

Thermochemistry of Dipotassium Magnesium Dodecaborate Decahydrate

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Abstract: The enthalpies of solution of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ in approximately $1\text{ mol} \cdot \text{dm}^{-3}$ aqueous hydrochloric acid, and of KCl in aqueous (hydrochloric acid + boric acid + magnesium oxide) were determined. Together with the previously determined enthalpies of solution of H_3BO_3 in approximately $1\text{ mol} \cdot \text{dm}^{-3}\text{HCl(aq)}$, and of MgO in aqueous (hydrochloric acid + boric acid), the standard molar enthalpy of formation of $-(12250.35 \pm 9.68)\text{ kJ} \cdot \text{mol}^{-1}$ for $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ was obtained from the standard molar enthalpies of formation of $MgO(s)$, $H_2BO_3(s)$, $KCl(s)$, and $H_2O(l)$. The standard molar entropy of formation of $-3848.23\text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and standard molar entropy of $765.96\text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ were calculated from the thermodynamic relations.

Key words: Dipotassium magnesium dodecaborate decahydrate; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy of solution; Aqueous hydrochloric acid solution

CLC number: O645.11 Document code: A Article ID: 1008-858X(2001)04-0041-07

1 Introduction

Besides lots of single metal borates found in nature and synthesized in laboratory, there are many double metal borates, mostly consisted of alkali and alkaline earth metals or alkaline earth and alkaline earth metals^[1]. These double metal borates could be triborates, tetraborates, pentaborates, and hexaborates, f. e. triborate $MgO \cdot CaO \cdot 3B_2O_3 \cdot 11H_2O$ (indorborite) tetraborate, $K_2O \cdot CaO \cdot 4B_2O_3 \cdot$

$12H_2O$, $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$ (ulexite pentaborate). In former series papers of the thermochemistry of hydrated borates^[2-9], we reported the standard molar enthalpies of hydrated alkali and alkaline earth metals borates and two kinds of double metal borates ulexite and $K_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$, and proposed a group contribution method to correlate and predict thermodynamic properties of hydrated borates. In this paper, we present the standard molar enthalpy of formation $\Delta_f H_m^0$ for $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$. There are several double potassium and magnesium borates^[1,10]. Possibly, $K_2O \cdot MgO \cdot 3B_2O_3 \cdot 9H_2O$ and $K_2O \cdot MgO \cdot 3B_2O_3 \cdot 15H_2O$ are tri-

收稿日期: 2001-04-23

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borates, $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ and $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 15H_2O$ are hexaborates, while kaliborite is a more complicated borate. By comparing IR spectrum of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ with that of $MgO \cdot 3B_2O_3 \cdot 7.5H_2O$, Gode^[10] assumed that $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ is a kind of hexaborates and assigned its structure to be $K_2Mg[B_6O_7(OH)_6]_2 \cdot 4H_2O$. There is no report on the standard molar enthalpy of formation $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ in the literature.

2 Experimental

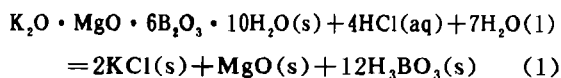
The sample $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$, used in this work was synthesized in laboratory according to the method in the literature^[10]. All the reagents used in synthesis were analytical grade (made in P. R. China). 19.6 g KOH, 53.4 g H_3BO_3 , and 66.8 g KCl were dissolved in approximately 211 cm³ of H_2O ; 213.6 g $MgCl_2 \cdot 6H_2O$ was dissolved in 106.8 cm³ of H_2O , then these two solutions were mixed, transferred into a flask, and stirred at 75°C. Drystallization began after a few days. The solids were separated after 15 days, and washed thoroughly with distilled water then with acetone, and dried at room temperature to constant weight finally. The sample was characterized by chemical analysis (Table. 1), X-ray powder diffraction (Fig. 1), FT-IR spectroscopy (Fig. 2), and thermal analysis. The X-ray powder diffraction was recorded on a Rigaku D/MAX-B with Ni-filtered and Cu-radiation, FT-IR spectrum on a NICOLET MAGNA-IR 760 spectrometer with KBr pellets, and thermal analysis on a TA Instrument 2100 with the heating rate of 0.17K · s⁻¹ at the N₂ flow rate of 2.33cm³ · s⁻¹. Except for a little difference in X-ray powder diffraction with that

reported by Gode^[10], the IR spectrum of our sample is as the same as that by Gode. We think the synthesized sample is a pure compound being of formula of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$, and suitable for calorimetric experiment from all physical and chemical characterizations. There was no need for impurity corrections.

Thermochemical reaction designed for the derivation of $\Delta_f H_m^\circ$ of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ as follows:

Table 1 The chemical composition of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ (mass %)

	K ₂ O	MgO	B ₂ O ₃	H ₂ O
theoretical	13.04	5.64	56.15	25.17
determined	12.86	5.50	57.04	24.60



The standard molar enthalpy of formation of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of $MgO(s)$, $H_3BO_3(s)$, $KCl(s)$, and $H_2O(l)$. The solution calorimetric procedure used here is similar to that in our previous paper^[6]. The H_3BO_3 and $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ were dissolved in approximately 1 mol · dm⁻³ aqueous hydrochloric acid, the stoichiometric amount of substance of $MgO(s)$ 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 + magnesium oxide). The temperature of the calor-

imetric experiments was $(298.15 \pm 0.005)\text{K}$.

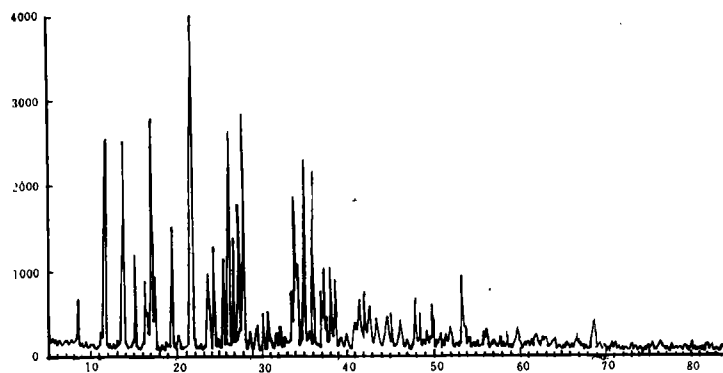


Fig. 1 The XRD of synthetic $\text{K}_2\text{O} \cdot \text{MgO} \cdot 6\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$

X—axis label: $2\theta/\text{degree}$

Y—axis label: Intensity

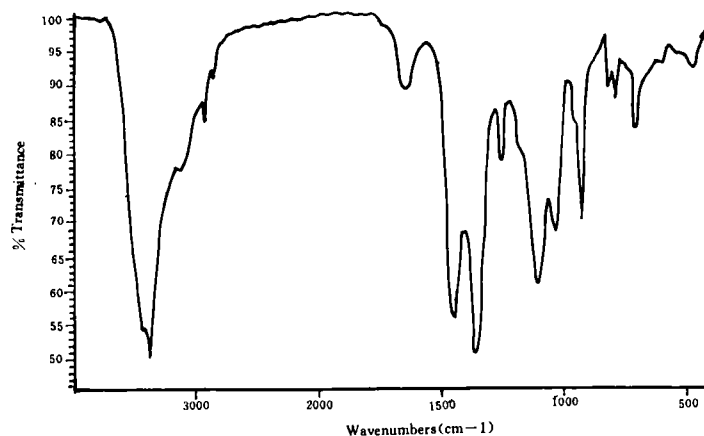


Fig. 2 The FT—IR spectrum of synthetic $\text{K}_2\text{O} \cdot \text{MgO} \cdot 6\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$

X—axis label: Wavenumber/ cm^{-1}

Y—axis label: Transmittance

In the previous paper, We have carried out the determination on the enthalpy of solution of H_3BO_3 in $\text{HCl}(\text{aq})$, and $\text{MgO}(\text{s})$ in aqueous $(\text{HCl} + \text{H}_3\text{BO}_3)^{[2]}$. Here, we only determine $\Delta_{\text{sol}} H_m$ of KCl in aqueous $(\text{HCl} + \text{H}_3\text{BO}_3 + \text{MgO})$ and of $\text{K}_2\text{O} \cdot \text{MgO} \cdot 6\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ in aqueous hydrochloric acid. The KCl (mass fraction > 0.9995 , made in P. R. China) was heated at the temperature 700 K for 2 h and stored in a desic-

cator. Analytical grade HCl and deionized water were used for preparation of the solvent, and its concentration was determined by titration to standardized sodium carbonate.

An LKB 8700 precision calorimetric system was used, and as described in detail previously^[2]. The calibrations were repeated after each experiment. No solid residues was found after the reactions in any of the calorim-

etric experiments.

3 Results and discussion

Figure 2 is the FT-IR spectrum of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$. Actually, this spectrum is very similar to that of $MgO \cdot 3B_2O_3 \cdot 7.5H_2O$ ^[11]. Gode's assignment that $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ is a kind of hexaborates is reasonable, and we adopted his assignment. The most possible structure of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ should be $K_2Mg[B_6O_7(OH)_8]_2 \cdot 4H_2O$.

Tables 2 and 3 present the results of the calorimetric experiments. In these tables, m is the mass of sample, $\Delta_{sol}H_m$ the molar enthalpy of solution of solute, and the uncertainty twice the standard deviation of the mean. Table 4 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$. The addition of $MgO(s)$ of 4.17×10^{-4} mole into the aqueous ($HCl + H_3BO_3$) has little influence on the enthalpy of solution of KCl compared with that in aqueous ($HCl + H_3BO_3$)^[4]. The molar enthalpies of solution of $H_3BO_3(s)$ of $(21.83 \pm 0.08) \text{ kJ} \cdot \text{mol}^{-1}$ in approximately $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl(aq)}$, and of $MgO(s)$ of $-(146.20 \pm 0.36) \text{ kJ} \cdot \text{mol}^{-1}$ in the mixture of HCl and H_3BO_3 were taken from our previous works separately^[2]. The enthalpy of dilution of $HCl(aq)$ was calculated from NBS tables^[12]. The standard molar enthalpies of formation of $-(285.830 \pm 0.040) \text{ kJ} \cdot \text{mol}^{-1}$ for $H_2O(l)$, of

$-(601.60 \pm 0.30) \text{ kJ} \cdot \text{mol}^{-1}$ for $MgO(s)$ and of $-(1094.8 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ for $H_3BO_3(s)$ were taken from the CODATA Key Values^[13]

The standard molar enthalpy of formation of $HCl(aq)$ was calculated from the NBS tables^[14]. Thus the standard molar enthalpy of formation of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ could be calculated and the result is $-(12250.35 \pm 9.68) \text{ kJ} \cdot \text{mol}^{-1}$. Applying the group contribution method developed by Li^[9] for the calculation of thermodynamic properties of hydrated borates, we calculated the $\Delta_f H_m^0$ of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ to be $-12051.91 \text{ kJ} \cdot \text{mol}^{-1}$. This value agrees with the experimental result quite well. This calculation gives the additional support for the structural assignment of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$. Because of no experimental data on $\Delta_f G_m^0$ of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ available, we used the group contribution method to calculate it to be $-11103 \text{ kJ} \cdot \text{mol}^{-1}$. Combining the standard molar enthalpy of formation of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$, the standard molar entropy of formation of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ has been calculated at $-3848.23 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Finally, the standard molar entropy of $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ of $765.96 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was obtained according to reaction (11) in Table 4. The standard molar entropies of the elements were taken from CODATA Key Values^[13] as $64.68, 32.67, 5.90, 130.571$, and $205.043 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $K(s)$, $Mg(s)$, $B(s)$, $H_2(g)$, and $O_2(g)$, respectively.

Table 2 The molar enthalpies of solution $\Delta_{\text{sol}}H_{\text{m}}$ of KCl in aqueous ($\text{HCl} + \text{H}_3\text{BO}_3 + \text{MgO}$) at $T = 298.15\text{K}$

No.	m/mg	$\Delta_{\text{sol}}H_{\text{m}}/(\text{kJ} \cdot \text{mol}^{-1})$
1	62.1	20.14
2	64.0	20.41
3	61.7	20.51
4	63.2	20.40
5	62.8	20.18
Mean		20.33 ± 0.14^a

^a Uncertainty is twice the standard derivation of the mean.

Table 3 The molar enthalpies of solution $\Delta_{\text{sol}}H_{\text{m}}$ of $\text{K}_2\text{O} \cdot \text{MgO} \cdot 6\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ in approximately $1 \text{ mol} \cdot \text{dm}^{-3}$ aqueous hydrochloric acid at $T = 298.15\text{K}$

No.	m/mg	$\Delta_{\text{sol}}H_{\text{m}}/(\text{kJ} \cdot \text{mol}^{-1})$
1	303.2	123.71
2	313.3	124.01
3	306.4	123.11
4	311.1	124.45
5	307.2	123.33
Mean		123.72 ± 0.48^a

^a Uncertainty is twice the standard derivation of the mean.

Table 4 Thermochemical cycles and results for the derivation of $\Delta_f H_m^\circ$ ($K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$, 298.15K)

Reaction	$\Delta_f H_m^\circ / (kJ \cdot mol^{-1})$
1. $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O(s) + 242(HCl \cdot 54.105H_2O) = 2K^+(aq) + Mg^{2+}(aq) + 4Cl^-(aq) + 12H_3BO_3(aq) + 238(HCl \cdot 54.989H_2O)$	123.72 ± 0.48
2. $12H_3BO_3(aq) + 240(HCl \cdot 54.527H_2O) = 12H_3BO_3(s) + 240(HCl \cdot 54.527H_2O)$	-261.96 ± 0.96
3. $Mg^{2+}(aq) + 2Cl^-(aq) + 12H_3BO_3(aq) + 238(HCl \cdot 54.989H_2O) = MgO(s) + 12H_3BO_3(aq) + 240(HCl \cdot 54.527H_2O)$	146.20 ± 0.36
4. $2K^+(aq) + 2Cl^-(aq) + 12H_3BO_3(aq) + Mg^{2+}(aq) + 2Cl^-(aq) + 238(HCl \cdot 54.989H_2O) = 2KCl(s) + Mg^{2+}(aq) + 12H_3BO_3(aq) + 238(HCl \cdot 54.989H_2O)$	-40.66 ± 0.28
5. $242(HCl \cdot 54.527H_2O) = 242(HCl \cdot 54.105H_2O) + 102.124H_2O(l)$	2.01 ± 0.08
6. $H_2(g) + Cl_2(g) + 109.054H_2O(l) = 2(HCl \cdot 54.527H_2O)$	-330.84 ± 0.20
7. $2KCl(s) = 2K(s) + Cl_2(g)$	873.49 ± 0.20
8. $12H_3BO_3(s) = 12B(s) + 18H_2(g) + 18O_2(g)$	13137.6 ± 9.6
9. $MgO(s) = Mg(s) + 1/2O_2(g)$	601.60 ± 0.30
10. $7H_2(g) + 7/2O_2(g) = 7H_2O(l)$	-2000.81 ± 0.28
11. $(K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O(s) = 2K(s) + Mg(s) + 12B(s) + 10H_2(g) + 15O_2(g)$	12250.35 ± 9.68

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$K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ 的热化学研究

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摘要: 在大约 $1 \text{ mol} \cdot \text{dm}^{-3}$ 的盐酸水溶液中测定了 $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ 的溶解焓。结合已获得的其它热化学数据, 得出 $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$ 的标准摩尔生成焓为 $-(12250.35 \pm 9.68) \text{ kJ} \cdot \text{mol}^{-1}$, 并利用“基团贡献法”计算出标准摩尔吉布斯自由能为 $-11103 \text{ kJ} \cdot \text{mol}^{-1}$ 。从而计算出其标准摩尔生成熵和标准摩尔焓。

关键词: $K_2O \cdot MgO \cdot 6B_2O_3 \cdot 10H_2O$; 标准摩尔生成焓; 溶液量热法; 摩尔溶解焓; 盐酸水溶液