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Short communication

Thermochemistry of hydrated rubidium tetraborate

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Abstract

The enthalpies of solution of $Rb_2B_4O_7 \cdot 5.6H_2O$ in approximately $1\,\mathrm{mol\,dm^{-3}}$ aqueous hydrochloric acid and of RbCl in aqueous (hydrochloric acid + boric acid) were determined. From these results and the enthalpy of solution of H_3BO_3 in approximately $1\,\mathrm{mol\,dm^{-3}}$ HCl(aq), the value of the molar enthalpy of formation of $-5023.36 \pm 3.26\,\mathrm{kJ\,mol^{-1}}$ for $Rb_2B_4O_7 \cdot 5.6H_2O$ was obtained by using the values for the standard molar enthalpies of formation of RbCl(s), H_3BO_3(s), and H_2O(l). The standard molar entropy of formation of $Rb_2B_4O_7 \cdot 5.6H_2O$ was calculated from the thermodynamic relation of the standard molar enthalpy of formation with the standard molar Gibbs free energy of formation of $Rb_2B_4O_7 \cdot 5.6H_2O$ computed from a group contribution method.

Keywords: $Rb_2B_4O_7 \cdot 5.6H_2O$; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy of solution; Aqueous hydrochloric acid solution

1. Introduction

Three hydrated rubidium borates, namely, triborate $Rb_3[B_3O_4(OH)_4] \cdot 2H_2O$ [1], tetraborate $Rb_2[B_4O_5(OH)_4] \cdot 3.6H_2O$ [2], and pentaborate $Rb[B_5O_6(OH)_4] \cdot 2H_2O$ [3] have been synthesized and their structural features have been given in the literature. But, there are no reports on standard molar enthalpies of formation of hydrated rubidium borates. In previous papers, Li et al. [4–7] reported the standard molar enthalpies of formation of hydrated magnesium borates, hydrated calcium borates, hydrated lithium borates, hydrated sodium borates and hydrated potassium borates, as well as three hydrated double metal borates (Ulexite ($NaCaB_5O_6(OH)_6 \cdot 5H_2O$) [8], $K_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ [9] and $Rb_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ [10]), and proposed a group contribution method to correlate and predict thermodynamics properties of hydrated borates. In this paper, as part of a systematic study of borates, the standard molar enthalpy of formation $\Delta_f H_m^\circ$ of $Rb_2B_4O_7 \cdot 5.6H_2O$ has been determined by solution calorimetry, and other thermochemical parameters have been calculated.

2. Experimental

Hydrated rubidium tetraborate was obtained from an aqueous solution of Rb_2CO_3 and H_3BO_3 in a mole ratio of $Rb_2O:B_2O_3 = 2:1$. After CO_2 release, the evaporation of the solution at 323.15 K led to the desired compound as a white powder. The product was analyzed by standard methods as follows. Boron was determined by titration with a standard solution of NaOH in the presence of manitol; rubidium was determined as $RbB(C_6H_5)_4$ by a gravimetric method;

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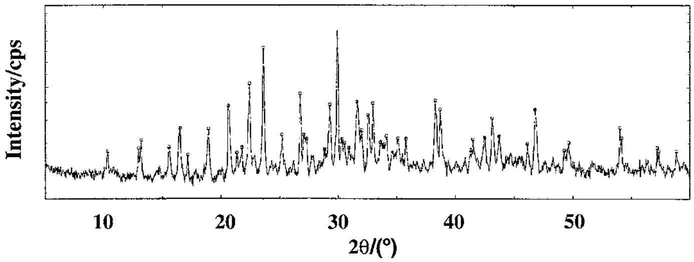

Fig. 1. The X-ray diffraction pattern of $Rb_2B_4O_7{\cdot}5.6H_2O$.

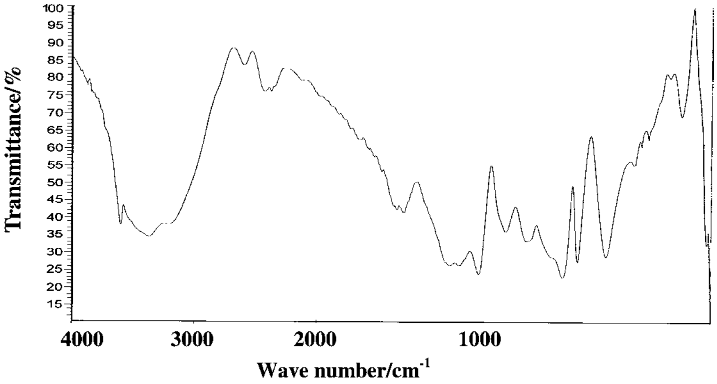

Fig. 2. The infrared spectra of $Rb_2B_4O_7{\cdot}5.6H_2O$.

and H_2O content was determined by thermal dehydration. The powder X-ray diffraction data (Fig. 1) of the synthesized compound was obtained by using a Rigaku DMAX/III diffractometer. The IR spectra (Fig. 2) was recorded in the 4000–400 cm^{-1} region by using a Nicolet NEXUS 670 FT-IR spectrometer with sample in KBr matrix and the Raman spectra (Fig. 3) in the 3600–400 cm^{-1} region by using a Nicolet Almega Dispersine Raman spectrometer. TG and DSC measurements were obtained in a SETARAM TGDTA92, in a flow of N_2 with a heating rate of 10 °C min^{-1}. The analytical data of the compound is given in Table 1. It is shown that the compound obtained is pure and has a general formula $Rb_2B_4O_7{\cdot}5.6H_2O$, being suitable for calorimetric experiment.

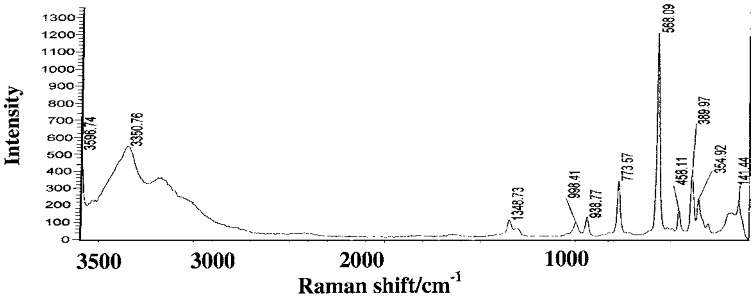

Fig. 3. Raman spectra of $Rb_2B_4O_7{\cdot}5.6H_2O$.

Table 1
The chemical composition of $Rb_2B_4O_7{\cdot}5.6H_2O$ (mass%)

	Rb_2O	B_2O_3	H_2O
Experimental	43.86	32.62	23.52
Calculated	43.78	32.61	23.61

The thermochemical reaction used for obtaining the value of $\Delta_f H_m^\circ$ of $Rb_2B_4O_7{\cdot}5.6H_2O$ was

$$\begin{aligned} &Rb_2B_4O_7 \cdot 5.6H_2O(s) + 2HCl(aq) \\ &\quad = 2RbCl(aq) + 4H_3BO_3(aq) + 0.6H_2O(l) \qquad (1) \end{aligned}$$

The standard molar enthalpy of formation of $Rb_2B_4O_7{\cdot}5.6H_2O$ could be obtained by using $\Delta_r H^\circ$ in combination with the standard molar enthalpies of formation of RbCl(s), H_3BO_3(s), and H_2O(l). The H_3BO_3(s) and $Rb_2B_4O_7{\cdot}5.6H_2O$(s) were dissolved in approximately 1mol dm^{-3} aqueous hydrochloric acid, and the calculated amount of RbCl(s) was dissolved in aqueous (hydrochloric acid + boric acid) which consisted of approximately 1 mol dm^{-3} HCl(aq) and the calculated amount of H_3BO_3.

The potassium chloride (mass fraction > 0.9999) and RbCl (mass fraction > 0.9999), both made in PR China, were heated at $T = 700$ and 873 K during 3 h, respectively, and stored in a desiccator. The boric acid (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 standard borax.

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 298.150 ± 0.005 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.

Table 2
The molar enthalpy of solution $\Delta_{sol}H_m$ of $Rb_2B_4O_7{\cdot}5.6H_2O$ in approximately 1 mol dm^{-1} aqueous hydrochloric acid at T = 298.15 K[a]

Experiment number	m (mg)	$\Delta_{sol}H_m$ (kJ mol^{-1})
1	8.29	55.70
2	8.20	55.73
3	8.25	55.84
4	8.24	55.90
5	8.27	55.61
Mean		55.76 ± 0.23

[a] In each experiment, 2.00 cm^3 of HCl(aq) was used.

Tables 2 and 3 give the results of the calorimetric experiments. In these tables, m is the mass of the sample, $\Delta_{sol}H_m$ is the molar enthalpy of solution of solute, and the uncertainty is twice the standard deviation of the mean. Table 4 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $Rb_2B_4O_7{\cdot}5.6H_2O$. The molar enthalpy of solution of H_3BO_3(s) of 21.83 ± 0.08 kJ mol^{-1} in approximately 1 mol dm^{-1}HCl(aq) was taken from our previous work [4]. The standard molar enthalpies of formation of H_2O(l) and H_3BO_3(s) were taken from the CODATA key values [13], namely, -285.83 ± 0.04 kJ mol^{-1} and -1094.80 ± 0.80 kJ mol^{-1}, respectively. The standard molar enthalpy of dilution of HCl(aq) was calculated and the enthalpies of formation of RbCl(s) and HCl(aq) taken from the NBS tables [14]. Therefore, the standard molar enthalpy

Table 3
The molar enthalpies of solution $\Delta_{sol}H_m$ of RbCl in aqueous (hydrochloric acid + boric acid) at $T = 298.15$ K[a]

Experiment number	m (mg)	$\Delta_{sol}H_m$ (kJ mol^{-1})
1	4.63	18.95
2	4.65	18.92
3	4.68	18.90
4	4.60	18.94
5	4.64	18.88
Mean		18.92 ± 0.06

[a] In each experiment, 2.00 cm^3 of HCl(aq) was used.

Table 4
Thermochemical cycle and results for the derivation of $\Delta_f H_m(Rb_2B_4O_7{\cdot}5.6H_2O$, at $T = 298.15\,K)$

Reaction	$\Delta_r H_m$ (kJ mol^{-1})
(1) $Rb_2B_4O_7{\cdot}5.6H_2O(s) + 104.18(HCl{\cdot}54.530H_2O) = 2Rb^+(aq) + 2Cl^-(aq) + 4H_3BO_3(aq) + 102.18(HCl{\cdot}55.603H_2O)$	55.76 ± 0.23
(2) $4H_3BO_3(aq) + 102.18(HCl{\cdot}55.603H_2O) = 4H_3BO_3(s) + 102.18(HCl{\cdot}55.603H_2O)$	−87.32 ± 0.32
(3) $2Rb^+(aq) + 2Cl^-(aq) + 4H_3BO_3(aq) + 102.18(HCl{\cdot}55.603H_2O) = 2RbCl(s) + 4H_3BO_3(aq) + 102.18(HCl{\cdot}55.603H_2O)$	−37.84 ± 0.12
(4) $104.18(HCl{\cdot}55.603H_2O) = 104.18(HCl{\cdot}54.530H_2O) + 111.785H_2O(l)$	2.22 ± 0.04
(5) $H_2(g) + Cl_2(g) + 111.206H_2O(l) = 2(HCl{\cdot}55.603H_2O)$	−330.86 ± 0.20
(6) $0.6H_2O(l) = 0.6H_2(g) + 0.3O_2(g)$	171.50 ± 0.20
(7) $2RbCl(s) = 2Rb(s) + Cl_2(g)$	870.70 ± 0.40
(8) $4H_3BO_3(s) = 4B(s) + 6H_2(g) + 6O_2(g)$	4379.20 ± 3.20
(9) $Rb_2B_4O_7{\cdot}5.6H_2O(s) = 2Rb(s) + 4B(s) + 5.6H_2(g) + 6.3O_2(g)$	5023.36 ± 3.26

of formation of $Rb_2B_4O_7{\cdot}5.6H_2O(s)$ was calculated as $-5023.36 \pm 3.26\,kJ\,mol^{-1}$. According to a group contribution method developed by Li et al. [15] for the calculation of thermodynamic properties of hydrated borates, the $\Delta_f H_m^\circ$ or $\Delta_f G_m^\circ$ of a hydrated borate should be the sum of the contributions of the corresponding cation in aqueous solution, of the polyborate anion and of liquid water, and could be expressed by Eqs. (2) and (3):

$$\Delta_f H_m^\circ(Rb_2B_4O_7 \cdot 5.6H_2O) = 2\Delta_f H_m^\circ(Rb^+, aq) + \Delta_f H_m^\circ\{[B_4O_5(OH)_4]^{2-}\} + 3.6\Delta_f H_m^\circ(H_2O, l) \quad (2)$$

$$\Delta_f G_m^\circ(Rb_2B_4O_7 \cdot 5.6H_2O) = 2\Delta_f G_m^\circ(Rb^+, aq) + \Delta_f G_m^\circ\{[B_4O_5(OH)_4]^{2-}\} + 3.6\Delta_f G_m^\circ(H_2O, l) \quad (3)$$

we calculated $\Delta_f H_m^\circ$ of $Rb_2B_4O_7{\cdot}5.6H_2O$ to be $-5012.21\,kJ\,mol^{-1}$and $\Delta_f G_m^\circ$ of $Rb_2B_4O_7{\cdot}5.6H_2O$ to be $-4517.80\,kJ\,mol^{-1}$. This $\Delta_f H_m^\circ$ value is in good agreement with the experimental result. The relative error is 0.22%. By using the experimental standard molar enthalpy formation of $Rb_2B_4O_7{\cdot}5.6H_2O$, the standard molar entropy of formation of $Rb_2B_4O_7{\cdot}5.6H_2O(s)$ has been calculated as $-1695.66\,J\,K^{-1}\,mol^{-1}$ according to the following equation:

$$\Delta_f S_m^\circ = \frac{\Delta_f H_m^\circ - \Delta_f G_m^\circ}{T} \quad (4)$$

Otherwise, the standard molar entropy of $Rb_2B_4O_7{\cdot}5.6H_2O$ was calculated to be $504.47\,J\,K^{-1}\,mol^{-1}$ according to the following reaction:

$$Rb_2B_4O_7 \cdot 5.6H_2O(s) = 2Rb(s) + 4B(s) + 5.6H_2(g) + 6.3O_2(g) \quad (5)$$

The standard molar entropies of the elements were taken from CODATA key values as 76.78, 5.90, 130.571, and $205.043\,J\,K^{-1}\,mol^{-1}$ for Rb(s), B(s), $H_2(g)$, and $O_2(g)$, respectively.

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