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Short communication

Thermochemistry of rubidium calcium octaborate dodecahydrate

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Abstract

The enthalpies of solution of $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid and of RbCl in aqueous (hydrochloric acid + boric acid +calcium oxide) were determined. From these result and the enthalpies of solution of H_3BO_3 in approximately 1 mol dm^{-3} HCl (aq), and of CaO in aqueous (hydrochloric acid + boric acid), the standard molar enthalpy of formation of $-10, 308.06 \pm 6.57$ kJ mol^{-1} for $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ was obtained from the standard molar enthalpy of formation of CaO (s), RbCl (s), H_3BO_3 (s) and H_2O (l). The standard molar entropy of formation of $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ was calculated from the thermodynamic relation with the standard molar Gibbs free energy of formation of $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ computed from a group contribution method.

Keywords: $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy of solution; Aqueous hydrochloric acid solution

1. Introduction

Most of hydrated double borates found in nature and synthesized in laboratory contain alkali metals and alkali earth metals, for example, Ulexite [$NaCaB_5O_6(OH)_6{\cdot}5H_2O$], Aristarainite {$Na_2Mg[B_6O_9(OH)_4]_2{\cdot}6H_2O$}, Hydroboracite [$CaMgB_6O_8(OH)_6{\cdot}3H_2O$] and Inderborite {$CaMg[B_3O_3(OH)_5]_2{\cdot}6H_2O$} [1]. Until now, eight kinds of hydrated double metal tetraborates have been synthesized in laboratory among which the structure of six compounds such as $K_{1.67}Na_{0.33}[B_4O_5(OH)_4]{\cdot}3H_2O$, $NaRb[B_4O_5(OH)_4]{\cdot}4H_2O$, $K_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$, $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$, $Rb_2Sr[B_4O_5(OH)_4]_2{\cdot}8H_2O$ and $(NH_4)_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ [2–6] have been established. All compounds contain the $[B_4O_5(OH)_4]^{2-}$ tetraborate anion which is the same that of borax. The rubidium calcium octaborate dodecahydrate $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ was firstly reported in 1981, and it's physicochemical properties have not been presented.

Thermodynamic properties play very important roles in scientific researches and industrial applications. In previous papers, Li et al. [7–10] reported the standard molar enthalpies of formation of hydrated magnesium borates, hydrated calcium borates, hydrated lithium borates, hydrated sodium borates and hydrated potassium borates. Besides, thermodynamic properties of two hydrated double metal borates, namely Ulexite ($NaCaB_5O_6(OH)_6{\cdot}5H_2O$) [11]and $K_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ [12] have also been studied. In this paper, the standard molar enthalpy of

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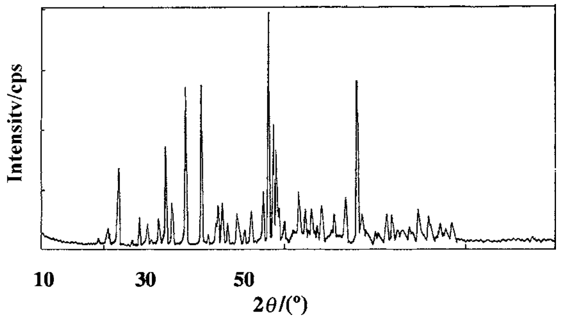

Fig. 1. The XRD of synthetic $Rb_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$.

formation $\Delta_f H_m^\circ$ of $Rb_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ has been determined by solution calorimetry, and other thermochemical parameters have also been calculated.

2. Experimental

All the reagents used in the synthesis were analytic grade. 46.2 g of a Rb_2CO_3 (Jiangxi Lithium Factory, China) and 53.0 g of a H_3BO_3 were dissolved in approximately 300 ml H_2O. After CO_2 release, the above solution was mixed with 23 g of a $CaCl_2$ to form an amorphous precipitate, the mixture was stirred during 20 min at 75 °C and leaving at room temperature. The crystallization begins in a few days. Large single crystals are obtained after 10 days. The prodoct was analyzed according to standard methods as following: calcium was titrated by a standard solution of Na–EDTA in an alkaline condition by the addition of buffer solution (pH = 9.56). 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. H_2O content was determined by thermal dehydration. The powder X-ray diffraction data (Fig. 1) of the synthesized compound was obtained using Rigaku D/MAX-2400 with Cu Kα radiation ($\lambda = 1.5418$ Å). Thermogravimetric analysis (TGA) and DSC were conducted on a NETZSCH-Geratebau STA 449c, in a flow of N_2 with a heating rate of 10 °C min^{-1}. FT-IR spectra (Fig. 2) was recorded in the 4000–400 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer using KBr pellets. The analytical data of the compound are given in Table 1. The data shows that the compound obtained is pure and has the general compound formula $Rb_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$ and it is suitable for calorimetric experiment.

Thermochemical reaction used for getting the derivation of $\Delta_f H_m^\circ$ of $Rb_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$

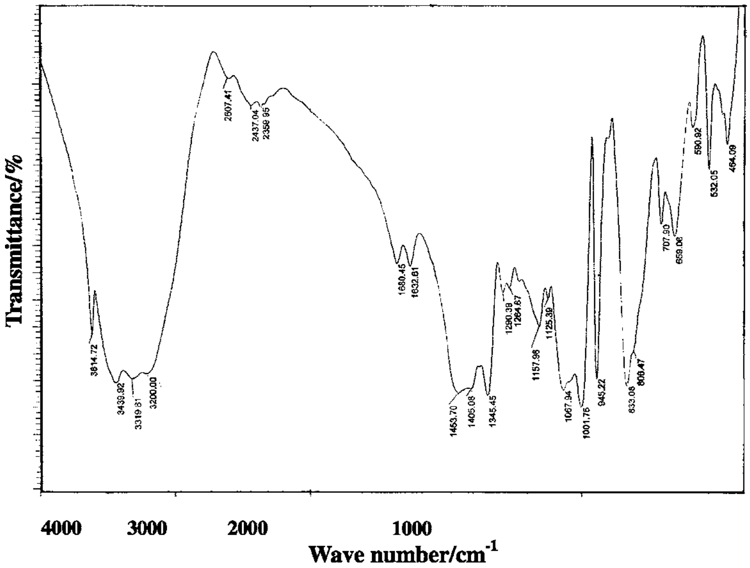

Fig. 2. The FT-IR spectrum of synthetic $Rb_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O$.

Table 1
The chemical composition of $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ (mass%)

	Rb_2O	CaO	B_2O_3	H_2O
Analytical	25.42	7.58	37.81	29.22[a]
Theoretical	25.35	7.60	37.76	29.29

[a] Determined by thermal analysis method.

was:

$$Rb_2Ca[B_4O_5(OH)_4]_2 \cdot 8H_2O(s) + 4HCl(aq) = 2RbCl(aq) + CaCl_2(aq) + 8H_3BO_3(aq) + 2H_2O \quad (1)$$

The standard molar enthalpy of formation of $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of RbCl (s), CaO (s), H_3BO_3 (s) and H_2O (l). The H_3BO_3(s) and $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$ (s) were dissolved in approximately 1 mol dm^{-3} aqueous hydrochloric acid, the calculated amount of CaO (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, and then the calculated amount RbCl was dissolved in the former mixed solution (hydrochloric acid + boric acid + calcium oxide).

High-purity CaO (mass fraction > 0.9999, PR China) was heated at the temperature of 1098 K during 3 h, and stored in a desiccator. The CaO sealed in a glass ampoules inside a box containing P_2O_5 as a drying agent. Before sealing, high-purity Ar gas was admitted to the glove box to expel the air. Both KCl (mass fraction > 0.9999, PR China) and RbCl (mass fraction > 0.9999, PR China) were heated at 700 and 873 K respectively for 3 h and stored in a desiccator. The H_3BO_3 (mass fraction > 0.9999, PR China) was used. 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 Microcalorimeter (Southwest Institute of Electronic Engineering, China) was used. The sensitivity of the instrument was measured through electrical calibration and the accuracy and precision were determined by chemical calibration. The calibration was repeated after each experiment and the average calibration constant was used. The temperature of the calorimetric experiments was 298.15 ± 0.005 K. The experimental data was saved and processed by using a computer. A detailed description is found elsewhere [13]. A glass ampoule containing a sample to be measured, put in the stainless steel reaction cell of the Microcalorimeter and broken after the thermal equilibrium was reached (at least 2 h). The total time required for the complete reaction was about 1 h, depending on the samples. No solid residues were observed in the solution after the calorimetric experiments.

3. Results and discussion

To check the performance of the RD496-III Microcalorimeter, the enthalpy of solution of KCl in deionized water was measured at 298.15 K and the results are listed in Table 2, the experimental value 17.24 ± 0.06 kJ mol^{-1} is in excellent agreement with that of 17.241 ± 0.018 kJ mol^{-1} reported [14]. This indicated that the device used in this work was reliable.

Tables 3 and 4 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 5 gives the thermochemical cycles for the derivation of the standard molar enthalpies of formation of $Rb_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$. The molar enthalpies of solution of H_3BO_3(s) of 21.83 ± 0.08 kJ mol^{-1} in approximately 1 mol dm^{-3} HCl (aq) and of CaO (s) of -188.63 ± 0.88 kJ mol^{-1} in the mixture of HCl and H_3BO_3 were taken from our previous works separately [7,8]. The standard molar enthalpies of formation of H_2O (l), CaO (s), and H_3BO_3 (s) were taken from the CODATA Key

Table 2
The molar enthalpies of solution $\Delta_{sol}H_m$ of KCl in water at 298.15[a]

Number	m (mg)	$\Delta_{sol}H_m$ (kJ mol^{-1})
1	12.02	17.29
2	8.01	17.23
3	13.32	17.25
4	15.02	17.24
5	15.00	17.21
	Mean	17.24 ± 0.06[b]

[a] Determined with an RD496-III Microcalorimeter; in each experiment, 8.00 cm^3 of H_2O (l) was used.

[b] Uncertainty is twice the standard deviation of the mean.

Table 3
The molar enthalpies of solution $\Delta_{\mathrm{sol}} H_{\mathrm{m}}$ of $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ in approximately $1\,\mathrm{mol\,dm^{-1}}$ aqueous hydrochloric acid at $T = 298.15\,\mathrm{K}$[a]

Number	m (mg)	$\Delta_{\mathrm{sol}} H_{\mathrm{m}}$ ($\mathrm{kJ\,mol^{-1}}$)
1	9.16	110.67
2	9.19	110.81
3	9.30	110.61
4	9.17	110.76
5	9.16	110.74
	Mean	110.72 ± 0.16[b]

[a] Determined with an RD496-III Microcalorimeter; in each experiment, $2.00\,\mathrm{cm^3}$ of HCl (aq) was used.

[b] Uncertainty is twice the standard deviation of the mean.

Table 4
The molar enthalpies of solution $\Delta_{\mathrm{sol}} H_{\mathrm{m}}$ of RbCl in aqueous (hydrochloric acid+boric acid + calcium oxide) at $T = 298.15\,\mathrm{K}$[a]

Number	m (mg)	$\Delta_{\mathrm{sol}} H_{\mathrm{m}}$ ($\mathrm{kJ\,mol^{-1}}$)
1	2.98	18.95
2	3.08	18.93
3	3.07	18.94
4	3.06	18.94
5	3.04	18.93
	Mean	18.94 ± 0.02[b]

[a] Determined with an RD496-III Microcalorimeter; in each experiment, $2.00\,\mathrm{cm^3}$ of HCl (aq) was used.

[b] Uncertainty is twice the standard deviation of the mean.

Values [15], namely -285.830 ± 0.04, -643.9 ± 0.9 and $-1094.8 \pm 0.8\,\mathrm{kJ\,mol^{-1}}$, respectively. The standard molar enthalpies of dilution of HCl (aq) were taken from the NBS table [16]; The enthalpies of formation of RbCl (s) and HCl (aq) were taken from the NBS table [16]. Therefore, the standard molar enthalpy of formation of $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ (s) could be calculated and the result is $-10308.06 \pm 6.57\,\mathrm{kJ\,mol^{-1}}$. Applying the group contribution method developed by Li et al. [17] for the calculation of thermodynamic properties of hydrated borates, we calculated $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}$ of the $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ to be $-10297.45\,\mathrm{kJ\,mol^{-1}}$. This value agrees with the experimental result very well. The relative error is 0.10%. Because of no experimental data on $\Delta_{\mathrm{f}} G^{\circ}_{\mathrm{m}}$ of $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ available, we used a group contribution method to calculate $\Delta_{\mathrm{f}} G^{\circ}_{\mathrm{m}}$ of the $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ to be $-9211.72\,\mathrm{kJ\,mol^{-1}}$. Combining with the standard molar enthalpy of formation of $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$, the standard molar entropy of formation of $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ (s) has been calculated as $-3677.14\,\mathrm{J\,K^{-1}\,mol^{-1}}$ according with the following equation:

$$\Delta_{\mathrm{f}} S^{\circ}_{\mathrm{m}} = \left(\frac{\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}} - \Delta_{\mathrm{f}} G^{\circ}_{\mathrm{m}}}{\mathrm{T}}\right)$$

Otherwise, the standard molar entropy of $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ has been calculated to be $797.62\,\mathrm{J\,K^{-1}\,mol^{-1}}$ according to reaction (11) in Table 5. The standard molar entropies of the elements were taken

Table 5
Thermochemical cycles and results for the derivation of $\Delta_{\mathrm{sol}} H_{\mathrm{m}}$ $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$, 298.15 K

Reaction	$\Delta_{\mathrm{sol}} H_{\mathrm{m}}$ ($\mathrm{kJ\,mol^{-1}}$)
1. $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ (s) + 156.73($HCl\cdot 55.828\ H_2O$) = $2Rb^+$(aq) + Ca^{2+}(aq) + $4Cl^-$(aq) + $8H_3BO_3$(aq) + 152.73 ($HCl\cdot 57.303H_2O$)	110.72 ± 0.14
2. $8H_3BO_3$(aq) + 156.73 ($HCl\cdot 55.828\ H_2O$) = $8H_3BO_3$(s) + 156.73($HCl\cdot 55.828H_2O$)	−174.64 ± 0.64
3. Ca^{2+}(aq) + $2Cl^-$(aq) + $8H_3BO_3$(aq) + 154.73 ($HCl\cdot 56.556\ H_2O$) = CaO (s) + $8H_3BO_3$(aq) + 156.73 ($HCl\cdot 55.828\ H_2O$)	188.63 ± 0.88
4. $2Rb^+$(aq) + Ca^{2+}(aq) + $4Cl^-$(aq) + $8H_3BO_3$(aq) + 154.73($HCl\cdot 56.556\ H_2O$) = 2RbCl (s) + Ca^{2+}(aq) + $2Cl^-$(aq) + $8H_3BO_3$(aq) + 154.73($HCl\cdot 56.556\ H_2O$)	−37.88 ± 0.04
5. 152.73($HCl\cdot 57.303\ H_2O$) = 152.73 ($HCl\cdot 56.556\ H_2O$) + $114.089H_2O$ (l)	2.24 ± 0.08
6. H_2(g) + Cl_2(g) + 113.112 H_2O (l) = 2($HCl\cdot 56.556H_2O$)	−330.86 ± 0.20
7. 2RbCl (s) = 2Rb (s) + Cl_2(g)	870.70 ± 0.40
8. CaO (s) = Ca (s) + (1/2) O_2 (g)	634.92 ± 0.90
9. $8H_3BO_3$(s) = 8B (s) + $12H_2$(g) + $12O_2$(g)	8758.40 ± 6.40
10. H_2O (l) = H_2(g) + (1/2)O_2(g)	285.83 ± 0.04
11. $Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$ (s) = 2Rb (s) + Ca (s) + 8B (s) + $12H_2$(g) + $13O_2$(g)	10308.06 ± 6.57

from CODATA Key Values as 76.78, 41.59, 5.90, 130.571, and 205.043 $\mathrm{J\,K^{-1}\,mol^{-1}}$ for Rb(s), Ca (s), B (s), H_2(g), and O_2(g), respectively.

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