Synthesis and Determination of Standard Molar Enthalpies of Formation for the Two Hydrated Ammonium Borates, $(NH_4)_2B_8O_{13}\cdot nH_2O$ ($n = 5.5, 6$)[†]

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Two pure hydrated ammonium borates, new $(NH_4)_2B_8O_{13}\cdot 5.5H_2O$ (**I**) and known $(NH_4)_2B_8O_{13}\cdot 6H_2O$ (**II**), have been synthesized and characterized by X-ray diffraction, infrared spectra, thermogravimetric analysis, differential thermal analysis, elemental analyses, and chemical analysis. The enthalpies of solution of **I** and **II** in 1 $mol\cdot dm^{-3}$ HCl(aq) were measured to be (89.58 ± 0.18) $kJ\cdot mol^{-1}$ and (97.84 ± 0.18) $kJ\cdot mol^{-1}$. From a combination of these results with measured enthalpies of solution of H_3BO_3(s) in 1 $mol\cdot dm^{-3}$ HCl(aq) and of NH_4Cl(s) in (HCl + H_3BO_3) aqueous solution, together with the standard molar enthalpies of formation of NH_4Cl(s), H_3BO_3(s), HCl(aq), and H_2O(l), the standard molar enthalpies of formation were found to be −(7361.4 ± 6.5) $kJ\cdot mol^{-1}$ for **I** and −(7226.7 ± 6.5) $kJ\cdot mol^{-1}$ for **II**.

Introduction

There are many kinds of borates because of the complexity of the structures involved. Some borates show interesting physical properties, such as nonlinear optical behavior for β-BaB_2O_4 (BBO) and CsB_3O_5(CBO). Therefore, the studies of borates have attracted much interest in recent years. Several hydrated ammonium borates have been reported, such as $(NH_4)_2B_4O_7\cdot 4H_2O$,[1] $NH_4[B_5O_7(OH)_2]\cdot H_2O$,[2] $(NH_4)_2[B_{10}O_{14}(OH)_4]\cdot H_2O$,[3] and $(NH_4)_3[B_{15}O_{20}(OH)_8]\cdot 4H_2O$.[4]

Thermodynamic properties play an important role in scientific research and industrial applications. As for the determination of the standard molar enthalpies of formation of ammonium borates, only two data for $(NH_4)_2B_4O_7\cdot 4H_2O$ and $NH_4B_5O_8\cdot 4H_2O$ have been reported.[5] This paper reports the synthesis and determination of the standard molar enthalpies of formation of the two ammonium borates, new $(NH_4)_2B_8O_{13}\cdot 5.5H_2O$ (**I**) and known $(NH_4)_2B_8O_{13}\cdot 6H_2O$ (**II**), using a heat conduction microcalorimeter.

Experimental Section

Synthesis and Characterization of Samples. All reagents used in the synthesis of the $(NH_4)_2B_8O_{13}\cdot nH_2O$ ($n = 5.5, 6$) were of analytical grade. The compound $(NH_4)_2B_8O_{13}\cdot 5.5H_2O$ (**I**) was prepared from a mixture of 0.961 g of $(NH_4)_2CO_3$, 3.091 g of H_3BO_3, and 2 cm^3 of H_2O, which was sealed in a Teflon-lined bomb and heated at 200 °C for 5 days and then cooled to room temperature. The compound $(NH_4)_2B_8O_{13}\cdot 6H_2O$ (**II**) was prepared from a mixture of 24 cm^3 of $NH_3\cdot H_2O$ (mass fraction = 0.25 to 0.28), 18 g of H_3BO_3, and 30 cm^3 of H_2O, in which the white powder was crystallized at room temperature after 5 days. The resulting two kinds of white powders were recovered by filtration, washed with distilled water, and dried in a vacuum dryer to a constant mass at room temperature, respectively. The samples **I** and **II** were characterized by FT-IR spectroscopy (recorded over the (400 to 4000) cm^{-1} region on a Bruker Equinox 55 spectrometer with KBr pellets at room temperature), X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target at $8°\cdot min^{-1}$), elemental analyses (determined on Vario EL III Elemental Analyzer), thermogravimetric analysis (TGA), and differential thermal analysis (DTA) (performed on a SDT Q600 simultaneous thermal analyzer under N_2 atmosphere with a heating rate of 10 $K\cdot min^{-1}$). The B_2O_3 content was determined by NaOH titration in the presence of mannitol.

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

no.	m/mg	$\Delta_{sol}H_m$/$kJ\cdot mol^{-1}$
	I	
1	6.47	89.59
2	6.42	89.42
3	6.41	89.40
4	6.34	89.60
5	6.43	89.89
Mean		89.58 ± 0.18[b]
	II	
1	6.44	97.80
2	6.48	97.73
3	6.49	98.19
4	6.57	97.79
5	6.50	97.68
Mean		97.84 ± 0.18[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, namely, $\delta = 2\sqrt{\Sigma(x_i - \bar{x})^2/n(n-1)}$, 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.

Calorimetric Experiment. The thermochemical reactions designed for the derivation of the $\Delta_f H_m°$ of $(NH_4)_2B_8O_{13}\cdot nH_2O$ ($n = 5.5, 6$) are given below

$$(NH_4)_2B_8O_{13}\cdot 5.5H_2O(s) + 2(HCl\cdot 54.506H_2O) = 2NH_4Cl(s) + 8H_3BO_3(s) + 103.512H_2O(l)$$

$$(NH_4)_2B_8O_{13}\cdot 6H_2O(s) + 2(HCl\cdot 54.506H_2O) = 2NH_4Cl(s) + 8H_3BO_3(s) + 104.012H_2O(l)$$

The 1 $mol\cdot dm^{-3}$ HCl(aq) solvent can dissolve all components of reactions, and its concentration of 0.9996 $mol\cdot dm^{-3}$ was

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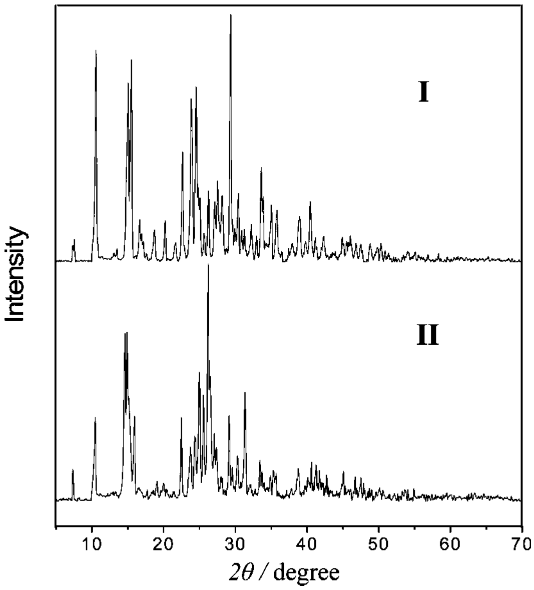

Figure 1. XRD patterns of the samples.

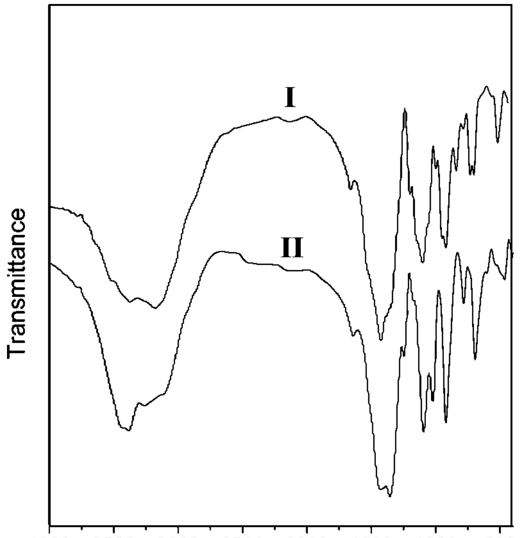

Figure 2. FT-IR spectra of the samples.

determined by titration with standard sodium carbonate. The standard molar enthalpies of formation of **I** and **II** could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of $NH_4Cl(s)$, $H_3BO_3(s)$, HCl(aq), and $H_2O(l)$.

The RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) used was described in detail previously.[6,7] To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction ≥ 0.9999) in deionized water was determined to be (17.31 ± 0.20) $kJ \cdot mol^{-1}$, which is in agreement with that of 17.234 $kJ \cdot mol^{-1}$ reported in the literature.[8] This shows that the device used for measuring the enthalpy of solution in this work is reliable.

Calorimetric experiments were performed five times at 298.15 K as previously described.[7] No solid residues were observed after the reactions.

Results and Discussion

Characterization of the Synthetic Samples. The chemical and elemental analytical data of samples are (found/calcd, %) B_2O_3(64.98/64.82), N(6.94/6.52), H(4.34/4.46) for **I** and B_2O_3(63.49/63.92), N(6.38/5.92), H(4.60/4.30) for **II**. The analytical results are consistent with the theoretical values.

Figure 1 shows the powder XRD patterns of samples **I** and **II**. The main characteristic *d* values of the XRD pattern for **I** are: (8.6510, 6.8896, 5.8221, 5.1212, 4.2306, 3.7952, 3.7232, 3.1081, 2.9190, 2.5376, 2.4715, 2.2616, 2.2468, 2.2077, and 2.1954) Å. Moreover, no peaks from H_3BO_3 or $(NH_4)_2CO_3$ are observed, which shows absence of other crystalline forms in the synthetic sample. The main *d* values for **II** are: (12.030, 8.450, 6.094, 5.940, 5.580, 3.950, 3.760, 3.720, 3.340, 3.580, 3.480, 3.390, 3.250, 3.050, 2.940, and 2.850) Å, which correspond with those of the JCPDS card (File No.19-0072) and show an absence of any other crystalline forms in this synthetic sample. It can be seen that the data of XRD patterns of **I** are different from those of **II**, which confirms that $(NH_4)_2B_8O_{13} \cdot 5.5H_2O$ (**I**) is a new compound.

The FT-IR spectra (Figure 2) of the samples exhibited the following absorption bands, and they were assigned referring to the literature.[9] For **I**: 3374 cm^{-1} (O−H), 1634 cm^{-1} (H−O−H), 3176 cm^{-1} (N−H), 1168 cm^{-1} (B−O−H), (1399, 963, and 926) cm^{-1} (B(3)−O), (1070, 888, and 744) cm^{-1} (B(4)−O), (696 and 667) cm^{-1} (B(3)−O), 480 cm^{-1} (B(4)−O). For **II**: 3390 cm^{-1} (O−H), 1641 cm^{-1} (H−O−H), 3273 cm^{-1} (N−H), 1244 cm^{-1} (B−O−H), (1430, 1361, and 925) cm^{-1} (B(3)−O), (1088, 1027, and 785) cm^{-1} (B(4)−O), 692 cm^{-1} (B(3)−O), 467 cm^{-1} (B(4)−O).

The simultaneous TG−DTA curves of sample **I** (Figure 3) indicated that it had a three-step mass loss between (20 and 584) °C, and the total mass loss was 35.12 %, which corresponds to the loss of 6.5 water molecules and 2 ammonium molecules and is in good agreement with calculated value of 35.18 %. The first mass loss was 8.22 % at (20 to 149) °C, which corresponds to the loss of 2 crystalline water molecules and is in good agreement with a calculated value of 8.39 %. In the second step, the mass loss was 16.03 % at (149 to 300) °C, which corresponds to the loss of 2 crystalline water molecules and 2 ammonium molecules and can be compared with a calculated value of 16.31 %. In the

Table 2. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^o$ ($(NH_4)_2B_8O_{13} \cdot 5.5H_2O$, 298.15 K)

no.	reaction	$\Delta_r H_m^\circ/(kJ \cdot mol^{-1})$
(1)	$(NH_4)_2B_8O_{13} \cdot 5.5H_2O(s) + 133.91(HCl \cdot 54.506H_2O) = 2NH_4^+(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 131.91(HCl \cdot 55.291H_2O)$	89.58 ± 0.18
(2)	$131.91(HCl \cdot 55.291H_2O) = 131.91(HCl \cdot 54.506H_2O) + 103.512H_2O(l)$	2.11 ± 0.08
(3)	$8H_3BO_3(aq) + 131.91(HCl \cdot 55.291H_2O) = 8H_3BO_3(s) + 131.91(HCl \cdot 55.291H_2O)$	−174.64 ± 0.64
(4)	$2NH_4^+(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 131.91(HCl \cdot 55.291H_2O) = 2NH_4Cl(s) + 8H_3BO_3(aq) + 131.91(HCl \cdot 55.291H_2O)$	−39.96 ± 0.24
(5)	$H_2(g) + Cl_2(g) + 109.012H_2O(l) = 2(HCl \cdot 54.506H_2O)$	−330.91 ± 0.20
(6)	$2NH_4Cl(s) = N_2(g) + Cl_2(g) + 4H_2(g)$	628.86 ± 0.40
(7)	$8H_3BO_3(s) = 8B(s) + 12H_2(g) + 12O_2(g)$	8758.4 ± 6.4
(8)	$11/2H_2(g) + 11/4O_2(g) = 11/2H_2O(l)$	−1572.07 ± 0.22
(9)	$(NH_4)_2B_8O_{13} \cdot 5.5H_2O(s) = N_2(g) + 8B(s) + 19/2H_2(g) + 37/4O_2(g)$	7361.4 ± 6.5[a]

[a] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

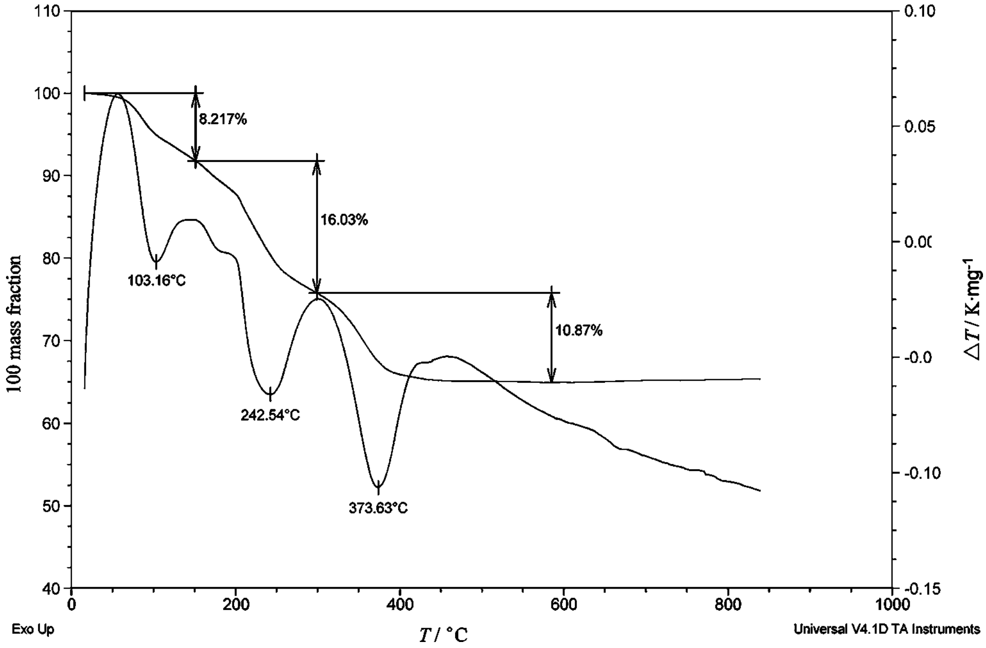

Figure 3. Simultaneous TG−DTA curves of sample **I**.

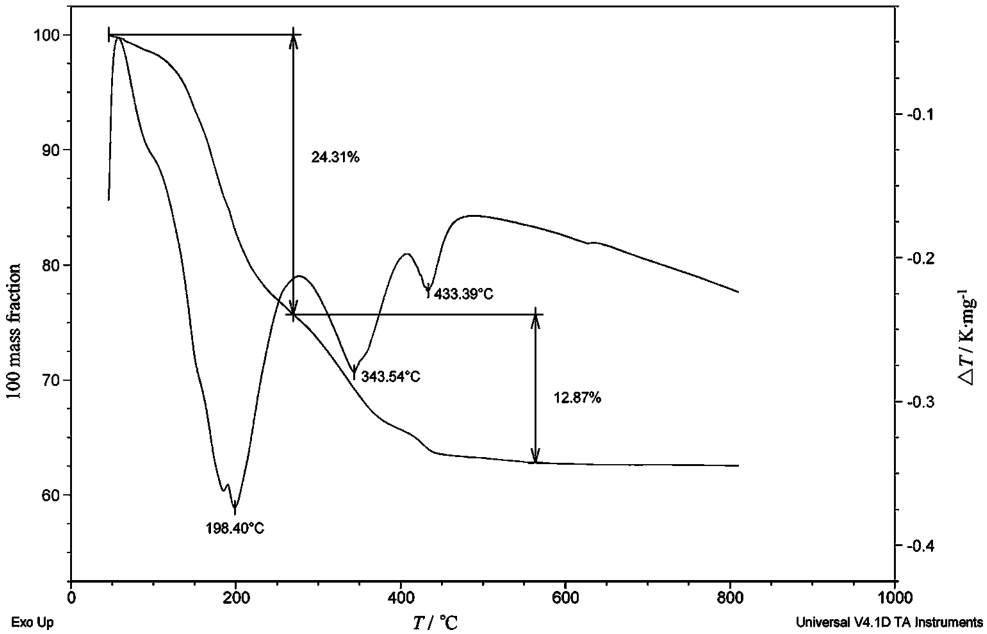

Figure 4. Simultaneous TG−DTA curves of sample **II**.

Table 3. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^\circ$ ($(NH_4)_2B_8O_{13}\cdot 6H_2O$, 298.15 K)

no.	reaction	$\Delta_r H_m^\circ/(kJ\cdot mol^{-1})$
(1)	$(NH_4)_2B_8O_{13}\cdot 6H_2O(s) + 135.29(HCl\cdot 54.506H_2O) = 2NH_4^+(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 133.29(HCl\cdot 55.286H_2O)$	97.84 ± 0.18
(2)	$133.29(HCl\cdot 55.286H_2O) = 133.29(HCl\cdot 54.506H_2O) + 103.012H_2O(l)$	2.13 ± 0.08
(3)	$8H_3BO_3(aq) + 133.29(HCl\cdot 55.286H_2O) = 8H_3BO_3(s) + 133.29(HCl\cdot 55.286H_2O)$	−174.64 ± 0.64
(4)	$2NH_4^+(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 133.29(HCl\cdot 55.286H_2O) = 2NH_4Cl(s) + 8H_3BO_3(aq) + 133.29(HCl\cdot 55.286H_2O)$	−39.96 ± 0.24
(5)	$H_2(g) + Cl_2(g) + 109.012H_2O(l) = 2(HCl\cdot 54.506H_2O)$	−330.91 ± 0.20
(6)	$2NH_4Cl(s) = N_2(g) + Cl_2(g) + 4H_2(g)$	628.86 ± 0.40
(7)	$8H_3BO_3(s) = 8B(s) + 12H_2(g) + 12O_2(g)$	8758.4 ± 6.4
(8)	$6H_2(g) + 3O_2(g) = 6H_2O(l)$	−1714.98 ± 0.24
(9)	$(NH_4)_2B_8O_{13}\cdot 6H_2O(s) = N_2(g) + 8B(s) + 10H_2(g) + 19/2O_2(g)$	7226.74 ± 6.5[a]

[a] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

third step, the mass loss was 10.87 % at (300 to 584) °C, which corresponds to the loss of 2.5 structural water molecules and can be compared with a calculated value of 10.48 %. In the DTA curve, there were three endothermic peaks at (103, 243, and 374) °C, which are related to the three-step decomposition and formation of the B_2O_3 phase.

The simultaneous TG−DTA curves of the sample **II** (Figure 4) indicated that it had a two-step mass loss between (46 and 562) °C, and the total mass loss was 37.18 %, which corresponds to the loss of 7 water molecules and 2 ammonium molecules and can be compared with a calculated value of 36.43 %. The first mass loss was 24.31 % at (46 to 269) °C, which corresponds to the loss of 4 crystalline water molecules and 2 ammonium molecules and is in good agreement with a calculated value of 24.17 %. In the second step, the weight loss was 12.87 % at (269 to 562) °C, which corresponds to the loss of 3 water molecules and can be compared with a calculated value of 12.89 %. In the DTA curve, there were three endothermic peaks at (198, 343, and 433) °C, which are related to the decomposition and formation of the B_2O_3 phase.

The results of XRD, TG, elemental analyses, and chemical analysis indicate that the two synthetic samples are pure and suitable for the calorimetric experiments.

Results of the Calorimetric Experiment. The molar enthalpies of solution of **I** and **II** in 1 $\text{mol}\cdot\text{dm}^{-3}$ HCl(aq) at 298.15 K are listed in Table 1, in which m is the mass of sample, $\Delta_{\text{sol}}H_{\text{m}}$ is the molar enthalpy of solution of solute, and the uncertainty is estimated as twice the standard deviation of the mean.

Tables 2 and 3 give the thermochemical cycles for the derivation of the standard molar enthalpies of formation of **I** and **II**. The molar enthalpy of solution of H_3BO_3(s) of (21.83 ± 0.08) $\text{kJ}\cdot\text{mol}^{-1}$ in 1 $\text{mol}\cdot\text{dm}^{-3}$ HCl(aq) was taken from the literature.[10] The molar enthalpy of solution of NH_4Cl(s) of (19.98 ± 0.12) $\text{kJ}\cdot\text{mol}^{-1}$ in (1 $\text{mol}\cdot\text{dm}^{-3}$ HCl + H_3BO_3)(aq) was taken from the literature.[5] The standard molar enthalpy of formation of HCl(aq) and the enthalpy of dilution of HCl(aq) were calculated from the NBS tables.[11] The standard molar enthalpy of formation of −(314.43 ± 0.20) $\text{kJ}\cdot\text{mol}^{-1}$ of NH_4Cl(s) was also taken from the NBS tables.[11] The standard molar enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values,[12] namely, −(1094.8 ± 0.8) $\text{kJ}\cdot\text{mol}^{-1}$ and −(285.830 ± 0.040) $\text{kJ}\cdot\text{mol}^{-1}$, respectively. From these data, the standard molar enthalpies of formation of **I** and **II** were calculated to be −(7361.4 ± 6.5) $\text{kJ}\cdot\text{mol}^{-1}$ and −(7226.7 ± 6.5) $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

Conclusions

Through an appropriate thermochemical cycle, the standard molar enthalpies of formation of $(NH_4)_2B_8O_{13}\cdot nH_2O$ ($n = 5.5$, 6) have been obtained from measured enthalpies of solution, together with the standard molar enthalpies of formation of NH_4Cl(s), H_3BO_3(s), HCl(aq), and H_2O(l).

Literature Cited

(1) Janda, R.; Heller, G. The structure of synthetic ammoniumtetraborat-dihydrat, $(NH_4)_2[B_4O_5(OH)_4]_2\cdot H_2O$. *Z. Kristallogr.* **1981**, *154*, 1–9.

(2) Merlino, S.; Sartori, F. The crystal structure of larderellite, $NH_4B_5O_7(OH)_2\cdot H_2O$. *Acta Crystallogr.* **1969**, *B25*, 2264–2270.

(3) Li, L. Y.; Li, G. B.; Xiong, M.; Wang, Y. X.; Lin, J. H. A new hydrated ammonium hydroxyborate, $(NH_4)_2[B_{10}O_{14}\ (OH)_4]\cdot H_2O$. *Acta Crystallogr.* **2003**, *C59*, 115–116.

(4) Merlino, S.; Sartori, F. Ammonioborite: new borate polyion and its structure. *Science.* **1971**, *B6*, 377–379.

(5) Wang, J.; Zhu, L. X.; Wang, B.; Xia, S. P. Thermochemistry of hydrated ammonium borates. *Thermochim. Acta* **2005**, *425*, 23–26.

(6) 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.

(7) 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 4, $y = 5$ and 7). *J. Chem. Eng. Data* **2006**, *51*, 272–275.

(8) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL, 1989.

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

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

(11) Wagman, D. D.; Evans, W. H.; Parker, 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.

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

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