\text{BO}_3(\text{aq}) + 140.062(\text{HCl}\cdot 54.561\text{H}_2\text{O}) = 2\text{ZnCl}_2(\text{aq}) + 6\text{H}_3\text{BO}_3(\text{aq}) + 136.062(\text{HCl}\cdot 56.180\text{H}_2\text{O})$	$-160.02 \pm 0.30$	This work
3	$140.062(\text{HCl}\cdot 54.561\text{H}_2\text{O}) + 2\text{H}_2\text{O}(\text{l}) = 140.062(\text{HCl}\cdot 54.575\text{H}_2\text{O})$	$-0.04 \pm 0.01$	[15]
4	$\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}(\text{s}) + 140.062(\text{HCl}\cdot 54.575\text{H}_2\text{O}) = 2\text{ZnCl}_2(\text{aq}) + 6\text{H}_3\text{BO}_3(\text{aq}) + 136.062(\text{HCl}\cdot 56.180\text{H}_2\text{O})$	$15.42 \pm 0.03$	This work
5	$2\text{ZnO}(\text{s}) + 6\text{H}_3\text{BO}_3(\text{s}) = \text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	$-44.36 \pm 0.43^{\text{b}}$	

<sup>a</sup>  $\Delta_f H_{\text{m}}^{\circ}(\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}, \text{s}) = \Delta_r H_{\text{m}}^{\circ}(5) + 2\Delta_f H_{\text{m}}^{\circ}(\text{ZnO}, \text{s}) + 6\Delta_f H_{\text{m}}^{\circ}(\text{H}_3\text{BO}_3, \text{s}) - 2\Delta_f H_{\text{m}}^{\circ}(\text{H}_2\text{O}, \text{l})$ .

<sup>b</sup> Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

**Table 5**

Thermochemical cycle and results for the derivation of  $\Delta_f H_{\text{m}}^{\circ}$  ( $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$ ,  $298.15 \text{ K}$ )<sup>a</sup>.

No.	Reaction	$\Delta_r H^{\circ}$ ( $\text{kJ mol}^{-1}$ )	Ref.
1	$10\text{H}_3\text{BO}_3(\text{s}) + 233.365(\text{HCl}\cdot 54.561\text{H}_2\text{O}) = 10\text{H}_3\text{BO}_3(\text{aq}) + 233.365(\text{HCl}\cdot 54.561\text{H}_2\text{O})$	$218.40 \pm 0.50$	[11]
2	$3\text{ZnO}(\text{s}) + 10\text{H}_3\text{BO}_3(\text{aq}) + 233.365(\text{HCl}\cdot 54.561\text{H}_2\text{O}) = 3\text{ZnCl}_2(\text{aq}) + 10\text{H}_3\text{BO}_3(\text{aq}) + 227.365(\text{HCl}\cdot 56.014\text{H}_2\text{O})$	$-240.03 \pm 0.45$	This work
3	$233.365(\text{HCl}\cdot 54.561\text{H}_2\text{O}) + \text{H}_2\text{O}(\text{l}) = 233.365(\text{HCl}\cdot 54.565\text{H}_2\text{O})$	$-0.02 \pm 0.01$	[15]
4	$\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}(\text{s}) + 233.365(\text{HCl}\cdot 54.565\text{H}_2\text{O}) = 3\text{ZnCl}_2(\text{aq}) + 10\text{H}_3\text{BO}_3(\text{aq}) + 227.365(\text{HCl}\cdot 56.014\text{H}_2\text{O})$	$57.78 \pm 0.11$	This work
5	$3\text{ZnO}(\text{s}) + 10\text{H}_3\text{BO}_3(\text{s}) = \text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l})$	$-79.39 \pm 0.68^{\text{b}}$	

<sup>a</sup>  $\Delta_f H_{\text{m}}^{\circ}(\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}, \text{s}) = \Delta_r H_{\text{m}}^{\circ}(5) + 3\Delta_f H_{\text{m}}^{\circ}(\text{ZnO}, \text{s}) + 10\Delta_f H_{\text{m}}^{\circ}(\text{H}_3\text{BO}_3, \text{s}) - \Delta_f H_{\text{m}}^{\circ}(\text{H}_2\text{O}, \text{l})$ .

<sup>b</sup> Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

**Table 3**

The molar enthalpies of solution of  $\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$  and  $\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$  in  $1 \text{ mol dm}^{-3} \text{ HCl}(\text{aq})$  at  $298.15 \text{ K}^{\text{a}}$ .

No.	$m$ (mg)	$\Delta_r H$ (mJ)	$\Delta_{\text{sol}} H_{\text{m}}$ ( $\text{kJ mol}^{-1}$ )
$\text{Zn}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$			
1	7.08	219.388	15.42
2	7.10	220.050	15.43
3	7.12	220.862	15.44
4	7.08	218.614	15.36
5	7.18	222.581	15.43
Mean			$15.42 \pm 0.03^{\text{b}}$
$\text{Zn}_3\text{B}_{10}\text{O}_{18}\cdot 14\text{H}_2\text{O}$			
1	7.14	488.146	57.73
2	7.19	492.291	57.82
3	7.28	496.969	57.65
4	7.20	492.205	57.73
5	7.22	495.594	57.96
Mean			$57.78 \pm 0.11^{\text{b}}$

<sup>a</sup> In each experiment,  $2.00 \text{ cm}^3$  of  $\text{HCl}(\text{aq})$  was used.

<sup>b</sup> Uncertainty is estimated as twice the standard deviation of the mean.

molar enthalpies of formation of  $\text{H}_3\text{BO}_3(\text{s})$  and  $\text{H}_2\text{O}(\text{l})$  were taken from the CODATA Key Values [16], namely  $-1094.8 \pm 0.8 \text{ kJ mol}^{-1}$  and  $-285.830 \pm 0.040 \text{ kJ mol}^{-1}$ , respectively. The standard molar enthalpy of formation of  $\text{ZnO}(\text{s})$  of  $-348.28 \text{ kJ mol}^{-1}$  was taken from the NBS tables [15]. From these data, the standard molar enthalpies of formation for  $\text{Zn}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$  and  $\text{Zn}_3\text{B}_{10}\text{O}_{18} \cdot 14\text{H}_2\text{O}$  were calculated to be  $-6738.1 \pm 4.8 \text{ kJ mol}^{-1}$  and  $-11,786.4 \pm 8.0 \text{ kJ mol}^{-1}$ , respectively.

The very big values of standard molar enthalpies of formation show that the two zinc borates are quite thermodynamic stable. It also can be found that the bigger the molecular weight of zinc borate, the larger the  $\Delta_f H_m^\circ$  of zinc borate, which shows that the total numbers of B(3)–O and B(4)–O groups in  $\text{Zn}_3\text{B}_{10}\text{O}_{18} \cdot 14\text{H}_2\text{O}$  are more than those in  $\text{Zn}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$ .

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