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Standard Molar Enthalpies of Formation for the Two Hydrated Calcium Borates xCaO·5B_2O_3·$y$$H_2O$ ($x = 2$ and 4, $y = 5$ and 7)

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Two pure calcium borates of 2CaO·5B_2O_3·5H_2O (**I**) and β-4CaO·5B_2O_3·7H_2O (**II**) have been synthesized under hydrothermal condition and characterized by X-ray diffraction, infrared spectra, and thermogravimetric analysis as well as by chemical analysis. All the enthalpies of solution were measured at 298.15 K by using a heat conduction microcalorimeter. The molar enthalpies of solution of (**I**) and (**II**) in 2.00 cm^3 of 1 mol·dm^{-3} HCl(aq) were measured to be $-(60.30 \pm 0.78)$ kJ·mol^{-1} and $-(158.63 \pm 0.72)$ kJ·mol^{-1}, respectively. The molar enthalpies of solution of H_3BO_3(s) in 2.00 cm^3 of 1 mol·dm^{-3} HCl(aq) and of CaO(s) in 2.00 cm^3 of (HCl + H_3BO_3) aqueous solution were measured to be (21.84 ± 0.05) kJ·mol^{-1} and $-(188.59 \pm 0.42)$ kJ·mol^{-1}, respectively. The enthalpies change of borates (**I**) and (**II**) formation from the reaction of reagents in the solid phase, $-(98.3 \pm 1.3)$ kJ·mol^{-1} and $-(377.2 \pm 1.9)$ kJ·mol^{-1} were calculated respectively on the basis of the appropriate thermochemical cycles. From these data and the standard molar enthalpies of formation of CaO(s), H_3BO_3(s), and H_2O(l), the standard molar enthalpies of formation were calculated as $-(9457.9 \pm 8.3)$ kJ·mol^{-1} for (**I**) and $-(11578.7 \pm 8.9)$ kJ·mol^{-1} for (II), respectively.

Introduction

Borate compounds have considerable mineralogical and industrial importance. Boron exists as polyborate anions composed of BO_3 (Δ) and BO_4 (T) groups. These BO_3 and BO_4 groups may further link together via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets, and networks. 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. Li and co-workers[1,2] determined the standard molar enthalpies of formation of six hydrated calcium borates using a Calvet low-temperature calorimeter and LKB 8700 precision calorimeter. This paper reports in detail the determination of standard molar enthalpies of formation of two hydrated calcium borates using a heat conduction microcalorimeter.

Experimental Section

Reagents and Instruments. $CaCO_3$ (mass fraction ⩾ 0.998), H_3BO_3 (mass fraction ⩾ 0.998), hydrochloric acid (mass fraction ⩾ 0.3800), and KCl (mass fraction ⩾ 0.9999) were produced by Xi'an Chemical Factory, China.

A Rigaku D/MAX -III C X-ray diffraction meter (with Cu target at 8°·min^{-1}), a Nicolet NEXUS 670 FT-IR spectrometer (recorded over the 400 to 4000 cm^{-1} region with KBr pellets at room temperature), and a Perkin-Elmer TGA7 (at a heating rate of 10 K·min^{-1} in flowing N_2) were used in the measurements.

Hydrothermal Synthesis. A 1.401 g sample (0.814 g for **II**) of CaO (obtained by the decomposition of $CaCO_3$ at 1223 K for 3 h), 6.178 g (1.855 g for **II**) of H_3BO_3, and 30 cm^3 (15 cm^3 for **II**) of redistilled water were put in the Teflon-lined small autoclave (40 cm^3). The mixture was stirred with a glass rod, and then the autoclave was sealed and placed in a oven at 513 K (393 K for **II**). The autoclave was cooled naturally and opened after 5 days of reaction time. The solid phase was separated and washed thoroughly with hot distilled water and then with alcohol and ether. Finally, the solid phase was dried at 353 K to constant mass.

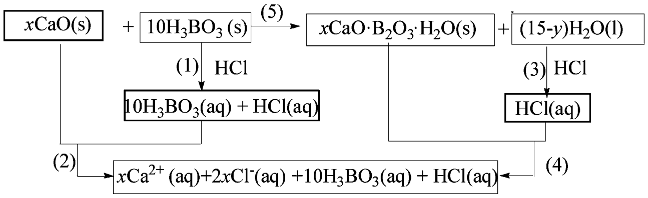

Figure 1. Schematic drawing of the thermodynamic circle.

Characterization and Analytical Methods. The synthetic samples were characterized by X-ray powder diffraction, FT-IR spectroscopy, and thermogravimetric analysis, respectively. The chemical compositions of the samples 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.

Thermochemical Cycles. **I** and **II** can be regarded as the products of the following reactions (5), and the thermochemical cycle was designed as in Figure 1.

The 1 mol·dm^{-3} HCl(aq) solvent can dissolve all components of the five reactions, and its concentration of 1.0004 mol·dm^{-3} was determined by titration with standard sodium carbonate. The molar enthalpies of solution of H_3BO_3(s), (**I**), and (**II**) in 1 mol·dm^{-3} HCl(aq) were measured, respectively. The calculated amount of CaO (s) was dissolved in (hydrochloric acid + boric acid) aqueous solution, which consisted of 1 mol·dm^{-3} HCl(aq) and the calculated amount of H_3BO_3(s). In all these determinations, strict control of the stoichiometries in each step of the calorimetric cycle must be observed [namely, n(CaO):n(H_3BO_3):n(xCaO·5B_2O_3·$y$$H_2O$) = 2:10:1 for (**I**) and 4:10:1 for (**II**)], with the objective that the dissolution of the reactants gives

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Table 1. Enthalpy of Solution in Water of KCl(s) at 298.15 K[a]

no.	m/mg	$\Delta_{sol}H$/mJ	$\Delta_{sol}H_m$/kJ·mol^{-1}
1	14.34	3299.115	17.15
2	14.92	3501.255	17.49
3	13.85	3164.742	17.03
4	13.85	3219.834	17.33
5	15.76	3713.466	17.56
mean			17.31 ± 0.20[b]

[a] In each experiment, 8.00 cm^3 of H_2O was used. [b] Uncertainty is twice the standard deviation of the mean.

the same composition as those of the products. Applying Hess's law, $\Delta_r H_m{}^\circ$ (5) can be calculated according to the following expression:

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

The standard molar enthalpies of formation of **I** and **II** can be obtained by the values of $\Delta_r H_m{}^\circ$ (5) in combination with the standard molar enthalpies of formation of CaO(s), H_3BO_3(s), and H_2O(l).

Calorimeter. All the enthalpies of solution were measured using an RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which is a totally automatic instrument utilizing computer control. This microcalorimeter is composed of the precision temperature-controlling system, the electric energy calibration system, the constant-temperature thermostat, and the data processing system. The working temperature of the calorimeter lies in the range of T = (77.15 to 473.15) K. It has a 16 cm^3 sample cell and a 16 cm^3 reference cell. The thermal effect can be determined through a thermoelectric pile composed of 496 thermocouples, which is converted to an electric voltage. The electric voltage is amplified through a microvolt amplifier, converted by the modulus, collected, and processed by a computer. The functions of controlling the temperature of the system (running on chemical and electrical calibrations) and a sensitivity calibration (measuring the thermal effect) and acquiring and storing the results are achieved by a program.[3,4]

To check the performance of RD496-III heat conduction microcalorimeter, the calorimetric constant at 298.15 K was determined by the Joule effect before the experiments. The Joule cell was supplied with 100 mW electric power for 100 s. The calorimetric constant obtained in this way was (63.99 ± 0.03) μV·mW^{-1}. The reliability of the calorimeter was verified by measuring the enthalpy of solution of KCl(s) in deionized water, and the results are shown in Table 1. 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 17.234 kJ·mol^{-1} reported in the literature.[5] The relative error between the literature value and the measuring value was 0.4 %. This shows that the device for measuring the enthalpy of solution used in this work is reliable.

Method of Calorimetric Experiments. Each of calorimetric experiment was performed 5 times. The temperature of the calorimetric experiment was (298.15 ± 0.01) K. Additional double-layer glass tubes were put in the 16 cm^3 stainless steel sample cell and reference cell of the calorimeter. This was done to prevent corrosion of the stainless steel sample cell and reference cell by HCl(aq). This device used for calorimetry is shown in Figure 2. The lining in the double-layer glass tube containing 2.00 cm^3 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.

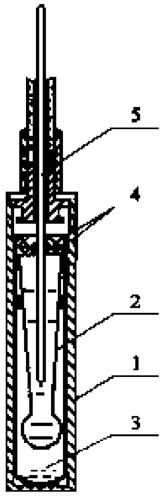

Figure 2. Schematic drawing of the device used for the study of enthalpy of solution: 1, calorimetric cell; 2, tube containing 1 mol·dm^{-3} HCl(aq); 3, tube containing solid sample; 4, silicone rubber cover; 5, glass rod.

Table 2. Chemical Analytical Results of Synthetic Samples/100 *w*

				mole ratio
	CaO	B_2O_3	H_2O	CaO:B_2O_3:H_2O
calcd for **I**	20.38	63.25	16.37	2.00:5.00:5.00
found	20.34	63.27	16.39	2.00:5.01:5.01
	20.36	63.23	16.41	2.00:5.01:5.01
calcd for **II**	31.89	50.32	17.78	4.00:5.00:7.00
found	32.14	49.79	18.07	4.00:4.98:7.02
	32.09	49.90	18.01	4.00:5.01:6.97

Results and Discussion

Characterization of the Synthetic Samples. Chemical analytical results of synthetic samples are listed in Table 2. The uncertainties in the measurement of the mass fraction of each species were estimated to be ± 0.2 %. The analytical results are consistent with the theoretical values.

Characteristic d values of XRD pattern for **I**: (0.5618, 0.5035, 0.4503, 0.3720, 0.3245, 0.3112, 0.2972, 0.2793, 0.2725, 0.2499, 0.2239, 0.2121, 0.2083, 0.2040, 0.1984, 0.1910, and 0.1841) nm, which correspond with those of JCPDS card (File No. 22-146) and shows absence of other crystalline forms in the synthetic sample **I**. Characteristic d values for **II**: (1.0800, 0.5949, 0.5407, 0.4462, 0.4275, 0.3610, 0.3474, 0.3366, 0.2963, 0.2882, 0.2841, 0.2771, 0.2712, 0.2665, 0.2580, 0.2456, 0.2414, 0.2301, 0.2222, and 0.2168) nm, which correspond with those of JCPDS card (File No. 10-463) and shows absence of other crystalline forms in the synthetic sample **II**.

The FT-IR spectra of these two compounds exhibit the following absorption bands, and they are assigned referring to literature.[6] In **I**, the band at 3436 cm^{-1} is the stretching mode of O−H. The band at 1643 cm^{-1} is the H−O−H bending mode, which shows that the compound contains crystal water. The bands at 1412 cm^{-1}, 1363 cm^{-1}, and 940 cm^{-1} might be the asymmetric and symmetric stretching modes of B(3)−O, respectively. The band at 1183 cm^{-1} is the in-plane bending of B−O−H. The bands at 1091 cm^{-1} and 803 cm^{-1} are assigned as the asymmetric and symmetric stretching of B(4)−O, respectively. The band at 620 cm^{-1} is the out-of-plane bending

Table 3. Molar Enthalpies of Solution of $H_3BO_3(s)$ in 1 mol·dm^{-3} HCl(aq) at 298.15 K[a]

no.	m/mg	$\Delta_r H$/mJ	$\Delta_{sol}H_m$/kJ·mol^{-1}
1	5.30	1877.30	21.89
2	5.27	1868.38	21.91
3	5.32	1874.91	21.78
4	5.34	1887.15	21.84
5	5.26	1854.62	21.79
mean			21.84 ± 0.05[b]

[a] In each experiment, 2.00 cm^3 of HCl(aq) was used. [b] Uncertainty is estimated as twice the standard deviation of the mean.

Table 4. Molar Enthalpies of Solution of CaO(s) in (Hydrochloric Acid + Boric Acid) Aqueous Solution That Consisted of 1 mol·dm^{-3} HCl(aq) and the Calculated Amount of $H_3BO_3(s)$[a]

no.	m/mg	$\Delta_r H$/mJ	$\Delta_{sol}H_m$/kJ·mol^{-1}
1	1.94	−6509.45	−188.17
2	1.92	−6443.71	−188.21
3	1.93	−6482.43	−188.36
4	1.91	−6441.14	−189.12
5	1.92	−6473.50	−189.08
mean			−188.59 ± 0.42[b]

[a] In each experiment, 2.00 cm^3 of HCl(aq) was used. [b] Uncertainty is estimated as twice the standard deviation of the mean.

Table 5. Molar Enthalpies of Solution of I and II in 1 mol·dm^{-3} HCl(aq) at 298.15 K[a]

no.	m/mg	$\Delta_r H$/mJ	$\Delta_{sol}H_m$/kJ·mol^{-1}
		I	
1	6.02	−651.015	−59.51
2	5.98	−653.298	−60.12
3	6.05	−653.943	−59.48
4	6.02	−672.107	−61.44
5	5.97	−661.005	−60.93
mean			−60.30 ± 0.78[b]
		II	
1	5.95	−1350.119	−158.50
2	6.21	−1414.215	−159.07
3	5.94	−1360.186	−158.37
4	6.00	−1354.656	−158.95
5	6.01	−1361.639	−158.26
mean			−158.63 ± 0.72[b]

[a] In each experiment, 2.00 cm^3 of HCl(aq) was used. [b] Uncertainty is estimated as twice the standard deviation of the mean.

mode of B(3)−O. The band at 469 cm^{-1} is the bending mode of B(4)−O. In **II**, the bands at (3461 and 3102) cm^{-1} are the stretching modes of O−H. The band at 1651 cm^{-1} is the H−O−H bending mode, which shows that the compound contains crystal water. The bands at 1365 cm^{-1}, 1306 cm^{-1}, and 906 cm^{-1} might be the asymmetric and symmetric stretching modes of B(3)−O, respectively. The bands at 1069 cm^{-1} and 797 cm^{-1} are assigned as the asymmetric and symmetric stretching of B(4)−O, respectively. The band at 719 cm^{-1} should be the out-of-plane bending mode of B(3)−O. The band at 587 cm^{-1} is the bending mode of B(3)−O. The band at 431 cm^{-1} is the bending mode of B(4)−O.

The TGA curve of **I** indicates that there is a mass loss of 16.28 % between (90 and 750) °C, which corresponds to the loss of five water molecules (calculated mass loss: 16.37 %). The TGA curve of **II** shows it has a mass loss of 17.96 % between (180 and 650) °C, which corresponds to the loss of seven water molecules, and can be compared with the calculated value of 18.05 %. All of above results indicate that the synthetic samples **I** and **II** are pure and are suitable for the calorimetric experiments, respectively.

Enthalpies of Solution. Table 3, Table 4, and Table 5 give the results of the calorimetric measurements. The uncertainty is twice the standard deviation of the mean, namely

$$\delta = 2\sqrt{\sum (x_i - \bar{x}^2)/n(n-1)}$$

in which n is experimental number ($n = 5$); x_i, experimental value of each series of repeated measurement; $\bar{x}$, mean value. The molar enthalpies of solution of (**I**) and (**II**) in 2.00 cm^3 of 1 mol·dm^{-3} HCl(aq) were measured to be −(60.30 ± 0.78) kJ·mol^{-1} and −(158.63 ± 0.72) kJ·mol^{-1}, respectively. The molar enthalpies of solution of $H_3BO_3(s)$ in 2.00 cm^3 of 1 mol·dm^{-3} HCl(aq) and of CaO(s) in 2.00 cm^3 of (HCl + H_3BO_3) aqueous solution were measured to be (21.84 ± 0.05) kJ·mol^{-1} and −(188.59 ± 0.42) kJ·mol^{-1} respectively.

Standard Molar Enthalpies of Formation. Table 6 and Table 7 give the thermochemical cycles for the derivation of the standard molar enthalpy of formation of (**I**) and (**II**). The enthalpies change of borates (**I**) and (**II**) formation from the reaction of reagents in the solid phase, −(98.3 ± 1.3) kJ·mol^{-1} and −(377.2 ± 1.9) kJ·mol^{-1} were calculated on the basis of the thermochemical cycles. The standard molar enthalpies of formation of $H_2O(l)$, CaO(s), and $H_3BO_3(s)$ were taken from the CODATA Key Values,[7] 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.[8] From these data, the standard molar enthalpies of formation of −(9457.9 ± 8.3) kJ·mol^{-1} for (**I**) and −(11578.7 ± 8.9) kJ·mol^{-1} for (**II**) were obtained, respectively.

Table 6. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^\circ$ ($2CaO\cdot 5B_2O_3\cdot 5H_2O$, 298.15 K)

no.	reaction	$\Delta_r H^\circ$/kJ·mol^{-1}
1	$10H_3BO_3(s) + 183.515\ (HCl\cdot 54.561H_2O) = 10H_3BO_3(aq) + 183.515\ (HCl\cdot 54.561H_2O)$	218.4 ± 0.5
2	$2CaO(s) + 10H_3BO_3(aq) + 183.515(HCl\cdot 54.561H_2O) = 2CaCl_2(aq) + 10H_3BO_3(aq) + 179.515(HCl\cdot 55.788H_2O)$	−377.18 ± 0.84
3	$183.515(HCl\cdot 54.561H_2O) + 10H_2O(l) = 183.515(HCl\cdot 54.616H_2O)$	−0.20 ± 0.04
4	$2CaO\cdot 5B_2O_3\cdot 5H_2O(s) + 183.515(HCl\cdot 54.616H_2O) = 2CaCl_2(aq) + 10H_3BO_3(aq) + 179.515(HCl\cdot 55.788H_2O)$	−60.30 ± 0.78
5	$2CaO(s) + 10H_3BO_3(s) = 2CaO\cdot 5B_2O_3\cdot 5H_2O(s) + 10H_2O(l)$	−98.3 ± 1.3

Table 7. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^\circ$ (β-$4CaO\cdot 5B_2O_3\cdot 7H_2O$, 298.15 K)

no.	reaction	$\Delta_r H^\circ$/kJ·mol^{-1}
1	$10H_3BO_3(s) + 232.927\ (HCl\cdot 54.561H_2O) = 10H_3BO_3(aq) + 232.927\ (HCl\cdot 54.561H_2O)$	218.4 ± 0.5
2	$4CaO(s) + 10H_3BO_3(aq) + 232.927(HCl\cdot 54.561H_2O) = 4CaCl_2(aq) + 10H_3BO_3(aq) + 224.927(HCl\cdot 56.519H_2O)$	−754.36 ± 1.68
3	$232.927\ (HCl\cdot 54.561H_2O) + 8H_2O(l) = 232.927\ (HCl\cdot 54.595H_2O)$	−0.16 ± 0.04
4	$4CaO\cdot 5B_2O_3\cdot 7H_2O(s) + 232.927(HCl\cdot 54.595H_2O) = 4CaCl_2(aq) + 10H_3BO_3(aq) + 224.927(HCl\cdot 56.519H_2O)$	−158.63 ± 0.72
5	$4CaO(s) + 10H_3BO_3(s) = 4CaO\cdot 5B_2O_3\cdot 7H_2O(s) + 8H_2O(l)$	−377.2 ± 1.9

The very big values of standard molar enthalpies of formation show that the two calcium borates are quite thermodynamic stable. It also can be found that the bigger the molecular weight of calcium borate, the larger the $\Delta_f H_m^\circ$ of calcium borate.

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