Thermodynamic Properties of $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$

Wei-He Han, Zhi-Hong Liu,* Wen-Juan Zhang, Chuan-Feng Zuo, and Sheng-Jun Liang

School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, People's Republic of China

A pure hydrated calcium double borate, $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$, has been synthesized and identified by chemical analysis, elemental analysis, X-ray diffraction, infrared spectra, and thermogravimetric analysis. The molar enthalpy of solution of $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ in 1 mol·dm^{-3} HCl(aq) and of NH_4Cl(s) in (HCl + H_3BO_3 +CaO)(aq) were measured to be (104.50 ± 0.34) kJ·mol^{-1} and (17.71 ± 0.30) kJ·mol^{-1}, respectively. From a combination of these results with measured enthalpies of solution of H_3BO_3(s) in 1 mol·dm^{-3} HCl(aq) and of CaO(s) in (HCl + H_3BO_3) aqueous solution together with the standard molar enthalpies of formation of HCl(aq), NH_4Cl(s), CaO(s), H_3BO_3(s), and H_2O(l), the standard molar enthalpy of formation of $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ was found to be −(10062.3 ± 6.5) kJ·mol^{-1}. Thermodynamic properties of the compound were also estimated by a group contribution method. The standard molar free energy of formation ($\Delta_f G_m°$) was estimated to be −8802.38 kJ·mol^{-1}. From these values, the standard molar entropy of formation ($\Delta_f S_m°$) was estimated to be −4225.8 J·mol^{-1}·K^{-1}. The standard molar entropy ($S_m°$) was estimated to be 809.3 J·mol^{-1}·K^{-1}.

Introduction

There are many kinds of hydrated calcium borates, both natural and synthetic. Some of them are useful chemical industrial materials and are used in the glass, pottery, and porcelain enamel industries. Thermodynamic properties play very important roles in scientific research and industrial applications. Li and co-workers[1−3] determined the standard molar enthalpies of formation of seven hydrated calcium borates using a Calvet low-temperature calorimeter and LKB 8700 precision calorimeter. The standard molar enthalpies of formation of two hydrated calcium borates have also been determined in this laboratory using a heat conduction microcalorimeter.[4] This paper reports the determination of the standard molar enthalpy of formation of $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ and an estimate of the $\Delta_f G_m°$ and $S_m°$ of the hydrated calcium double borate by a group contribution method.

Experimental Section

Reagents and Instruments. H_3BO_3 (mass fraction ⩾ 0.998), $CaCl_2\cdot 2H_2O$ (mass fraction ⩾ 0.980), $NH_3\cdot H_2O$ (mass fraction ⩾ 0.280), hydrochloric acid (mass fraction ⩾ 0.380), and KCl (mass fraction ⩾ 0.9999) were produced by the 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 (recording over the 400 to 4000 cm^{-1} region with KBr pellets at room temperature), a Vario EL III elemental analyzer, and a TA-SDT Q600 simultaneous thermal analyzer (at a heating rate of 10 K·min^{-1} in flowing N_2) were used in the experiments.

Synthesis and Characterization. To a mixed solution of 11.9339 g of H_3BO_3 in 200 cm^3 of deionized water and 2.1956 g of $CaCl_2\cdot 2H_2O$ in 2 cm^3 of deionized water was added 17.50 cm^3 of $NH_3\cdot H_2O$ (mass fraction ⩾ 0.280). The mixture was stirred until homogeneous. After 20 days, the solid that crystallized out was separated. The crystals were washed with absolute alcohol and ether. The obtained solids were dried in a vacuum-dryer to a constant mass at room temperature and were identified by X-ray powder diffraction, FT-IR spectroscopy, and simultaneous DTA-TG. The chemical composition was determined by C, H, and N elemental analysis, Ca^{2+} by EDTA titration, and B_2O_3 by NaOH standard solution in the presence of mannitol.

Thermochemical Cycle. The thermochemical reaction designed for the derivation of the $\Delta_f H_m°$ of $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ is shown in reaction 1, and the thermochemical cycle is shown in Table 4:

$$(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O(s) + 2HCl(aq) = 2NH_4Cl(s) + CaO(s) + 8H_3BO_3(s) + H_2O(l) \quad (1)$$

The 1 mol·dm^{-3} HCl(aq) solvent can dissolve all components of reaction 1, and its concentration of 0.9996 mol·dm^{-3} was determined by titration with standard sodium carbonate. In all these determinations, strict control of the stoichiometries in each step of the calorimetric cycle must be maintained, with the objective that the dissolution of the reactants give the same composition as those of the products. The molar enthalpies of solution of H_3BO_3(s) and $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$(s) in 1 mol·dm^{-3} HCl(aq) were measured. The stoichiometric amount of CaO(s) was dissolved in a (hydrochloric acid + boric acid) aqueous solution, which consisted of 1 mol·dm^{-3} HCl(aq) and the calculated amount of H_3BO_3. Then the stoichiometric amount of NH_4Cl(s) was dissolved in the mixed solution of (HCl + H_3BO_3 + CaO)(aq).

The standard molar enthalpy of formation of $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ can be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of HCl(aq), NH_4Cl(s), CaO(s), H_3BO_3(s), and H_2O(l).

Calorimeter and Method of Calorimetric Experiments. 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 a precision temperature-controlling system, an

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* Corresponding author. Tel.: +86-29-85307765. Fax: +86-29-85307774. E-mail: liuzh@snnu.edu.cn.

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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.

Table 2. Molar Enthalpies of Solution of $(NH_4)_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ in 1 mol·dm^{-3} HCl(aq) at 298.15 K[a]

no.	m/mg	$\Delta_{sol}H$/mJ	$\Delta_{sol}H_m$/kJ·mol^{-1}
1	6.96	1201.964	104.10
2	7.00	1210.484	104.24
3	6.94	1207.470	104.88
4	6.95	1209.735	104.93
5	6.93	1199.509	104.34
mean			104.50 ± 0.34[b]

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

Table 3. Molar Enthalpies of Solution of NH_4Cl(s) in Aqueous (1 mol·dm^{-3} HCl) and Calculated Amounts of H_3BO_3 and CaO at 298.15 K[a]

no.	m/mg	$\Delta_{sol}H$/mJ	$\Delta_{sol}H_m$/kJ·mol^{-1}
1	1.31	423.867	17.31
2	1.10	374.602	18.22
3	1.20	398.365	17.76
4	1.15	376.494	17.51
5	1.10	365.278	17.76
mean			17.71 ± 0.30[b]

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

electric energy calibration system, a constant-temperature thermostat, and a data processing system, which has been described in detail previously.[4−6]

To check the performance of the 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 of $\Delta_{sol}H_m$(KCl) was determined to be (17.31 ± 0.20) kJ·mol^{-1}, which is in excellent agreement with that of 17.234 kJ·mol^{-1} reported in the literature.[7] The relative error between the literature and the measured value was 0.4 %. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

Each calorimetric experiment was performed five 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). The lining in the double-layer glass tube containing 2.00 cm^3 of HCl(aq) was broken by a rod after thermal equilibration for at least 2 h, and the HCl(aq) was mixed with the solid sample in the outer glass tube. The thermal effect was then recorded automatically on a computer. The 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

Characterization of the Synthetic Sample. Anal. Calcd. for $(NH_4)_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$: H, 5.35 %; N, 4.65 %; B, 14.35 %; Ca, 6.65 %. Found: H, 5.43 %; N, 4.53 %; B, 14.30 %; Ca, 6.61 %. The analytical results are consistent with the theoretical values. The uncertainties in the measurement of the mass fraction of each species were estimated to be ± 0.2 %.

The XRD pattern of the synthetic sample indicated that the characteristic d values are 0.9522, 0.8699, 0.8339, 0.7596, 0.6440, 0.6348, 0.6294, 0.5902, 0.5786, 0.5317, 0.5254, 0.5024, 0.4667, 0.4255, 0.3924, 0.3841, 0.3818, 0.3394, 0.3225, 0.3147, 0.3095, 0.3068, 0.2984, 0.2462, 0.2433, 0.2358, 0.2151, 0.2083, 0.2065, 0.1951, and 0.1874 nm, which corresponds with those of JCPDS card (File No. 15-0532: formula $(NH_4)_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$). No other crystalline forms in the synthetic sample were observed.

The FT-IR absorption spectrum of the synthetic sample was assigned by referring to the literature.[8] The bands at (3440 and 3222) cm^{-1} are the O−H stretching mode. The band at 1628 cm^{-1} is the bending mode of H−O−H, which shows that the compound contains crystalline water. The bands at (1404, 1347, and 943) cm^{-1} are likely to relate to the asymmetric and symmetric stretching of B(3)−O. The band at 1156 cm^{-1} is the in-plane bending of B−O−H. The bands at (1063, 1004, and 831) cm^{-1} are the asymmetric and symmetric stretching of B(4)−O. The bands at 707 cm^{-1} and 658 cm^{-1} are the out-of-plane bending of B(3)−O. The band at 537 cm^{-1} is assigned as the characteristic peak of the tetraborate anion. The band at 472 cm^{-1} is the bending of B(4)−O.

Simultaneous DTA-TG curves of the synthetic sample indicate that a total mass loss of 44.93 % occurred from (25 to 650) °C. This is likely to correspond to the continuous loss of 13 H_2O molecules and 2 NH_3 molecules, the loss of which would have a calculated value of 44.51 %.

All of the above results indicate that the synthetic sample is pure $(NH_4)_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ and is suitable for the calorimetric experiment.

Enthalpies of Solution. The molar enthalpy of solution of $(NH_4)_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ is (104.50 ± 0.34) kJ·mol^{-1} in 1 mol·dm^{-3} HCl(aq), and that of NH_4Cl(s) is (17.71 ± 0.30) kJ·mol^{-1} in (HCl + H_3BO_3 +CaO)(aq) at 298.15 K. The values are listed in Tables 2 and 3, in which m is the mass of sample, $\Delta_{sol}H_m$ is the molar enthalpy of solution of the sample. The uncertainty is estimated as twice the standard deviation of the mean, namely

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

in which n is the number of experimentals ($n = 5$); x_i is the experimental value of each repeated measurement; and $\bar{x}$ is the mean value. The molar enthalpy of solution of H_3BO_3(s) is (21.84 ± 0.05) kJ·mol^{-1} in 1 mol·dm^{-3} HCl(aq), and that of CaO(s) is −(188.59 ± 0.42) kJ·mol^{-1} in the (HCl + H_3BO_3) aqueous solution, the values of which were taken from our previous work.[4]

Standard Molar Enthalpy of Formation. Table 4 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $(NH_4)_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$. The standard molar enthalpy of formation of HCl(aq) in the calculated amount of water [$(HCl \cdot 55.149H_2O)$] is −(165.43 ± 0.06) kJ·mol^{-1}, and the enthalpy of dilution of HCl(aq) is −(2.20 ± 0.08) kJ·mol^{-1}, which were calculated from the NBS tables.[9] The standard molar enthalpy of formation of NH_4Cl(s) of −(314.43 ± 0.06) kJ·mol^{-1} was taken directly from the NBS

Table 4. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^\circ$ ($(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$, 298.15 K)

no.	reaction	$\Delta_r H_m^\circ$/kJ·mol^{-1}
1	$(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O(s) + 173.15(HCl{\cdot}54.506H_2O) = 2NH_4^+(aq) + Ca^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 169.15(HCl{\cdot}55.807H_2O)$	104.50 ± 0.34
2	$8H_3BO_3(aq) + 171.15(HCl{\cdot}55.149H_2O) = 8H_3BO_3(s) + 171.15(HCl{\cdot}55.149H_2O)$	−174.72 ± 0.40
3	$Ca^{2+}(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 169.15(HCl{\cdot}55.807H_2O) = CaO(s) + 8H_3BO_3(aq) + 171.15(HCl{\cdot}55.149H_2O)$	188.59 ± 0.42
4	$2NH_4^+(aq) + Ca^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 169.15(HCl{\cdot}55.807H_2O) = 2NH_4Cl(s) + Ca^{2+}(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 169.15(HCl{\cdot}55.807H_2O)$	−35.42 ± 0.60
5	$173.15(HCl{\cdot}55.149H_2O) = 173.15(HCl{\cdot}54.506H_2O) + 111.298H_2O(l)$	2.20 ± 0.08
6	$H_2(g) + Cl_2(g) + 110.298H_2O(l) = 2(HCl{\cdot}55.149H_2O)$	−330.86 ± 0.12
7	$2NH_4Cl(s) = N_2(g) + 4H_2(g) + Cl_2(g)$	628.86 ± 0.12
8	$CaO(s) = Ca(s) + 1/2O_2$	634.92 ± 0.90
9	$8H_3BO_3(s) = 8B(s) + 12H_2(g) + 12O_2(g)$	8758.4 ± 6.4
10	$H_2O(l)= H_2(g)+1/2O_2(g)$	285.83 ± 0.04
11	$(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O(s) = Ca(s) + 8B(s) + N_2(g) + 16H_2(g) + 13O_2(g)$	10062.3 ± 6.5

tables,[9] and the standard molar enthalpies of formation of CaO(s), H_3BO_3(s), and H_2O(l) were taken from the CODATA Key Values,[10] namely −(634.92 ± 0.90) kJ·mol^{-1}, −(1094.8 ± 0.8) kJ·mol^{-1}, and −(285.830 ± 0.040) kJ·mol^{-1}, respectively. From these data, the standard molar enthalpy of formation of $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ was calculated to be −(10062.3 ± 6.5) kJ·mol^{-1}.

Estimated Thermodynamic Properties by a Group Contribution Method. An accurate calculation of the $\Delta_f G_m^\circ$ of borates should take account the $\Delta_r G_m^\circ$ of the solubilization reaction. When the solubility data of borates are not known, Li et al. put forward a group contribution method to estimate the thermodynamic parameters approximatively, namely, the $\Delta_f H_m^\circ$ or $\Delta_f G_m^\circ$ of a hydrated borate phase should be the sum of the contributions of corresponding cations in aqueous solution, of borate polyanions, and of structural water.[11] The contributions of borate polyanions can be obtained from known experimental data of $\Delta_f H_m^\circ$ or $\Delta_f G_m^\circ$ for hydrated borates by using multiple linear regress technique. As such, use of this method assumes the $\Delta_r G_m^\circ$ is zero.

The molar enthalpy of formation of $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ can also be estimated by a group contribution method, which can be expressed as shown in following equation:

$$\begin{aligned}\Delta_f H_m^\circ((NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O)(s) = {}& 2\Delta_f H_m^\circ(NH_4^+)(aq) + \Delta_f H_m^\circ(Ca^{2+})(aq) + \\ & 2\Delta_f H_m^\circ([B_4O_5(OH)_4]^{2-})(aq) + 8\Delta_f H_m^\circ(H_2O)(l)\end{aligned}$$

The $\Delta_f H_m^\circ$ of Ca^{2+} is −542.83 kJ·mol^{-1}. The regressed $\Delta_f H_m^\circ$ of $[B_4O_5(OH)_4]^{2-}$ is −3464.46 kJ·mol^{-1}, and structural H_2O is −290.42 kJ·mol^{-1}, which were taken from the literature.[11] The $\Delta_f H_m^\circ$ of NH_4^+ is −132.51 kJ·mol^{-1}, which was taken from the NBS tables.[9] Using this scheme, the standard molar enthalpy of formation of $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ is −10060.13 kJ·mol^{-1}. The relative error is 0.02 %.

A group contribution method was also used to estimate $\Delta_f G_m^\circ$ of $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$, which was found to be −8802.38 kJ·mol^{-1} according to the following equation:

$$\begin{aligned}\Delta_f G_m^\circ((NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O)(s) = {}& 2\Delta_f G_m^\circ(NH_4^+)(aq) + \Delta_f G_m^\circ(Ca^{2+})(aq) + \\ & 2\Delta_f G_m^\circ([B_4O_5(OH)_4]^{2-})(aq) + 8\Delta_f G_m^\circ(H_2O)(l)\end{aligned}$$

The $\Delta_f G_m^\circ$ of Ca^{2+} is −553.54 kJ·mol^{-1}. The regressed $\Delta_f G_m^\circ$ of $[B_4O_5(OH)_4]^{2-}$ is −3095.99 kJ·mol^{-1} and −237.28 kJ·mol^{-1} for structural H_2O, which again were taken from the literature.[11] The $\Delta_f G_m^\circ$ of −79.31 kJ·mol^{-1} for NH_4^+ was taken from the NBS tables.[9] Combining the $\Delta_f H_m^\circ$ of $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$, the standard molar entropy of formation of $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ is estimated to be −4225.8 J·mol^{-1}·K^{-1} according to following equation:

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

Finally, the standard molar entropy (S_m°) of $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ was estimated to be 809.3 J·mol^{-1}·K^{-1} according to following reaction (eq 2):

$$Ca(s) + 8B(s) + N_2(g) + 16H_2(g) + 13O_2(g) = (NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O(s) \quad (2)$$

The standard molar entropies of the elements were taken from the CODATA Key Values,[10] namely, (41.59, 5.90, 191.61, 130.571, and 205.043) J·mol^{-1}·K^{-1} for Ca(s), B(s), N_2(g), H_2 (g), and O_2 (g), respectively.

Conclusions

Through designing the thermochemical cycle, the standard molar enthalpy of formation of $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ has been obtained from measured enthalpies of solution together with the standard molar enthalpies of formation of HCl (aq), NH_4Cl(s), CaO(s), H_3BO_3(s), and H_2O. The standard molar free energy of formation and the standard molar entropy of $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ have also been estimated by a group contribution method.

Supporting Information Available:

The XRD pattern, FT-IR absorption spectrum, and simultaneous DTA-TG curves of the synthetic sample. This material is available free of charge via the Internet at http://pubs.acs.org.

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