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Thermochemistry of dipotassium calcium octaborate dodecahydrate

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Abstract

The enthalpies of solution of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid, and of KCl in aqueous (hydrochloric acid+boric acid+calcium oxide) were determined. Together with the previously determined 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 $-(10308.00\pm6.56)$ kJ mol^{-1} for $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ was obtained from the standard molar enthalpies of formation of CaO(s), H_3BO_3(s), KCl(s), and H_2O(l). The standard molar entropy of formation of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ was calculated from the thermodynamic relation with the standard molar Gibbs free energy of formation of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ computed from the group contribution method.

Keywords: $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy of solution; Aqueous hydrochloric acid solution

1. Introduction

Most of hydrated double borates were synthesized at laboratory. Some of them such as ulexite, inderborite, hydroboracite etc. were found in the nature. These hydrated double borates dissolve incongruently in water when the cations of the double salt are of different groups. This feature can be used to synthesize it's component hydrated borates. Up to now, nine double salt of hydrated borates belong to $Me_2O{\cdot}MO{\cdot}4B_2O_3{\cdot}nH_2O$ (Me is alkali metal cation, M is alkaline earth metal cation, and n 12 or 14) are found. The polyborate anion of all these borates is $[B_4O_5(OH)_4]^{2-}$ which is the same as that of borax. Dipotassium calcium octaborate dodecahydrate, $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ of these hydrated double borates is first one synthesized by Gode [1], and its unit cell data been determined [2], the structure is $K_2Ca[B_4O_5(OH)_4]_2{\cdot}8H_2O$.

Thermodynamic properties play very important roles in scientific researches and industrial applications. Li Jun et al. reported [3–6] the standard molar enthalpies of formation of eight hydrated magnesium borates, five hydrated calcium borates, and some hydrated potassium and sodium borates. They also studied the thermodynamic properties of a hydrated double borates of calcium ulexite [8]. As part of the continuing study of the thermochemistry of hydrated borates and hydrated double borates of calcium, this paper presents the standard molar enthalpies of formation $\Delta_f H_m^0$ of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$.

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2. Experimental

$K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ sample was synthesized at laboratory according to method given in the literature [1]. All the reagents used in synthesis were analytical grade (made in Beijing Chemical Factory, China). 25.0 g KOH, 50.0 g H_3BO_3, and 4.5 g $CaCl_2{\cdot}6H_2O$ were dissolved in approximately 420 ml H_2O. The mixtures in a flask were stirred at room temperature. Crystallization begins in a few days. The solids were separated and washed thoroughly with distilled water, and then with alcohol and ether, finally, dried at room temperature to constant weight. The sample was characterized by chemical analyzed, X-ray powder diffraction (Fig. 1) and FT-IR spectrum (Fig. 2). FT-IR spectrum was recorded on a NICOLET 170SX FT-IR spectrometer with KBr pellets at room temperature; X-ray powder diffraction on Rigaku D/MAX-2400, Ni-filtered, Cu-radiation, and they show the sample is identical to that reported [7]. The composition of the sample is given in Table 1. It is shown that the synthetic sample is pure compound being of formula $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ and suitable for calorimetric experiment. The impurity corrections were unnecessary.

Thermochemical reaction designed for the derivation of $\Delta_f H_m^0$ of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ as follows:

$$\begin{aligned} &K_2O\cdot CaO\cdot 4B_2O_3\cdot 12H_2O(s) + 2HCl(aq) \\ &\quad = CaO(s) + 2KCl(aq) + 8H_3BO_3(aq) \\ &\qquad + H_2O(l). \end{aligned} \tag{1}$$

The standard molar enthalpy of formation of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of CaO(s), H_3BO_3(s), KCl(s), and H_2O(l). The solution calorimetric procedure used here is similar to that used in our previous paper [8]. The H_3BO_3(s) and $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ were dissolved in approximately 1 mol dm^{-3} aqueous hydrochloric acid, the stoichiometric amount of substance 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 substance of H_3BO_3, and then the stoichiometric amount KCl was dissolved in the former mixed solution (hydrochloric acid+boric acid+calcium oxide). The temperature of the calorimetric experiments was (298.15±0.005) K.

Table 1
The chemical composition of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ (mass %)

	K_2O	CaO	B_2O_3	H_2O
Analytical	14.59	8.70	43.19	33.52
Theoretical	14.61	8.70	43.19	33.50

In the previous paper, we have carried out the determination on the enthalpy of solution of H_3BO_3(s) in HCl(aq), and CaO(s) in aqueous ($HCl+H_3BO_3$). In this paper, we only determine $\Delta_{sol}H_m$ of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ in HCl(aq) and of KCl in aqueous ($HCl+H_3BO_3+CaO$). The KCl (mass fraction>0.9995, produced by China) was heated at the temperature 700 K for 2 h and stored in a desiccator. The HCl solvent was prepared from analytical grade hydrochloric acid and deionized water, and its concentration was determined by titration with standard sodium carbonate.

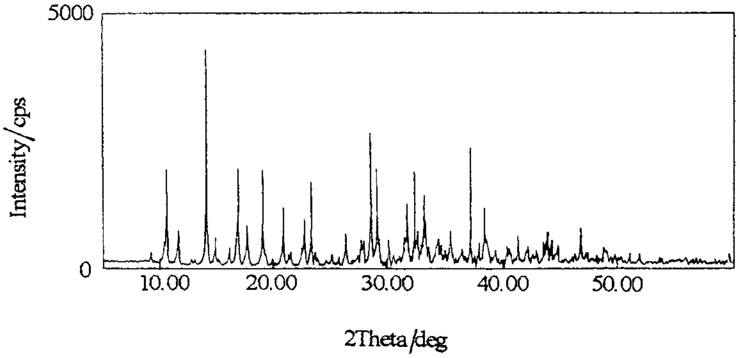

Fig. 1. The XRD of synthetic $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$: *X*-axis label -2θ in degrees; *Y*-axis label-Intensity.

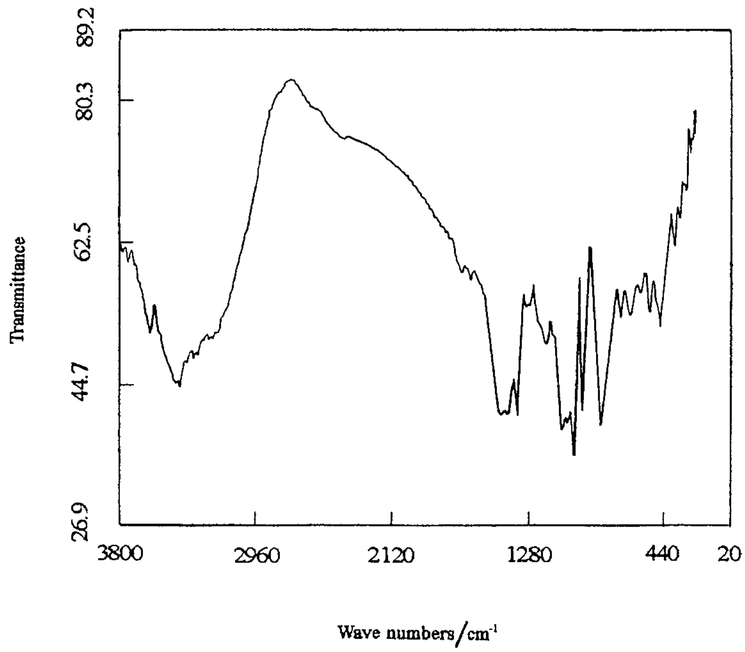

Fig. 2. The FT-IR spectrum of synthetic $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$: X-axis label-Wave number in cm^{-1}; Y-axis label-Transmittance in %.

An LKB 8700 precision calorimeter were used, and have been described in detail previously [3]. The calibrations were repeated after each experiment, and the average calibration constant was used. There were no solid residues observed after the reactions in each calorimetric experiment.

3. Results and discussion

Tables 2 and 3 present the results of the calorimetric experiments. In these tables, m is the mass of 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 enthalpies of formation of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$. The additive of CaO(s) of 6.25×10^{-4} mol into the aqueous ($HCl+H_3BO_3$) has very little influence on the enthalpy of solution of KCl in aqueous ($HCl+H_3BO_3+CaO$) compared with that in aqueous ($HCl+H_3BO_3$). The molar enthalpies of solution of H_3BO_3(s) of (21.83±0.08) kJ mol^{-1} in approximately

Table 2
The molar enthalpies of solution $\Delta_{sol}H_m$ of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid at T=298.15 K[a]

No.	m (mg)	$\Delta_{sol}H_m$ (kJ mol^{-1})
1	402.1	87.68
2	402.7	87.69
3	402.5	87.75
4	403.3	87.65
5	402.0	87.75
	Mean	87.70±0.04[b]

[a] Determined with an LKB precision calorimeter; in each experiment, 100.10 cm^3 of HCl(aq) was used.
[b] Uncertainty is twice the standard deviation of the mean.

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

No.	m (mg)	$\Delta_{sol}H_m$ (kJ·mol^{-1})
1	93.6	17.73
2	93.5	17.73
3	93.4	17.47
4	93.0	17.73
5	93.4	17.75
	Mean	17.68±0.11[b]

[a] Determined with an LKB precision calorimeter; in each experiment, 100.10 cm^3 of HCl(aq) was used.
[b] Uncertainty is twice the standard deviation of the mean.

Table 4
Thermochemical cycles and results for the derivation of $\Delta_f H_m^0$ $K_2O.CaO.4B_2O_3.12H_2O$, 298.15 K

Reaction	$\Delta_r H_m$ (kJ mol^{-1})
1. $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O(s)+159.29(HCl{\cdot}54.688H_2O) = 2K^+(aq)+Ca^{2+}(aq)+4Cl^-(aq)+8H_3BO_3(aq)$ $+155.29(HCl{\cdot}56.110H_2O)$	87.70±0.04
2. $8H_3BO_3(aq)+157.29(HCl{\cdot}55.390H_2O)=8H_3BO_3(s)+157.29(HCl{\cdot}55.390H_2O)$	−174.64±0.64
3. $Ca^{2+}(aq)+2Cl^-(aq)+8H_3BO_3(aq)+155.29(HCl{\cdot}56.110H_2O)=CaO(s)+8H_3BO_3(aq)+157.29(HCl{\cdot}55.390H_2O)$	188.63±0.88
4. $2K^+(aq)+Ca^{2+}(aq)+4Cl^-(aq)+8H_3BO_3(aq)+155.29(HCl{\cdot}56.110H_2O)=2KCl(s)+Ca^{2+}(aq)+2Cl^-(aq)$ $+8H_3BO_3(aq)+155.29(HCl{\cdot}56.110H_2O)$	−17.68±0.11
5. $159.29(HCl{\cdot}55.390H_2O)=159.29(HCl{\cdot}54.688H_2O)+111.821H_2O(l)$	2.21±0.08
6. $H_2(g)+Cl_2(g)+110.821H_2O(l)=2(HCl{\cdot}55.390H_2O)$	−330.86±0.20
7. $2KCl(s)=2K(s)+Cl_2(g)$	873.49±0.20
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. $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O(s)=2K(s)+Ca(s)+8B(s)+12H_2(g)+13O_2(g)$	10308.00±6.56

1 mol dm^{-3} HCl(aq), and of CaO(s) Of −(188.83±0.88) kJ mol^{-1} in the mixture of HCl and H_3BO_3 were taken from our previous works separately [4]. The standard molar enthalpies of formation of $H_2O(l)$, CaO(s), and $H_3BO_3(s)$ were taken from the CODATA Key Values [9], namely −(285.830±0.040), −(634.9±0.90), and −(1094.8±0.8) kJ mol^{-1}, respectively. The enthalpies of dilution of HCl (aq) were calculated from the NBS tables [10]; The standard molar enthalpies of formation of KCl(s), and HCl(aq) were taken from the NBS tables [10]. Therefore, the standard molar enthalpy of formation of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ could be calculated and the result is −(10308.00±6.56) kJ mol^{-1}. Applying the group contribution method developed by Li Jun et al. [11] for the calculation of thermodynamic properties of hydrated borated, we calculated the $\Delta_f H_m^0$ of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ to be −10299.87 kJ mol^{-1}. This value agrees with the experimental result very well. The relative error is 0.08%. Because of no experimental data on $\Delta_f G_m^0$ of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}$ $12H_2O$ available, we used the group contribution method to calculate $\Delta_f G_m^0$ of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ to be −9210.28 kJ mol^{-1}. Combining the standard molar enthalpy of formation of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}$ $12H_2O$, the standard molar entropy of formation of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ has been calculated at −3681.77 J K^{-1} mol^{-1} according to following equation:

$$\Delta_f S_m^0 = (\Delta_f H_m^0 - \Delta_f G_m^0)/T. \tag{2}$$

Finally, the standard molar entropy of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ has been calculated to be 768.79 J K^{-1} mol^{-1} according to reaction (11) in Table 4. The standard molar entropies of the elements were taken from CODATA Key Values as 64.68, 41.59, 5.90, 130.571, and 205.043J K^{-1} mol^{-1} for K(s), Ca(s), B(s), $H_2(g)$, and $O_2(g)$, respectively.

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