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Synthesis and Thermodynamic Properties of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$

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A new hydrated double borate, $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$, has been synthesized and characterized by chemical analysis, elemental analysis, X-ray diffraction, infrared spectrum, and thermogravimetric analysis. The molar enthalpies of solution of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ in 1 $mol \cdot dm^{-3}$ HCl(aq) and of KCl(s) in $[Ba(OH)_2 \cdot 8H_2O(aq) + H_3BO_3(aq) + HCl(aq)]$ were measured to be (90.74 ± 0.27) $kJ \cdot mol^{-1}$ and (17.37 ± 0.31) $kJ \cdot mol^{-1}$, respectively. With the incorporation of the previously determined enthalpy of solution of $Ba(OH)_2 \cdot 8H_2O(s)$ in $[HCl + H_3BO_3](aq)$ and that of $H_3BO_3(s)$ in HCl(aq), together with the standard molar enthalpies of formation of HCl(aq), $H_2O(l)$, $Ba(OH)_2 \cdot 8H_2O(s)$, $H_3BO_3(s)$, and KCl(s), the standard molar enthalpy of formation of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ was found to be −(10295.2 ± 6.5) $kJ \cdot mol^{-1}$. The standard molar free energy of formation was estimated to be −9217.53 $kJ \cdot mol^{-1}$. The standard molar entropy was estimated to be 858.1 $J \cdot mol^{-1} \cdot K^{-1}$.

Introduction

Thermodynamic properties play very important roles in scientific research and industrial applications. As for the thermochemistry of alkaline-earth metal borates, the standard molar enthalpies of formation of many magnesium and calcium borates have been measured.[1–6] However, studies of the thermochemistry of the barium borates are rare. Recently, we have determined the standard molar enthalpies of formation of β-BaB_2O_4 and $BaB_2O_4 \cdot 4H_2O$ by the method of solution calorimetry.[7] As part of the continuing study of the thermochemistry of barium borates, this paper reports the synthesis and the determination of the standard molar enthalpy of formation of a new hydrated double barium borate $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$, which was unexpectedly obtained when we tried to synthesize the known $K_2Ba[B_4O_5(OH)_4]_2 \cdot 10H_2O$ according to the method given in the literature,[8] as well as an estimate of the $\Delta_f G_m^{\ominus}$ and $S_m^{\ominus}$ of this double borate by a group contribution method.

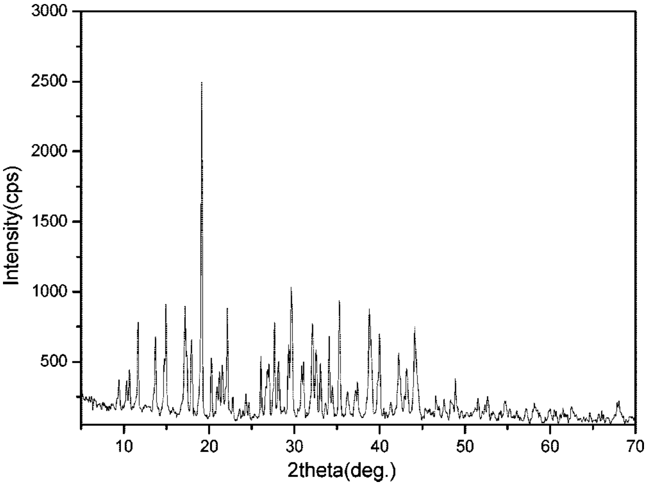

Figure 1. X-ray powder diffraction pattern of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$.

Experimental Section

Preparation and Characterization of the $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ Sample. All reagents used in the synthesis were of analytic grade (made in the Xi'an Chemical Factory, China). A solution of 1.2 g of $BaCl_2 \cdot 2H_2O$ in 20 cm^3 of water was added to a solution of 8.1 g of $K_2B_4O_7 \cdot 4H_2O$ in 50 cm^3 of water.[8] Crystallization began in a few days at room temperature. The resulting solids were separated and washed thoroughly with distilled water and then with alcohol and ether and, finally, dried in a vacuum-dryer to a constant mass. The synthetic sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target at $8° \cdot min^{-1}$), 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 $K \cdot min^{-1}$ in flowing N_2). The chemical composition of the sample was determined by EDTA titration for Ba^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by TG for H_2O.

Calorimetric Experiment. The thermochemical reaction designed for the derivation of $\Delta_r H_m^{\ominus}$ of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ is shown in reaction (1), and the thermochemical cycle is shown in Table 3.

$$\begin{aligned} &K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O(s) + \\ &\quad 178.983(HCl \cdot 54.506H_2O) = 2KCl(s) + Ba(OH)_2 \cdot \\ &\quad 8H_2O(s) + 8H_3BO_3(s) + 176.983(HCl \cdot 54.506H_2O) + \\ &\quad 101.012H_2O(l) \quad (1) \end{aligned}$$

HCl(aq) (1 $mol \cdot dm^{-3}$) solvent can rapidly dissolve all components of the reaction (1), which was prepared from analytical grade hydrochloric acid and deionized water, and its concentration, 0.9996 $mol \cdot dm^{-3}$, was determined by titration with standard sodium carbonate. In all determinations, strict control of the stoichiometries in each step of the calorimetric cycle must be maintained, with the objective that the dissolution

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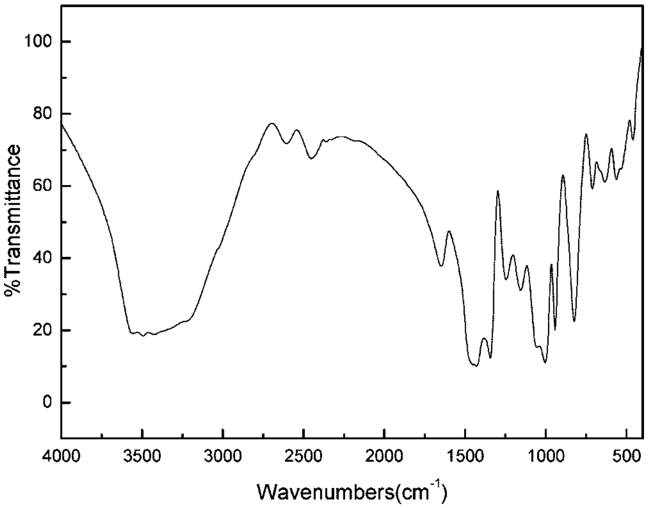

Figure 2. FT-IR spectrum of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$.

of the reactants gives the same composition as those of the products in the reaction (1).

The standard molar enthalpy of formation of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of KCl(s), H_3BO_3(s), $Ba(OH)_2 \cdot 8H_2O$(s), HCl(aq), and H_2O(l).

The RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) used was described in detail previously.[7,9] Each calorimetric experiment was performed five times at 298.15 K as previously described. The total time required for the complete reaction was about 0.5 h. No solid residues were observed after each reaction.

Results and Discussion

Characterization of the Synthetic Sample. Anal. Calcd for $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$: BaO, 20.66 %; B_2O_3, 37.52 %; H_2O, 29.13 %. Found: BaO, 20.49 %; B_2O_3, 37.40 %; H_2O, 30.00 %. The chemical 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 is shown in Figure 1. The characteristic *d* values are 0.7569, 0.6442, 0.5923, 0.5163, 0.5069, 0.4919, 0.4629, 0.4184, 0.3416, 0.3013, 0.2899, 0.2879, 0.2788, 0.2740, 0.2627, 0.2605, 0.2542, 0.2403, 0.2341, 0.2321, 0.2310, 0.2255, 0.2141, 0.2092, 0.2049, 0.2041, and 0.1660 nm.

The FT-IR spectrum of the synthetic sample (Figure 2) exhibits the following absorption bands, and they are assigned by referring to the literature.[10] The band at 3492 cm^{-1} is the stretching vibration of the O−H group. The band at 1648 cm^{-1} is assigned to the H−O−H bending mode, which shows this compound contains crystalline water. The bands at (1430, 1344, and 942) cm^{-1} are the asymmetric and symmetric stretching modes of B(3)−O, respectively. The bands at (1246 and 1157) cm^{-1} are the in-plane bending of B−O−H. The bands at (1005 and 824) cm^{-1} are the asymmetric and symmetric stretching modes of B(4)−O, respectively. The bands at (711 and 634) cm^{-1} are assigned to out-of-plane bending of B(3)−O. The band at 563 cm^{-1} is the characteristic peak of the tetraborate anion of $[B_4O_5(OH)_4]^{2-}$.

The simultaneous TG-DTA curves of a synthetic sample are shown in Figure 3. The TG curve indicates that the total mass loss is 30.00 % from (303 to 1073) K, which corresponds to the loss of 12 water molecules and is near the calculated value of 29.13 %. In the DTA curve, the endothermic peak appearing at 383.6 K is related to the dehydration of crystal water. The forming amorphous phase recrystallizes as shown by the exothermic peak at 884.8 K. The endothermic peaks appearing at (1034.4 and 1077.8) K are related to the melt of the forming phase of $K_2Ba[B_4O_7]_2$.

All of above results indicate that the obtained product is $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ instead of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 10H_2O$, according to the previously described synthetic method,[8] and is suitable for calorimetric experiment. It might be the higher room temperature (about 303 K) in summer in Xian of China that led to the formation of the octahydrate compound.

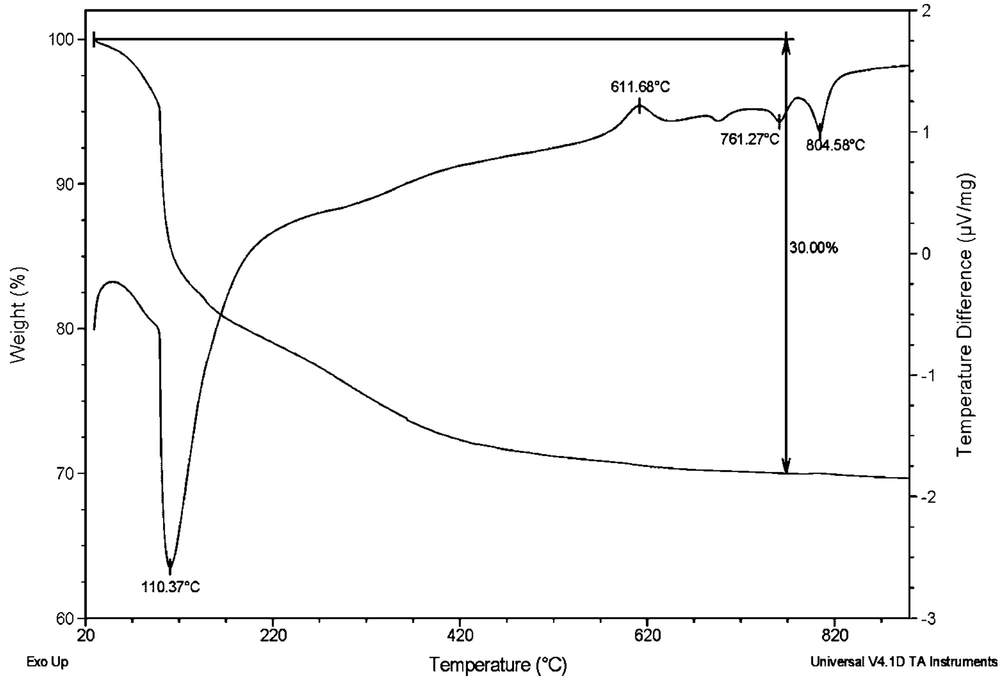

Figure 3. TG-DTA curve of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$.

Table 1. Molar Enthalpies of Solution of KCl(s) in Aqueous 1 mol·dm^{-3} HCl and Calculated Amount of H_3BO_3 and $Ba(OH)_2 \cdot 8H_2O$ at 298.15 K[a]

no.	m (mg)	$\Delta_{sol}H_m$ (kJ·mol^{-1})
1	1.43	17.55
2	1.36	17.63
2	1.47	17.03
4	1.48	17.68
5	1.47	16.97
mean		17.37 ± 0.31[b]

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

Table 2. Molar Enthalpies of Solution of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O(s)$ in 1 mol·dm^{-3} HCl(aq) at 298.15 K[a]

no.	m (mg)	Δ_rH (mJ)	$\Delta_{sol}H_m$ (kJ·mol^{-1})
1	8.12	989.353	90.43
2	8.43	1028.966	90.59
3	8.35	1022.634	90.90
4	8.40	1025.541	90.61
5	8.13	998.759	91.18
mean			90.74 ± 0.27[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.

Results of the Calorimetric Experiment. The molar enthalpy of solution of KCl(s) is (17.37 ± 0.31) kJ·mol^{-1} in the mixed solvent of [$Ba(OH)_2 \cdot 8H_2O$(aq) + H_3BO_3(aq) + HCl(aq)], and that of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ is (90.74 ± 0.27) kJ·mol^{-1} in 1 mol·dm^{-3} HCl(aq) at 298.15 K. The values are listed in Tables 1 and 2, in which m is the mass of sample; $\Delta_{sol}H_m$ is the molar enthalpy of solution of solute; and the uncertainty is estimated as twice the standard deviation of the mean, namely, $\delta = 2\sqrt{\Sigma(x_i - \overline{x})^2/n(n-1)}$, in which n is the number of experiments ($n = 5$); x_i is the experimental value of each repeated measurement; and x^- is the mean value.

Table 3 gives the thermochemical cycles for the derivation of the standard molar enthalpy of formation of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$. The molar enthalpy of solution of H_3BO_3(s) of (21.83 ± 0.08) kJ·mol^{-1} in 1 mol·dm^{-3} HCl(aq) was taken from the literature.[1] The molar enthalpy of solution of $Ba(OH)_2 \cdot 8H_2O$(s) of −(55.42 ± 0.36) kJ·mol^{-1} in aqueous [1 mol·dm^{-3} HCl(aq) + H_3BO_3(aq)] was taken from our previous work.[7] The standard molar enthalpies of formation of H_2O(l) and H_3BO_3(s) were taken from the CODATA Key Values,[11] namely, −(285.830 ± 0.040) and −(1094.8 ± 0.8) kJ·mol^{-1}, respectively. The standard molar enthalpy of formation of HCl(aq) and the enthalpy of dilution of HCl(aq) were calculated from the NBS tables.[12] The standard molar enthalpies of formation of KCl(s) and $Ba(OH)_2 \cdot 8H_2O$(s) were taken from the NBS tables,[12] namely, (−436.747 and −3342.2) kJ·mol^{-1}, respectively. From these data, the standard molar enthalpy of formation of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ was calculated to be −(10295.2 ± 6.5) kJ·mol^{-1}.

Estimate Thermodynamic Properties by a Group Contribution Method. An accurate calculation of the $\Delta_fG_m^\Theta$ of borates should take into account the $\Delta_rG_m^\Theta$ of the solubilization reaction. When the solubility data of borates are not known, Li et al.[13] put forward a group contribution method to approximatively estimate thermodynamic parameters; namely, the $\Delta_fH_m^\Theta$ or $\Delta_fG_m^\Theta$ 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. The contributions of borate polyanions can be obtained from known experimental data of $\Delta_fH_m^\Theta$ or $\Delta_fG_m^\Theta$ for hydrated borates by using a multiple linear regression technique. As such, use of this method assumes the $\Delta_rG_m^\Theta$ is zero.

According to this method, the molar enthalpy of formation of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ can also be estimated by the following equation

$$\Delta_fH_m^\Theta(K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O, s) = 2\Delta_fH_m^\Theta(K^+, aq) + \Delta_fH_m^\Theta(Ba^{2+}, aq) + 2\Delta_fH_m^\Theta([B_4O_5(OH)_4]^{2-}, aq) + 8\Delta_fH_m^\Theta(H_2O, l)$$

The $\Delta_fH_m^\Theta$ of regressed $[B_4O_5(OH)_4]^{2-}$ and structural H_2O are −3464.46 kJ·mol^{-1} and −290.42 kJ·mol^{-1}, respectively, which were taken from the literature.[13] The $\Delta_fH_m^\Theta$ of K^+ and Ba^{2+} are −252.38 kJ·mol^{-1} and −537.64 kJ·mol^{-1}, respectively, which were taken from the NBS tables.[12] Using this scheme, the standard molar enthalpy of formation is −10294.68 kJ·mol^{-1}, which is in good agreement with the measured value of − (10295.2 ± 6.5) kJ·mol^{-1}. The relative error is 0.01 %.

A group contribution method was also used to estimate $\Delta_fG_m^\Theta$ of $K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O$ which was found to be −9217.53 kJ·mol^{-1} according to the following equation

$$\Delta_fG_m^\Theta(K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O, s) = 2\Delta_fG_m^\Theta(K^+, aq) + \Delta_fG_m^\Theta(Ba^{2+}, aq) + 2\Delta_fG_m^\Theta([B_4O_5(OH)_4]^{2-}, aq) + 8\Delta_fG_m^\Theta(H_2O, l)$$

The $\Delta_fG_m^\Theta$ of regressed $[B_4O_5(OH)_4]^{2-}$ and structural H_2O are −3095.99 kJ·mol^{-1} and −237.28 kJ·mol^{-1}, which again were taken from the literature.[13] The $\Delta_fG_m^\Theta$ of K^+ and Ba^{2+}

Table 3. Thermochemical Cycle and Results for the Derivation of $\Delta_fH_m^\Theta$ ($K_2Ba[B_4O_5(OH)_4]_2 \cdot 8H_2O(s)$, 298.15 K)

no.	reaction	Δ_rH^Θ(kJ·mol^{-1})
1	$K_2O \cdot BaO \cdot 4B_2O_3 \cdot 12H_2O(s) + 178.983(HCl \cdot 54.506H_2O) = 2K^+ + Ba^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 174.983(HCl \cdot 55.763H_2O)$	90.74 ± 0.27
2	$Ba^{2+}(aq) + 2Cl^- + 8H_3BO_3(aq) + 174.983(HCl \cdot 55.763H_2O) = Ba(OH)_2 \cdot 8H_2O(s) + 8H_3BO_3(aq) + 176.983(HCl \cdot 55.076H_2O)$	55.42 ± 0.36
3	$2K^+(aq) + Ba^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 174.983(HCl \cdot 55.763H_2O) = Cl(s) + Ba^{2+}(aq) + 2Cl^-(aq) + 8H_3BO_3(s) + 174.983(HCl \cdot 55.763H_2O)$	−34.74 ± 0.62
4	$8H_3BO_3(aq) + 176.983(HCl \cdot 55.076H_2O) = 8H_3BO_3(s) + 176.983(HCl \cdot 55.076H_2O)$	−174.64 ± 0.60
5	$176.983(HCl \cdot 55.076H_2O) = 176.983(HCl \cdot 54.506H_2O) + 101.012H_2O(l)$	2.02 ± 0.08
6	$H_2(s) + Cl_2(g) + 109.012H_2O(l) = 2(HCl \cdot 54.506H_2O)$	−330.86 ± 0.20
7	$2KCl(s) = 2K(s) + Cl_2(g)$	873.49 ± 0.20
8	$Ba(OH)_2 \cdot 8H_2O(s) = Ba(s) + 5O_2 + 9H_2(g)$	3342.2 ± 0.40
9	$8H_3BO_3(s) = 8B(s) + 12H_2(g) + 12O_2(g)$	8758.4 ± 6.4
10	$8H_2(g) + 4O_2(g) = 8H_2O(l)$	−2286.64 ± 0.32
11	$K_2O \cdot BaO \cdot 4B_2O_3 \cdot 12H_2O(s) = 2K(s) + Ba(s) + 8B(s) + 12H_2(g) + 13O_2(g)$	10295.2 ± 6.5

are $-283.27\ \text{kJ}\cdot\text{mol}^{-1}$ and $-560.77\ \text{kJ}\cdot\text{mol}^{-1}$, respectively, which were taken from the NBS tables.[12]

Combining the $\Delta_f H_m^{\ominus}$ of $K_2Ba[B_4O_5(OH)_4]_2\cdot 8H_2O$, the standard molar entropy of formation of $K_2Ba[B_4O_5(OH)_4]_2\cdot 8H_2O$ is estimated to be $-3614.6\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ according to the following equation

$$\Delta_f S_m^{\ominus} = (\Delta_f H_m^{\ominus} - \Delta_f G_m^{\ominus})/T$$

Finally, the standard molar entropy of $K_2Ba[B_4O_5(OH)_4]_2\cdot 8H_2O$ is estimated to be $858.1\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ according to the following reaction (2)

$$2K(s) + Ba(s) + 8B(s) + 12H_2(g) + 13O_2(g) = K_2Ba[B_4O_5(OH)_4]_2\cdot 8H_2O(s) \quad (2)$$

The standard molar entropies of the elements were taken from the NBS tables,[12] namely, (64.18, 62.8, 5.86, 130.648, and 205.138) $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$for K(s), Ba(s), B(s), H_2(g), and O_2(g), respectively.

Conclusions

The standard molar enthalpy of formation of $K_2Ba[B_4O_5(OH)_4]_2\cdot 8H_2O$ has been obtained from measured enthalpies of solution, together with the standard molar enthalpies of formation of HCl (aq), KCl(s), $Ba(OH)_2\cdot 8H_2O$(s), H_3BO_3(s), and H_2O(l). The standard molar free energy of formation and the standard molar entropy of this borate have also been estimated by a group contribution method.

Literature Cited

(1) Li, J.; Gao, S. Y.; Xia, S. P.; Li, B. Thermochemistry of hydrated magnesium borates. *J. Chem. Thermodyn.* **1997**, *29*, 491–497.

(2) Li, J.; Gao, S. Y.; Xia, S. P.; Li, B.; Hu, R. Z. Thermochemistry of hydrated calcium borates. *J. Chem. Thermodyn.* **1997**, *29*, 1071–1075.

(3) Liu, Z. H.; Hu, M. C.; Gao, S. Y. Thermodynamic properties of chloropinnoite. *J. Chem. Thermodyn.* **2003**, *35*, 1831–1836.

(4) Liu, Z. H.; Hu, M. C. Synthesis, characterization and thermochemistry of a new form of $2MgO\cdot 3B_2O_3\cdot 17H_2O$. *Thermochim. Acta* **2004**, *414*, 215–218.

(5) Liu, Z. H.; Li, P.; Zuo, C. F. Standard molar enthalpies of formation for the two hydrated calcium borates $x\text{CaO}\cdot 5B_2O_3\cdot yH_2O$ ($x = 2$ and $4y = 5$ and 7). *J. Chem. Eng. Data* **2006**, *51*, 272–275.

(6) Han, W. H.; Liu, Z. H.; Zhang, W. J.; Zuo, C. F.; Liang, S. J. Thermodynamic properties of $(NH_4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$. *J. Chem. Eng. Data* **2006**, *51*, 1242–1245.

(7) Liu, Z. H.; Wang, Y.; Huang, H. S. Synthesis and thermochemistry of $BaB_2O_4\cdot 4H_2O$ and β-BaB_2O_4. *J. Chem. Eng. Data* **2007**, *52*, 487–490.

(8) Kesans, A.; Streipa, I. Potassium barium octaborate. *Latvijas PSR Zinatnu Akad. Vestis.* **1954**, *5*, 105.

(9) Ji, M.; Liu, M. Y.; Gao, S. L.; Shi, Q. Z. The enthalpy of solution in water of complexes of zinc with methionine. *Instrum. Sci. Technol.* **2001**, *29*, 53–57.

(10) Li, J.; Xia, S. P.; Gao, S. Y. FT-IR and Raman spectroscopic study of hydrated borates. *Spectrochim. Acta* **1995**, *51A*, 519–532.

(11) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(12) Wagman, D. D.; Evans, W. H.; Paker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Chumey, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Data*, **1982**, *11*, (Suppl. 2).

(13) Li, J.; Li, B.; Gao, S. Y. Calculation of thermodynamic properties of hydrated borates by group contribution method. *Phys. Chem. Miner.* **2000**, *27*, 342–346.

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