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Determination of standard molar enthalpies of formation for the two lead borates: $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$

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ABSTRACT

Two pure hydrated lead borates, $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$, have been synthesized and characterized by XRD, FT-IR, DTA-TG techniques and chemical analysis. The molar enthalpies of solution of $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$ in 1 mol dm^{-3} HNO_3(aq) were measured to be -51.44 ± 0.18 kJ mol^{-1} and -91.70 ± 0.19 kJ mol^{-1}, respectively. With the incorporation of the previously determined enthalpies of solution of H_3BO_3(s) in 1 mol dm^{-3} HNO_3(aq) and of PbO(s) in (HNO_3 + H_3BO_3)(aq), together with the use of the standard molar enthalpies of formation for PbO(s), H_3BO_3(s) and H_2O(l), the standard molar enthalpies of formation of -8231.4 ± 8.6 kJ mol^{-1} for $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ and -9967.5 ± 9.8 kJ mol^{-1} for $Pb_6B_{11}O_{18}\cdot 4.5H_2O$ were obtained on the basis of the appropriate thermochemical cycles.

1. Introduction

Lead borates are of special interest in the search for materials, since some of these compounds have pronounced nonlinear-optical properties [1], such as PbB_4O_7 [2], $Pb_2[B_5O_9](OH)\cdot H_2O$ [3], $Pb_5B_3O_8(OH)_3\cdot H_2O$ [4], $Pb_3B_9O_{16}(OH)\cdot B(OH)_3$ [5] and $Pb_6B_{11}O_{18}(OH)_9$ [6].

Thermodynamic properties play very important roles in scientific research and industrial applications. As for the thermochemistry of lead borates, we recently determined the standard molar enthalpies of the formation of $Pb(BO_2)_2\cdot H_2O$ and $PbB_4O_7\cdot 4H_2O$ [7]. As part of the continuing study of this work, this paper reports the determination of standard molar enthalpies of formation of two lead borates, $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$, by using a heat conduction microcalorimeter.

2. Experimental

2.1. Synthesis and characterization of samples

All reagents used in the synthesis were of analytic grade.

$Pb_4B_{10}O_{19}\cdot 2.5H_2O$ appeared in the system of $PbO–B_2O_3–H_2O$ at 75 °C [8]. In this work, it was synthesized from a mixture of $Pb(CH_3COO)_2\cdot 3H_2O$ (3.00 g, 0.0079 mol), H_3BO_3 (1.90 g, 0.030 mol) and H_2O (50 ml, 2.78 mol) in a molar ratio of 4:15:1408 with heating and vigorous stirring at 90 °C over a week. The resulting white suspended precipitate was filtered, then washed with absolute alcohol and absolute ether, and finally, dried at 30 °C to constant mass.

$Pb_6B_{11}O_{18}(OH)_9$ was synthesized referring to the literature [6]. The resulting colorless crystals were collected by filtration, washed with distilled water, and dried in air at ambient temperature.

These two synthetic samples were characterized by FT-IR spectroscopy (recorded over the 400–4000 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellets at room temperature), X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target at 8° min^{-1}) and TG (performed on a TA-SDT Q600 simultaneous thermal analyzer under N_2 atmosphere with a heating rate of 10 °C min^{-1}). The chemical compositions of the sample were determined by EDTA titration for Pb^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by the weight loss in the TG curve for H_2O.

2.2. Calorimetric experiment

$Pb_4B_{10}O_{19}\cdot 2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$ can be regarded as the products of reactions (5) in the designed thermochemical cycles (Fig. 1 and Tables 2 and 3).

The 1 mol dm^{-3} HNO_3(aq) solvent can dissolve all components of reaction (5), which was prepared from analytical grade nitric acid and deionized water, and its concentration, 1.0044 mol dm^{-3}, was determined by titration with standard sodium carbonate. With the use of its density of 1.032 g cm^{-3} (taken from chemical handbook), its concentration can also be expressed as the form of $HNO_3\cdot 53.59H_2O$.

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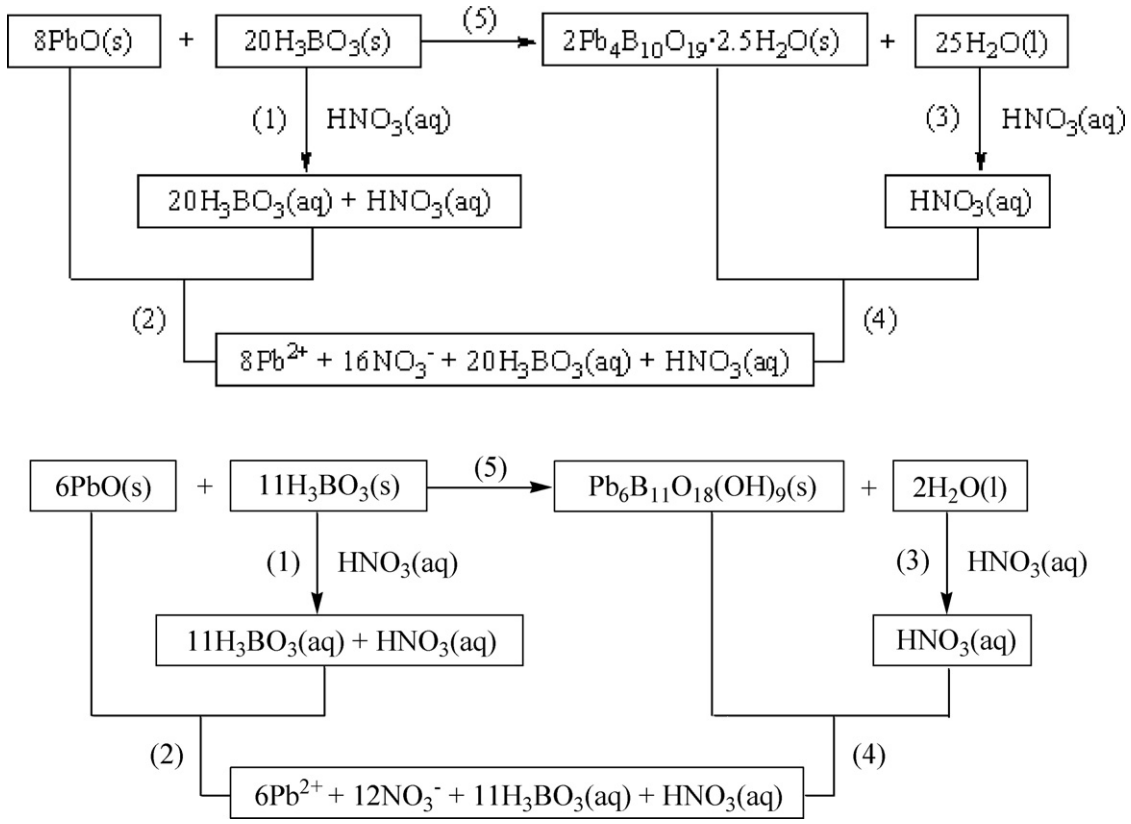

Fig. 1. Schematic drawings of the thermodynamic circles.

The molar enthalpies of solution of $Pb_4B_{10}O_{19}{\cdot}2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$ in 1 mol dm^{-3} HNO_3(aq) were measured, respectively. The calculated amount of PbO(s) was dissolved in aqueous solution which consisted of 1 mol dm^{-3} HNO_3(aq) and the calculated amount of H_3BO_3(s). In all these determinations, strict control of the stoichiometry 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 reaction (5). Applying Hess's law, the enthalpy of reaction (5) can be calculated according to the following expression:

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

The standard molar enthalpies of formation of $Pb_4B_{10}O_{19}{\cdot}2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$ can be obtained from the value of $\Delta_r H_m^\circ$ (5) in combination with the molar enthalpies of formation of H_3BO_3(s), PbO(s), and H_2O(l).

All the enthalpies of solution were measured with an RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which has been described in detail previously [9]. 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 deionized water was determined to be 17.54 ± 0.10 kJ mol^{-1}, which was in agreement with that of 17.524 ± 0.028 kJ mol^{-1} reported in the literature [10]. 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 $Pb_4B_{10}O_{19}{\cdot}2.5H_2O$ sample

The chemical analytical data of $Pb_4B_{10}O_{19}{\cdot}2.5H_2O$ are (calcd/found, %), PbO (69.43/69.49), B_2O_3 (27.08/26.46), and H_2O (3.49/3.79), which are consistent with the theoretical values.

The XRD pattern of synthetic sample of $Pb_4B_{10}O_{19}{\cdot}2.5H_2O$ is shown in Fig. 2. The characteristic *d* values are 8.0959, 5.7790, 5.1638, 4.0359, 3.5897, 3.3118, 3.1730, 3.0652, 2.8861, 2.7655, 2.6303, 2.5390, 2.4597, 2.3925, 2.2787, 2.2193, 2.1713, 2.0937,

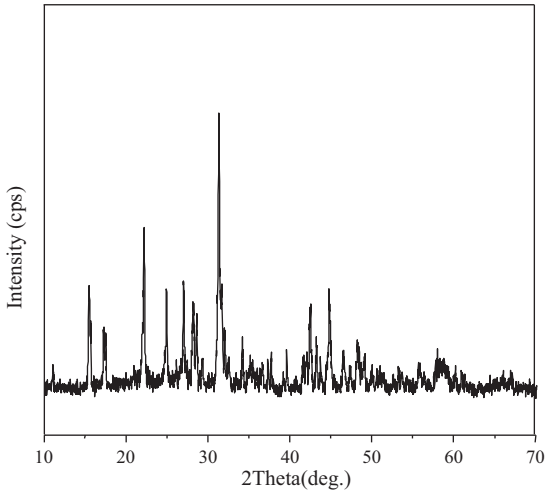

Fig. 2. Powder X-ray diffraction pattern for $Pb_4B_{10}O_{19}{\cdot}2.5H_2O$.