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Short communication

Standard molar enthalpy of formation of $Ca_2[B_4O_7(OH)_2]$

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Abstract

A pure calcium borate $Ca_2[B_4O_7(OH)_2]$ has been synthesized under hydrothermal condition and characterized by XRD, FT-IR and TG as well as by chemical analysis. The molar enthalpy of solution of $Ca_2[B_4O_7(OH)_2]$ in $HCl\cdot 54.549H_2O$ was determined. From a combination of this result with measured enthalpies of solution of H_3BO_3 in $HCl\cdot 54.517H_2O$ and of CaO in $(HCl+H_3BO_3)$ solution, together with the standard molar enthalpies of formation of CaO(s), H_3BO_3(s), and H_2O(l), the standard molar enthalpy of formation of $-(4398.9 \pm 3.8)\,kJ\,mol^{-1}$ for $Ca_2[B_4O_7(OH)_2]$ was obtained.

Keywords: $Ca_2[B_4O_7(OH)_2]$; Standard molar enthalpy of formation; Solution calorimetry

1. Introduction

There are many kinds of hydrated calcium borates, both natural and synthetic. Some of them are useful chemical industrial materials, which are used in glass, pottery and porcelain enamel industry, especially in unalkali glass industry. Thermodynamic properties play very important roles in scientific research and industrial applications. Li Jun et al. [1] reported the standard molar enthalpy of formation of seven hydrated calcium borates. We also determined the standard molar enthalpy of formation of hydrated calcium borate of $2CaO\cdot B_2O_3\cdot H_2O$ by the method of solution calorimetry [2], as part of the continuing study of the thermodynamic properties of hydrated calcium borates. This paper reports the determination of standard molar enthalpy of formation of $Ca_2[B_4O_7(OH)_2]$.

2. Experimental

2.1. Hydrothermal synthesis of $Ca_2[B_4O_7(OH)_2]$

$Ca_2[B_4O_7(OH)_2]$ was prepared by modification of the literature [3] method. 0.025 mol of CaO (obtained by the decomposition of $CaCO_3$ (mass fraction ≥ 0.998) at 1223 K for 3 h), 0.075 mol of H_3BO_3 (mass fraction ≥ 0.998), and $20\,cm^3$ of H_2O were put in the lining of small autoclave ($40\,cm^3$). The mixture was stirred and placed in a oven at 513 K. The autoclave was cooled naturally and opened after 5 days reaction time. The solid phase was separated, washed thoroughly with hot distilled water, and then with alcohol and ether. Finally, the solid phase was dried at 353 K to constant mass. The synthetic sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC, Cu target), FT-IR spectroscopy (Bruker Equinox 55 FT-IR spectrometer with KBr pellets at room temperature), and TG (Perkin-Elmer TGA7, heating rate of $10\,K\,min^{-1}$ in flowing N_2). The chemical compositions of the sample were determined by EDTA titration for Ca^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by difference for H_2O.

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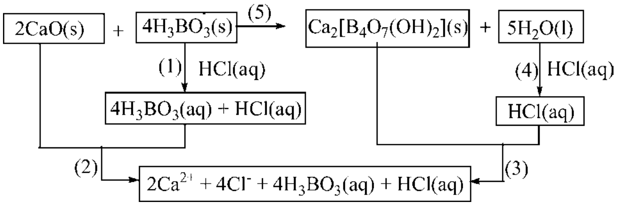

Fig. 1. Schematic drawing of the thermochemical cycle.

2.2. Method of calorimetric experiment

$Ca_2[B_4O_7(OH)_2]$ can be regarded as the product of the following reaction (5),and the thermochemical cycle was designed as Fig. 1.

The approximately 1 mol dm^{-3} HCl(aq) solvent can dissolve instantaneously all components of the reaction (5), which was prepared from analytical grade hydrochloric acid and deionized water, and its concentration was determined by titration with standard sodium carbonate.

The standard molar enthalpy of formation of $Ca_2[B_4O_7(OH)_2]$ could be obtained by the value of $\Delta_r H_m^o$ (5) in combination with the standard molar enthalpies of formation of CaO(s), H_3BO_3(s) and H_2O(l). Value of $\Delta_r H_m^o$ (5) could be obtained by means of the following reactions:

$$4H_3BO_3(s) + HCl(aq) = SolnX_1 \tag{1}$$

$$2CaO(s) + SolnX_1 = SolnX_2 \tag{2}$$

$$Ca_2[B_4O_7(OH)_2](s) + SolnX_4 = SolnX_3 \tag{3}$$

$$5H_2O(l) + HCl(aq) = SolnX_4 \tag{4}$$

$$SolnX_2 = SolnX_3$$

In all these determinations, a strict control of the stoichiometries in each step of the calorimetric cycle must be obeyed, with the objective that the dissolution of the reactants give the same composition as those of the products. Applying Hess's law, $\Delta_r H_m^o$ (5) could be calculated according to the following expression:

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

A RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which is a totally automatic instrument utilizing computer control, was used and has been described in detail previously [4,5]. The experiment was performed 5 times. The temperature of the calorimetric experiment was 298.15 K. Additional double-layer glass tubes were put in the 15 cm^3 stainless steel sample cell and reference cell of the calorimeter. This was done to prevent corrosion of the stainless steel sample and reference cell by HCl(aq). The lining in the double-layer glass tube containing HCl (aq) was broken by a rod after thermal equilibration for at least 2 h, and the HCl(aq) was mixed with solid sample in the outer glass tube. The thermal effect was then recorded automatically on a 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.

To check the performance of RD496-III heat conduction microcalorimeter, calorimetric measurements on the enthalpy of solution of KCl (mass fraction ≥ 0.9999) in deionized water were made 5 times. The average experimental value (17.31 ± 0.20) kJ mol^{-1} of $\Delta_{sol}H_m$ of KCl(s) is in excellent agreement with that of (17.241 ± 0.018) kJ mol^{-1} reported in the literature [6]. This shows that the device for measuring the enthalpy of solution used in this work is reliable.

3. Results and discussion

3.1. Characterization of the synthetic sample

Chemical analysis of synthetic sample were performed 3 times. One typical result is given as follows: CaO, 41.57%; B_2O_3, 51.87%; H_2O, 6.56%. Mole ratio of CaO: B_2O_3: H_2O is 2.00: 2.01: 0.98.

XRD pattern of synthetic sample is showed in Fig. 2. d/nm (I/I_o): 0.5647(33), 0.4345 (23), 0.3972 (12), 0.3618 (21), 0.3268 (28), 0.3166 (43), 0.3131 (43), 0.2801 (100), 0.2718 (48), 0.2132 (27), 0.2028 (62), 0.1911 (33), 0.1805 (30), and 0.1761 (20), which corresponds with those of JCPDS card (File No. 15-0532) and shows absence of other crystalline forms in the synthetic sample.

The IR spectrum (Fig. 3) of synthetic sample exhibited the following absorptions and they were assigned referring to literature [7]. The band at 3490 cm^{-1} is the O-H stretching mode. The absorption between 1600–1700 cm^{-1} which is due to the H-O-H bending mode is not seen in the spectrum, and this result shows that the compound does not contain crystal water. The bands at 1429 cm^{-1}, 1374 cm^{-1} and 893 cm^{-1} might be the asymmetric and symmetric stretching of B(3)-O, respectively. The bands at 1270 and 1226 cm^{-1} are the in-plane bending of B-O-H. The bands at 1068 cm^{-1}, 1021 cm^{-1} and 767 cm^{-1} might be the asymmetric and symmetric stretching of B(4)-O, respectively. The bands at 718 cm^{-1} and 655 cm^{-1} are the out-of-plane bending of B(3)-O. The band at 587 cm^{-1} is assigned as the characteristic peak of tetraborate anion.

TG-DTG curve indicates that the total weight loss is 6.10% from 683 to 934 K, which corresponds to the loss of 1 water molecule and can be compared with the calculated value of 6.68%. The high temperature for the water emission suggest that the H_2O molecule in $2CaO{\cdot}2B_2O_3{\cdot}H_2O$ molecule is structural water. So the structural formula for $2CaO{\cdot}2B_2O_3{\cdot}H_2O$ can be written as $Ca_2[B_4O_7(OH)_2]$ in combination with the result of the IR spectrum.

All of above results indicate that the synthetic sample is pure $Ca_2[B_4O_7(OH)_2]$ and is suitable for the calorimetric experiments.

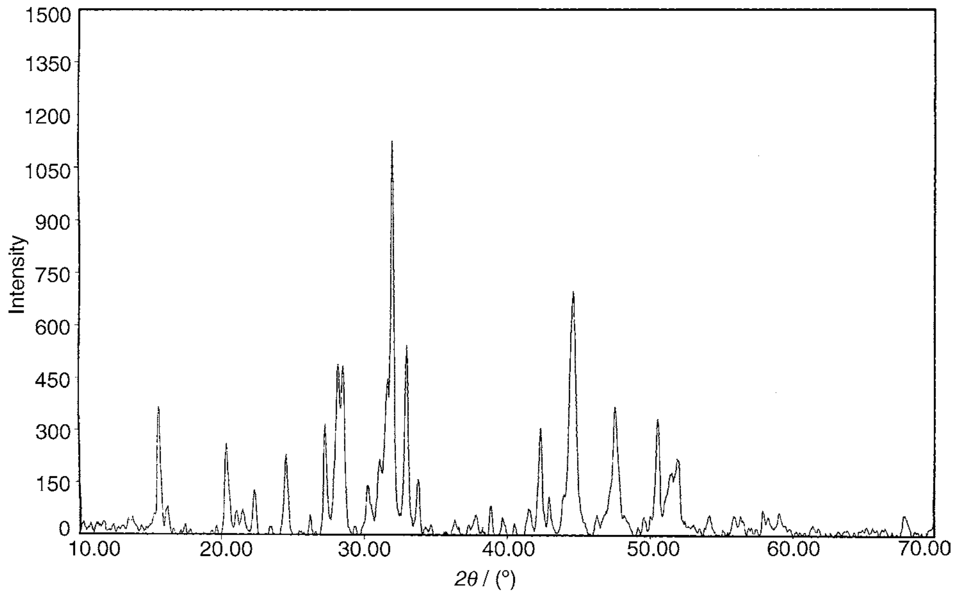

Fig. 2. X-ray powder diffraction pattern of $2CaO{\cdot}2B_2O_3{\cdot}H_2O$.

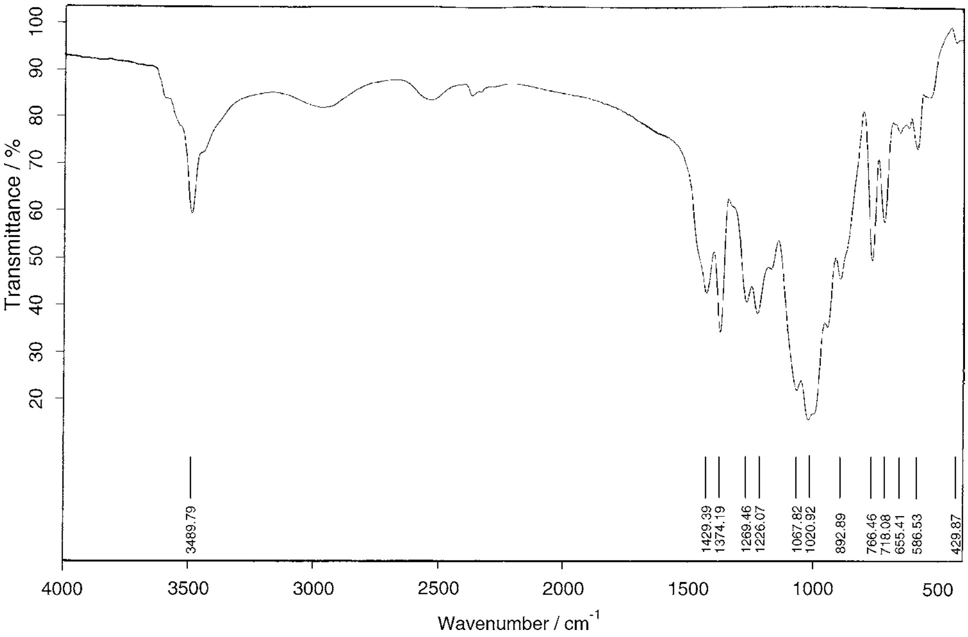

Fig. 3. IR spectrum of $2CaO{\cdot}2B_2O_3{\cdot}H_2O$.

3.2. Results of calorimetric experiment

The results of the calorimetric measurements are given in Table 1, in which m is the mass of sample, $\Delta_{\mathrm{sol}}H_m^o$ is the molar enthalpy of solution of solute, and the uncertainty is twice the standard deviation of the mean. Table 2 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $Ca_2[B_4O_7(OH)_2]$. The molar enthalpy of solution of H_3BO_3(s) of $(21.83 \pm 0.08)\,\mathrm{kJ\,mol^{-1}}$ in $(HCl{\cdot}54.517H_2O)$, and of CaO(s) of $-(188.63 \pm 0.36)\,\mathrm{kJ\,mol^{-1}}$ in the mixture of HCl and H_3BO_3 were taken from the literature [1]. The standard mo-

Table 1
The molar enthalpies of solution of $Ca_2[B_4O_7(OH)_2]$ in $HCl{\cdot}54.549H_2O$ at 298.15K[a]

No.	m (mg)	Δ_rH (mJ)	$\Delta_{sol}H_m$ ($\mathrm{kJ{\cdot}mol^{-1}}$)
1	6.00	−2466.05	−110.73
2	5.98	−2459.01	−110.78
3	6.04	−2483.18	−110.76
4	6.05	−2496.80	−111.18
5	6.03	−2474.99	−110.58
Mean			-110.81 ± 0.20[b]

[a] In each experiment, $2.00\,\mathrm{cm^3}$ of HCl(aq) was used.

[b] Uncertainty is estimated as twice the standard deviation of the mean.

Table 2
Thermochemical cycle and results for the derivation of $\Delta_f H_m^o(Ca_2[B_4O_7(OH)_2]$, 298.15K)

Reaction		$\Delta_r H_m^o (kJ \cdot mol^{-1})$
$4H_3BO_3(s) + 155.286(HCl \cdot 54.517H_2O) = 4H_3BO_3(aq) + 155.286(HCl \cdot 54.517H_2O)$	(1)	87.32±0.32
$2CaO(s) + 4H_3BO_3(aq) + 155.286(HCl \cdot 54.517H_2O) = 2CaCl_2(aq) + 4H_3BO_3(aq) + 151.286(HCl \cdot 55.972H_2O)$	(2)	−377.26±0.72
$Ca_2[B_4O_7(OH)_2](s) + 155.286(HCl \cdot 54.549H_2O) = 2CaCl_2(aq) + 4H_3BO_3(aq) + 151.286(HCl \cdot 55.972H_2O)$	(3)	-110.81±0.20
$155.286(HCl \cdot 54.517H_2O) + 5H_2O(l) = 155.286(HCl \cdot 54.549H_2O)$	(4)	−0.10±0.03
$2CaO(s) + 4H_3BO_3(s) = Ca_2[B_4O_7(OH)_2](s) + 5H_2O(l)$	(5)	-179.03±0.81

lar enthalpies of formation of $H_2O(l)$, CaO(s), and $H_3BO_3(s)$ were taken from the CODATA Key Values [8], namely –(285.830 ± 0.040) kJ mol^{-1}, –(634.92 ± 0.90) kJ mol^{-1}, and –(1094.8 ± 0.8) kJ mol^{-1}, respectively. The enthalpy of dilution of HCl(aq) was calculated from the NBS tables [9]. From these data, the standard molar enthalpy of formation of $Ca_2[B_4O_7(OH)_2]$ was calculated to be –(4398.9 ± 3.8) kJ mol^{-1}. The $\Delta_f H_m^o$ of $[B_4O_7(OH)_2]^{4-}$ (aq) can be estimated by a group contribution method [10], which can be expressed in following equation:

$$\Delta_f H_m^o(Ca_2[B_4O_7(OH)_2], s) = 2\Delta_f H_m^o(Ca^{2+}, aq) + \Delta_f H_m^o([B_4O_7(OH)_2]^{4-}, aq)$$

in which the $\Delta_f H_m^o$ of −542.83 kJ mol^{-1} of Ca^{2+} (aq) was taken from the literature [10]. Using this scheme, the standard molar enthalpy of formation of $[B_4O_7(OH)_2]^{4-}$ (aq) is −3313.24 kJ mol^{-1}.

Comparing the $\Delta_f H_m^o$ of the title compound with those reported for other calcium borates [1,2], it can be found that the bigger the molecular weight of calcium borate, the larger the $\Delta_f H_m^o$ of calcium borate, which support the group contribution method [10] from another point of view.

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