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Thermodynamic properties of microporous crystals for two hydrated borogermanates, $K_2[Ge(B_4O_9)]\cdot 2H_2O$ and $K_4[B_8Ge_2O_{17}(OH)_2]$

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ABSTRACT

Two pure hydrated borogermanates for microporous crystals, $K_2[Ge(B_4O_9)]\cdot 2H_2O$ and $K_4[B_8Ge_2O_{17}(OH)_2]$, have been synthesized and characterized by single X-ray diffraction, XRD, FT-IR, and TG techniques. The molar enthalpies of solution of $K_2[Ge(B_4O_9)]\cdot 2H_2O$(s) and $K_4[B_8Ge_2O_{17}(OH)_2]$(s) samples in 1 mol · dm^{-3} NaOH (aq) were measured, respectively. The molar enthalpies of solution of $K_2B_4O_7\cdot 4H_2O$(s) in NaOH (aq), and of GeO_2(s) in the mixture of (NaOH + $K_2B_4O_7\cdot 4H_2O$) (aq) were determined by microcalorimeter at T = 298.15 K, respectively. From these results, the enthalpy changes of (16.28 ± 0.29) kJ · mol^{-1} for the formation of $K_2[Ge(B_4O_9)]\cdot 2H_2O$ and (38.81 ± 0.42) kJ · mol^{-1} for the formation of $K_4[B_8Ge_2O_{17}(OH)_2]$ from the reagents in the solid phase were calculated on the basis of the thermochemical cycles. With the use of the standard molar enthalpies of formation for $K_2B_4O_7\cdot 4H_2O$(s), GeO_2(s) and H_2O(l), the values of the standard molar enthalpies of formation of −(4560.8 ± 3.4) kJ · mol^{-1} for $K_2[Ge(B_4O_9)]\cdot 2H_2O$ and −(8257.9 ± 6.8) kJ · mol^{-1} for $K_4[B_8Ge_2O_{17}(OH)_2]$ at 298.15 K were obtained respectively.

1. Introduction

Microporous materials have attracted considerable attention due to their widespread applications in catalysis, ion exchange, and adsorption [1]. Because of the flexible coordination geometries for Ge and B atoms, and the ability to form (Ge + O) and (B + O) clusters, the (B + Ge + O) system is the souse of searching for microporous materials. Until now, many borogermanates have been synthesized, some of which possessed open framework structures and might be used as microporous materials, such as $K_2[Ge(B_4O_9)]\cdot 2H_2O$ [2] and $K_4[B_8Ge_2O_{17}(OH)_2]$ [3].

Thermodynamic properties play very important roles in scientific research and industrial applications. Thermochemical data can provide information on stabilities and reactivities of molecules that are used, and also are a key factor in the safe and successful scale-up of chemical processes in the chemical industry. The Navrotsky group has done much work on the thermochemistry of microporous compounds such as zeolites, pure silica, gallosilicate, and aluminophosphates by using high-temperature calorimetry [4]. Recently, our group reported the determination of standard molar enthalpies of formation of several boron-containing microporous compounds for borophosphates and aluminoborates by using a heat conduction microcalorimeter [5–7].

However, the investigation of the thermodynamic properties of the microporous materials for borogermanates was not reported in the literature. This paper reports the determination of standard molar enthalpies of formation of two hydrated borogermanates of $K_2[Ge(B_4O_9)]\cdot 2H_2O$ and $K_4[B_8Ge_2O_{17}(OH)_2]$ determined by using a heat conduction microcalorimeter.

2. Experimental

2.1. Synthesis and characterization of samples

The $K_2[Ge(B_4O_9)]\cdot 2H_2O$ and $K_4[B_8Ge_2O_{17}(OH)_2]$ samples were synthesized referring to literature [2,3], and all reagents and solvents employed in the synthesis were commercially available and used without further purification. Table 1 summarizes relevant information on sample material purities.

A single crystal sample of $K_2[Ge(B_4O_9)]\cdot 2H_2O$ was synthesized referring to literature [2]. In a typical synthesis, 0.104 g of GeO_2 was added to a stirring colourless solution of water (0.5 cm^3) and diethylenetriamine (0.5 cm^3). After a few minutes, 0.30 g of $K_2B_4O_7\cdot 4H_2O$ was then added to the above mixture, and this mixture continued stirring for 4 h. The final mixture was heated in a Teflon-lined stainless steel autoclave at 170 °C for 7 days under constant pressure, and then cooled to room temperature.

The colourless crystal of $K_4[B_8Ge_2O_{17}(OH)_2]$ sample was synthesized according to the literature [3]. In a typical synthesis, the autoclave was charged with a mixture of $K_2B_4O_7\cdot 4H_2O$ (0.78 g) and GeO_2 (0.26 g), which was heated at 240 °C for 6 days, then cooled to room temperature.

The two kinds of colourless crystals that resulted were washed with distilled water, and dried in air at ambient temperature, which were characterized by single X-ray diffraction (recorded

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TABLE 1
Chemical samples used in this study.

Chemical name	Source	State	Initial mole fraction
$K_2B_4O_7{\cdot}4H_2O$	Sinopharm Chemical Reagent Co., Ltd	Solid	0.995
GeO_2	Sinopharm Chemical Reagent Co., Ltd.	Solid	0.9999
Diethylenetriamine	Sinopharm Chemical Reagent Co., Ltd.	Liquid	⩾0.98

by a CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.34.36 CCD automatic diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.071073$ nm)), X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target at $8^\circ \cdot min^{-1}$), FT-IR spectroscopy (recorded over the (400 to 4000) cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellet at room temperature), and TG (performed on a TA-SDT Q600 simultaneous thermal analyzer under N_2 atmosphere with a heating rate of $10\ K \cdot min^{-1}$).

2.2. Calorimetric experiment

The $K_2[Ge(B_4O_9)]{\cdot}2H_2O$ and $K_4[B_8Ge_2O_{17}(OH)_2]$ can be regarded as the product of the reaction (5) in the designed thermochemical cycle (Figure 1).

The 1 mol · dm^{-3} NaOH (aq) solvent dissolves all components of the reaction (5), and its concentration of 1.0210 mol · dm^{-3} was determined by titration with standard HCl(aq). With the use of its density of 1.042 g · cm^{-3}, its concentration can also be expressed as the form of $NaOH{\cdot}54.476H_2O$. The molar enthalpies of solution of $K_2[Ge(B_4O_9)]{\cdot}2H_2O$(s), $K_4[B_8Ge_2O_{17}(OH)_2]$(s), $K_2B_4O_7{\cdot}4H_2O$(s) and GeO_2(s) in corresponding solvents were measured, respectively. In all these determinations, strict control of the stoichiometries in each step of the calorimetric cycle must be observed, with the objective that the dissolution of the reactants give the same composition as those of the products.

In order to check whether the designed thermochemical cycles (Figure 1) are reasonable, the solutions obtained from the dissolution of the reactants and products in the reaction (5) in corresponding solvents were characterized by UV–Vis spectrophotometer (Shimadzu UV-1700).

Applying Hess's law, the $\Delta_r H_m^o$ (5) can be calculated according to the following expression:

$$\Delta_r H_m^\circ(5) = \Delta_r H_m^\circ(1) + \Delta_r H_m^\circ(2) - \Delta_r H_m^\circ(3) - \Delta_r H_m^\circ(4) \quad (1)$$

The standard molar enthalpies of formation of $K_2[Ge(B_4O_9)]{\cdot}2H_2O$(s) and $K_4[B_8Ge_2O_{17}(OH)_2]$(s) can be obtained by the values of $\Delta_r H_m^o$ (5) in combination with the standard molar enthalpies of formation of $K_2B_4O_7{\cdot}4H_2O$(s), and GeO_2(s), and H_2O(l).

All the enthalpies of solution were measured with a RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., LTD, China), which has been described in detail previously [8]. The total time required for the complete dissolution reaction was about 0.5 h. There were no solid residues observed after the reactions in each calorimetric experiment.

To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction ⩾ 0.9999) in deionised water was determined to be (17.54 ± 0.10) kJ · mol^{-1}, which is in agreement with that of (17.524 ± 0.028) kJ · mol^{-1} reported in the literature [9]. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

3. Results and discussion

3.1. Characterization of synthetic samples

The synthesized single crystal sample of $K_2[Ge(B_4O_9)]{\cdot}2H_2O$ crystallized in the monoclinic system, *Cc* space group, with

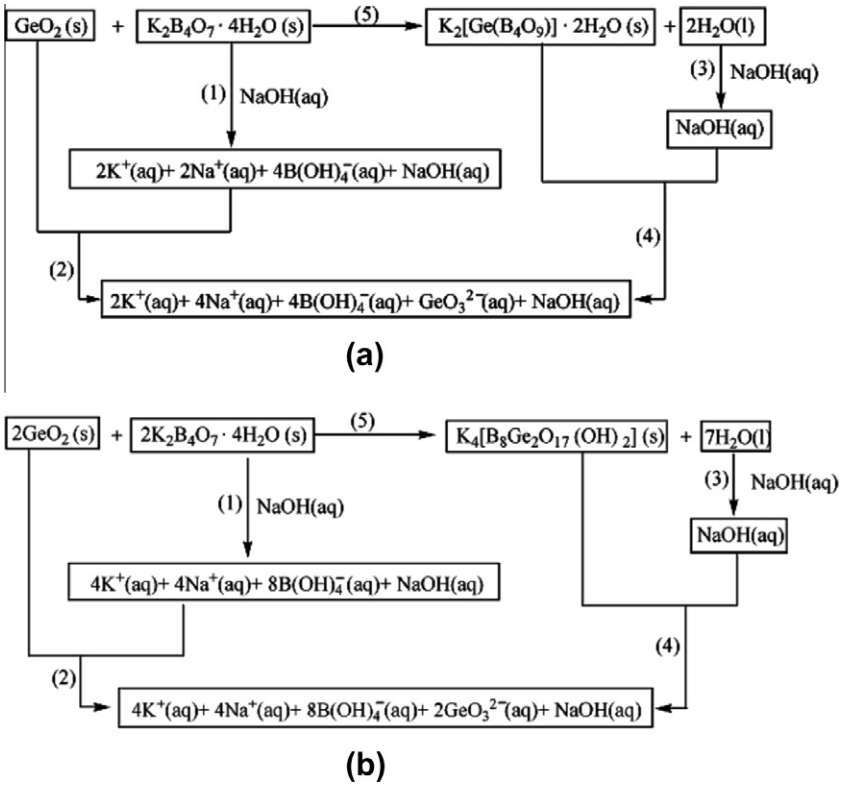

FIGURE 1. Schematic drawing of the thermodynamic circles.