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Thermochemistry of hydrated ammonium borates

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Abstract

The enthalpies of solution of $(NH_4)_2B_4O_7\cdot4H_2O$ (cr) and $NH_4B_5O_8\cdot4H_2O$ (cr) in approximately 1 mol dm^{-3} aqueous hydrochloric acid solution, as well as the enthalpy of solution of NH_4Cl (cr) in aqueous (hydrochloric acid + boric acid) have been measured by using a microcalorimeter. From these results and other auxiliary data, the standard molar enthalpies of formation $\Delta_f H_m^0$ of $(NH_4)_2B_4O_7\cdot4H_2O$ (cr) and $NH_4B_5O_8\cdot4H_2O$ (cr) have been derived to be (-4313.74 ± 3.26) and (-4703.56 ± 4.03) kJ mol^{-1} at 298.15 K, respectively. Some other thermodynamic properties of the title borates, such as the standard molar entropies of formation and the standard molar entropies have also been calculated.

Keywords: Hydrated ammonium borate; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy of solution

1. Introduction

The hydrated ammonium borates, $(NH_4)_2B_4O_7\cdot4H_2O$ and $NH_4B_5O_8\cdot4H_2O$, can be obtained from $(NH_4)_2O$–B_2O_3–H_2O system [1], and their structural features have been reported by Janda and Heller [2] and Domenech and Solans [3]. But there are no reports on the standard molar enthalpies of formation of the above two hydrated ammonium borates. Thermodynamic properties of borates play an important role in the research of the structures of borates and model aqueous solution systems containing hydrated borates. In continuation of a systematic investigation of the thermochemistry of hydrated borates, the standard molar enthalpies of formation of hydrated alkaline earth metal (Mg, Ca) borates, and hydrated alkaline metal (Li, Na, K, Rb) borates have been reported in our previous works [4–9]. The present study focuses on the relatively direct experimental determination of the standard molar enthalpies of formation $\Delta_f H_m^0$ of $(NH_4)_2B_4O_7\cdot4H_2O$ (cr) and $NH_4B_5O_8\cdot4H_2O$ (cr) by solution calorimetry.

2. Experimental

The colorless and transparent hydrated ammonium borate crystals, $(NH_4)_2B_4O_7\cdot4H_2O$ and $NH_4B_5O_8\cdot4H_2O$ were obtained from the supersaturated aqueous solutions of ammonium borates in molar ratios $(NH_4)_2O:B_2O_3 = 2.5:1$ and 1:3, respectively. The samples were analyzed as follows. Boron was determined by titration with a standard solution of NaOH in the presence of mannitol, nitrogen was determined by using an elemental analyzer (Elementar Vario EL), and H_2O content was calculated by difference. The analytical data of the synthetic samples are listed in Table 1. The results of the powder X-ray diffraction of $(NH_4)_2B_4O_7\cdot4H_2O$ and $NH_4B_5O_8\cdot4H_2O$ prepared for the present work are in agreement with those reported in the JCPDS X-ray diffraction files (Nos. 19–0061 and 31–0043). The FTIR spectra (Fig. 1) were recorded in the region from 4000 to 400 cm^{-1} on a Nicolet NEXUS 670 FTIR spectrometer with samples in KBr matrix. The spectrum of $(NH_4)_2B_4O_7\cdot4H_2O$ (Fig. 1a) is very similar to that of $K_2B_4O_7\cdot4H_2O$ [10]. The spectrum of $NH_4B_5O_8\cdot4H_2O$ (Fig. 1b) is in good agreement with that reported in the literature [10]. All these results show that above borates are pure compounds and suitable for calorimetric experiment.

In order to obtain the standard molar enthalpies of formation of the hydrated ammonium borates, a thermochem-

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Table 1
Chemical compositions of synthetic samples (mass%)

Sample		$(NH_4)_2O$	B_2O_3	H_2O
$(NH_4)_2B_4O_7{\cdot}4H_2O$	Experiment	19.72	52.94	27.34
	Calculated	19.77	52.87	27.36
$NH_4B_5O_8{\cdot}4H_2O$	Experimental	9.49	63.97	26.54
	Calculated	9.57	63.95	26.48

ical scheme was designed. The enthalpies of solution of $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr) and $NH_4B_5O_8{\cdot}4H_2O$ (cr) in approximately 1 mol dm^{-3} aqueous hydrochloric acid solution were determined according to Eqs. (1) and (2):

$$(NH_4)_2B_4O_7\cdot 4H_2O(cr) + 2HCl(aq) + H_2O(l) = 2NH_4Cl(aq) + 4H_3BO_3(aq) \quad (1)$$

$$NH_4B_5O_8\cdot 4H_2O(cr) + HCl(aq) + 3H_2O(l) = NH_4Cl(aq) + 5H_3BO_3(aq) \quad (2)$$

In addition, the enthalpy of solution of NH_4Cl (cr) in the aqueous solution that consisted of approximately 1 mol dm^{-3} aqueous hydrochloric acid and the calculated amount of H_3BO_3(cr) was also determined. Combining with other auxiliary data such as the standard molar enthalpies of formation of NH_4Cl (cr), H_3BO_3 (cr), and H_2O(l), etc., the standard molar enthalpies of formation of $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr) and $NH_4B_5O_8{\cdot}4H_2O$ (cr) could be derived.

The NH_4Cl (mass fraction > 0.999) was recrystallized from analytical grade NH_4Cl (mass fraction > 0.99, PR China) at room temperature, and heated at the temperature 373 K for 4 h, then stored in a desiccator. The H_3BO_3 (mass fraction > 0.9999, PR China) was used without further purification. The HCl standard solution was prepared from azeotropic hydrochloric acid and deionized water, and its concentration was determined by titration with standardized sodium carbonate.

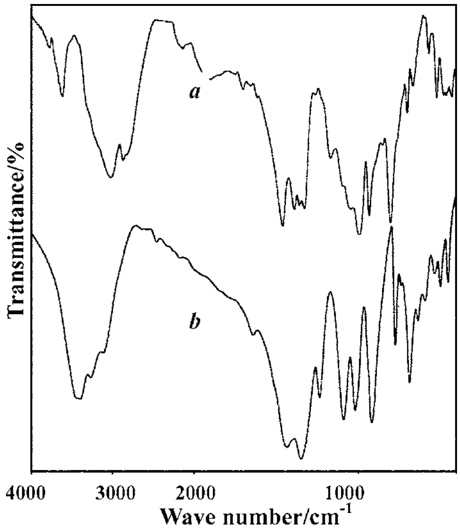

Fig. 1. The FTIR spectra of the synthetic samples *a*: $(NH_4)_2B_4O_7{\cdot}4H_2O$; *b*: $NH_4B_5O_8{\cdot}4H_2O$.

An RD496-III precise heat conduction microcalorimeter (made in the Southwest Institute of Electronic Engineering, PR China) was used for the calorimetric determinations. The equipment was calibrated by the Joule effect. The accuracy and precision of the microcalorimeter were determined by chemical calibration. The temperature of the calorimetric experiments was 298.15 ± 0.05 K. A detailed description of the procedure is given elsewhere [11]. No solid residues were observed in the solution after the calorimetric experiments.

3. Results and discussion

To check the performance of the microcalorimeter, the enthalpy of solution of KCl in deionized water was measured at $T = 298.15$ K. The experimental value 17.24 ± 0.06 kJ mol^{-1} is in excellent agreement with the value 17.241 ± 0.018 kJ mol^{-1} reported in the literature [12]. This result indicated that the device used in this work was reliable.

The molar enthalpies of solution of NH_4Cl (cr) in aqueous (hydrochloric + boric acid) and of the hydrated ammonium borates in approximately 1 mol dm^{-3} aqueous hydrochloric acid solution at $T = 298.15$ K are given in Tables 2 and 3, respectively. Here, *m* denotes the mass of the sample dissolved, *Q* the measured energy change, $\Delta_{sol}H_m$ the molar enthalpy of solution of solute, and the uncertainty is twice the standard deviation. The thermochemical cycles from which the standard molar enthalpies of formation of $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr) and $NH_4B_5O_8{\cdot}4H_2O$ (cr) have been derived are given in Tables 4 and 5. The molar enthalpy of solution of H_3BO_3 (cr) of (21.83 ± 0.08)kJ mol^{-1} in approximately 1 mol dm^{-3} aqueous hydrochloric acid solution was taken from our previous work [4]. The standard molar enthalpies of formation of H_2O(l) and H_3BO_3 (cr) were

Table 2
The molar enthalpy of solution of NH_4Cl (cr) in aqueous (hydrochloric + boric acid) at $T = 298.15$ K[a]

Experimental no.	*m* (mg)	*Q* (mJ)	$\Delta_{sol}H_m$ (kJ mol^{-1})
1	1.07	398.862	19.94
2	1.05	393.749	20.06
3	1.08	403.967	20.01
4	2.63	981.585	19.96
5	2.60	973.019	20.02
6	2.76	1027.452	19.91
Mean			19.98 ± 0.12[b,c]

[a] In each experiment, 2.00 cm^3 of aqueous solution containing HCl (c = 0.9972 mol dm^{-3}, aq.) and approximately 6.16 mg of H_3BO_3 (cr) was used.

[b] Uncertainty is twice the standard deviation.

[c] Molar enthalpy of solution based on a molar mass of 53.491 g mol^{-1} for NH_4Cl.

Table 3
The molar enthalpies of solution of $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr) and $NH_4B_5O_8{\cdot}4H_2O$ (cr) in approximately 1 mol dm^{-3} aqueous hydrochloric acid solution at $T = 298.15$ K[a]

Sample	Experiment no.	m (mg)	Q (mJ)	$\Delta_{sol}H_m$ (kJ mol^{-1})
$(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr)	1	6.50	1174.411	47.59
	2	6.53	1183.440	47.73
	3	6.55	1185.453	47.67
	4	6.52	1184.741	47.86
	5	6.51	1181.576	47.80
	Mean			47.73 ± 0.22[b,c]
$NH_4B_5O_8{\cdot}4H_2O$ (cr)	1	5.40	1315.062	66.28
	2	5.35	1302.454	66.25
	3	5.40	1314.264	66.24
	4	5.38	1310.162	66.27
	5	5.45	1326.033	66.22
	Mean			66.25 ± 0.04[b,c]

[a] In each experiment, 2.00 cm^3 of aqueous solution containing HCl ($c = 0.9972$ mol dm^{-3}, aq.) was used.
[b] Uncertainty is twice the standard deviation.
[c] Molar enthalpies of solution based on the molar mass of 263.377 and 272.149 g mol^{-1} for $(NH_4)_2B_4O_7{\cdot}4H_2O$ and $NH_4B_5O_8{\cdot}4H_2O$, respectively.

Table 4
Thermochemical cycle and results for the derivation of $\Delta_f H^0_m$ $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr), $T = 298.15$ K

Reaction	$\Delta_r H_m$ (kJ mol^{-1})
(1) $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr) + 80.032($HCl{\cdot}54.577H_2O$) = $2NH_4^+$(aq.) + $2Cl^-$(aq.) + $4H_3BO_3$(aq.) + 78.032($HCl{\cdot}55.963H_2O$)	47.73 ± 0.22
(2) $4H_3BO_3$(aq.) + 78.032($HCl{\cdot}55.963H_2O$) = $4H_3BO_3$ (cr) + 78.032($HCl{\cdot}55.963H_2O$)	−87.32 ± 0.32
(3) $2NH_4^+$(aq.) + $2Cl^-$(aq.) + $4H_3BO_3$(aq.) + 78.032($HCl{\cdot}55.963H_2O$) = $2NH_4Cl$ (cr) + $4H_3BO_3$(aq.) + 78.032($HCl{\cdot}55.963H_2O$)	−39.96 ± 0.24
(4) 80.032($HCl{\cdot}55.963H_2O$) = 80.032($HCl{\cdot}54.577H_2O$) + 110.924H_2O(l)	1.99 ± 0.04
(5) H_2(g) + Cl_2(g) + 111.926H_2O(l) = 2($HCl{\cdot}55.963H_2O$)	−330.93 ± 0.20
(6) $2NH_4Cl$ (cr) = N_2(g) + $4H_2$(g) + Cl_2(g)	628.86 ± 0.40
(7) $4H_3BO_3$ (cr) = $6H_2$(g) +$6O_2$(g) + 4B (cr)	4379.20 ± 3.20
(8) H_2(g) + (1/2)O_2(g) = H_2O(l)	−285.83 ± 0.04
(9) $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr) = N_2(g) + $8H_2$(g) + (11/2)O_2(g) + 4B (cr)	4313.74 ±3.26

taken from the CODATA key values for thermodynamics [13] to be (−285.830 ± 0.040) kJ mol^{-1} and (−1094.8 ± 0.8) kJ mol^{-1}, respectively. The standard molar enthalpy of formation of NH_4Cl (cr) was taken from the NBS tables [14]. The standard molar enthalpies of formation of HCl(aq.) in the calculated amount of water and of dilution of it were calculated from the NBS tables. From these values, the standard molar enthalpies of formation $\Delta_f H^0_m$ (298.15 K) of $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr) and $NH_4B_5O_8{\cdot}4H_2O$ (cr) have been derived to be (−4313.74 ± 3.26) and (−4703.56 ± 4.03) kJ mol^{-1}, respectively.

According to the group contribution method [15], the $\Delta_f H^0_m$ or $\Delta_f G^0_m$ of a hydrated borate should be the sum of contributions of the corresponding cations in aqueous solution, of polyborate anions, and of structural water. For a borate $M_a[B_xO_y(OH)_z]{\cdot}nH_2O$, which could be expressed as the following equations:

$$\begin{aligned}&\Delta_f H^0_m(M_a[B_xO_y(OH)_z]\cdot nH_2O, S)\\&\quad = a\,\Delta_f H^0_m(M^{v+}, aq) + \Delta_f H^0_m\{[B_xO_y(OH)_z]^{3x-2y-z}\}\\&\qquad + n\cdot\Delta_f H^0_m(H_2O, 1)\end{aligned} \tag{3}$$

Table 5
Thermochemical cycle and results for the derivation of $\Delta_f H^0_m$ $NH_4B_5O_8{\cdot}4H_2O$ (cr), $T = 298.15$ K

Reaction	$\Delta_r H_m$ (kJ mol^{-1})
(1) $NH_4B_5O_8{\cdot}4H_2O$ (cr) + 100.020($HCl{\cdot}54.577H_2O$) = NH_4^+(aq.) + Cl^-(aq.) + $5H_3BO_3$(aq.) + 99.020($HCl{\cdot}55.098H_2O$)	66.25 ± 0.04
(2) $5H_3BO_3$(aq.) + 99.020($HCl{\cdot}55.098H_2O$) = $5H_3BO_3$ (cr) + 99.020($HCl{\cdot}55.098H_2O$)	−109.15 ± 0.40
(3) NH_4^+(aq.) + Cl^-(aq.) + $5H_3BO_3$(aq.) + 99.020($HCl{\cdot}55.098H_2O$) = NH_4Cl (cr) + $5H_3BO_3$(aq.) + 99.020($HCl{\cdot}55.098H_2O$)	−19.98 ± 0.12
(4) 100.020($HCl{\cdot}55.098H_2O$) = 100.020($HCl{\cdot}54.577H_2O$) + 52.110H_2O(l)	0.95 ± 0.02
(5) (1/2)H_2(g) + (1/2)Cl_2(g) + 55.098H_2O(l) = ($HCl{\cdot}55.098H_2O$)	−165.45 ± 0.10
(6) NH_4Cl (cr) = (1/2)N_2(g) + $2H_2$(g) + (1/2)Cl_2(g)	314.43 ± 0.20
(7) $5H_3BO_3$ (cr) = (15/2)H_2(g) + (15/2)O_2(g) + 5B (cr)	5474.00 ± 4.00
(8) $3H_2$(g) + (3/2)O_2(g) = $3H_2O$(l)	−857.49 ± 0.12
(9) $NH_4B_5O_8{\cdot}4H_2O$ (cr) = (1/2)N_2(g) + $6H_2$(g) + $6O_2$(g) + 5B (cr)	4703.56 ± 4.03

Table 6

Experimental and calculated standard molar enthalpies of formation and standard molar Gibbs free energies of formation of $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr) and $NH_4B_5O_8{\cdot}4H_2O$ (cr) at 295.15 K

Species		$\Delta_f H_m^0/(\mathrm{kJ\,mol^{-1}})$	$\Delta_f G_m^0/(\mathrm{kJ\,mol^{-1}})$
NH_4^+(aq.) [14]		−132.51	−79.31
H_2O(l) [15]		−290.42	−237.28
$[B_4O_5(OH)_4]^{2-}$ [15]		−3464.46	−3095.99
$[B_5O_6(OH)_4]^{-}$ [15]		−3989.97	−3621.73
$(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr)	Calculated	−4310.32	−3729.17
	Experimental	−4313.74	−3724.60 [15]
	Error (%)	0.08	−0.12
$NH_4B_5O_8{\cdot}4H_2O$ (cr)	Calculated	−4703.32	−4175.60
	Experimental	−4703.56	−4173.14 [15]
	Error (%)	0.01	−0.06

$$\begin{aligned}&\Delta_f G_m^0(M_a[B_xO_y(OH)_z]\cdot nH_2O,\ S)\\&\quad = a\,\Delta_f G_m^0(M^{\upsilon+},\ aq) + \Delta_f G_m^0\{[B_xO_y(OH)_z]^{3x-2y-z}\}\\&\qquad + n\cdot\Delta_f G_m^0(H_2O,\ 1)\end{aligned} \tag{4}$$

where x, y, z, a, and n are the stoichiometric coefficients of boron, oxygen, hydroxyl, cation, and structural water in the borate, $\upsilon+$ is the valence of cation. For $(NH_4)_2B_4O_7{\cdot}4H_2O$ and $NH_4B_5O_8{\cdot}4H_2O$, their structural formulas are $(NH_4)_2[B_4O_5(OH)_4]{\cdot}2H_2O$ and $NH_4[B_5O_6(OH)_4]{\cdot}2H_2O$ [2,3], respectively. The thermodynamic parameters are listed in Table 6. It can be seen that the calculated values are in good agreement with experimental results.

Combining with the standard molar enthalpies of formation $\Delta_f H_m^0$ in this work and the standard molar Gibbs free energies $\Delta_f G_m^0$ [15], the standard molar entropies of formation $\Delta_f S_m^0$ of $(NH_4)_2B_4O_7{\cdot}4H_2O$ (cr) and $NH_4B_5O_8{\cdot}4H_2O$ (cr) at 298.15 K have also been calculated to be −1975.99 and −1779.04 $\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively, according to the following equation:

$$\Delta_f S_m^0 = \frac{\Delta_f H_m^0 - \Delta_f G_m^0}{T} \tag{5}$$

And then, the standard molar entropies S_m^0(298.15 K) of (NH4)2B4O7·4H2O (cr) and $NH_4B_5O_8{\cdot}4H_2O$ (cr) were calculated to be 412.79 and 361.00 $\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively, on the basis of the following reactions:

$$\begin{aligned}&N_2(g) + 8H_2(g) + \tfrac{11}{2}O_2(g) + 4B(cr)\\&= (NH_4)_2B_4O_7\cdot 4H_2O(cr)\end{aligned} \tag{6}$$

$$\begin{aligned}&\tfrac{1}{2}N_2(g) + 6H_2(g) + 6O_2(g) + 5B(cr)\\&= NH_4B_5O_8\cdot 4H_2O(cr)\end{aligned} \tag{7}$$

The standard molar entropies of the elements were taken from the NBS tables [14] as 191.61, 130.684, 205.138, and 5.86 $\mathrm{J\,K^{-1}\,mol^{-1}}$ for N_2(g), H_2(g), O_2(g), and B (cr), respectively.

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