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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 $-51.44 \pm 0.18\,kJ\,mol^{-1}$ and $-91.70 \pm 0.19\,kJ\,mol^{-1}$, 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 $-8231.4 \pm 8.6\,kJ\,mol^{-1}$ for $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ and $-9967.5 \pm 9.8\,kJ\,mol^{-1}$ 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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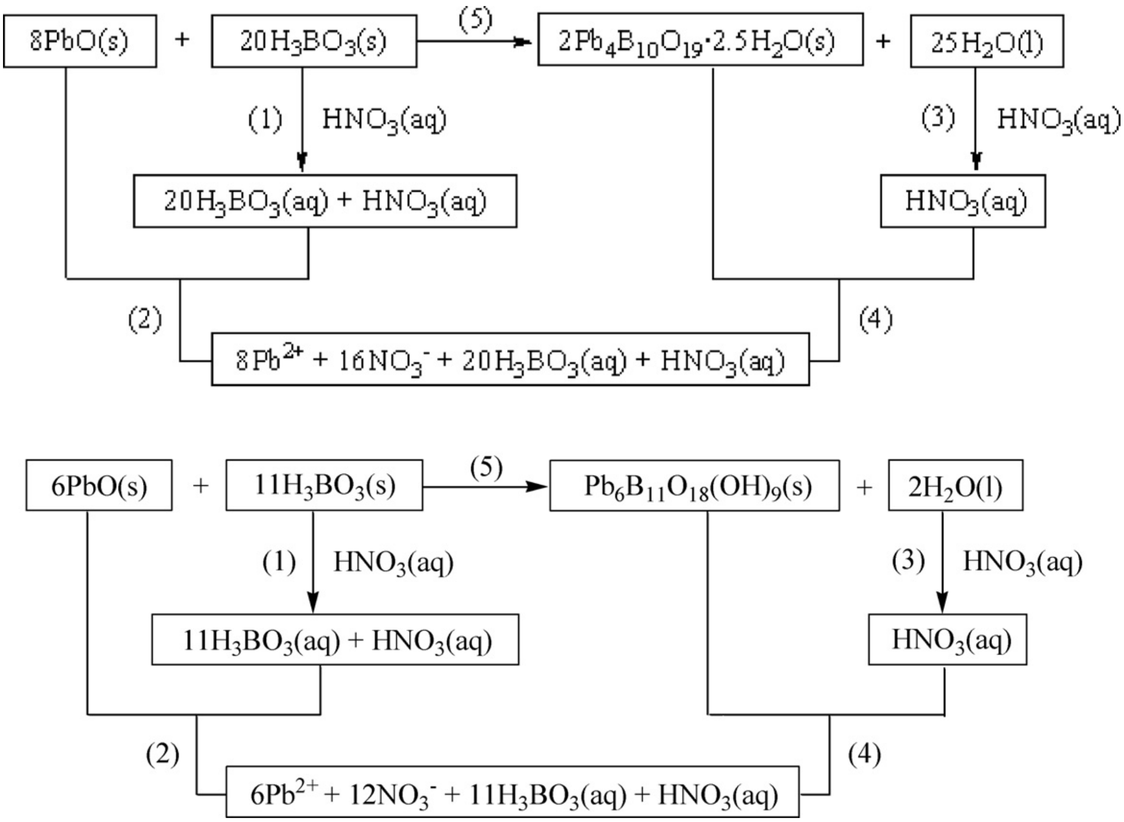

Fig. 1. Schematic drawings of the thermodynamic circles.

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 $17.54 \pm 0.10\,kJ\,mol^{-1}$, which was in agreement with that of $17.524 \pm 0.028\,kJ\,mol^{-1}$ 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,

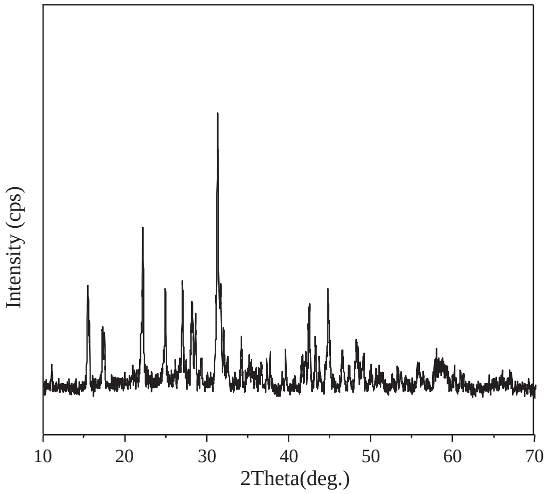

Fig. 2. Powder X-ray diffraction pattern for $Pb_4B_{10}O_{19}{\cdot}2.5H_2O$.

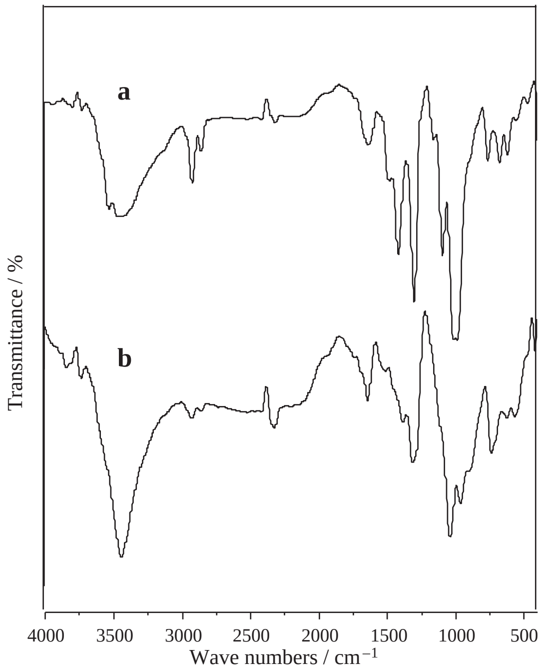

Fig. 3. FT-IR spectra of samples. a. $Pb_4B_{10}O_{19}\cdot 2.5H_2O$; b. $Pb_6B_{11}O_{18}(OH)_9$.

1.9561, 1.9217, 1.8907 and 1.5920 Å, which correspond with those of JCPDS card (File No. 28-0519).

The FT-IR spectrum of $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ sample (Fig. 3a) exhibited the following absorption bands and they were assigned referring to the literature [11]. The band at 3460 cm^{-1} is the stretching vibration of the O–H group. The bands at 2918 and 2852 cm^{-1} are the O–H stretching because of hydrogen bond. The band at 1632 cm^{-1} is assigned to the H–O–H bending mode, which shows this compound contains crystal water. The bands at 1296 and 1154 cm^{-1} are the in-plane bending of B–O–H. The bands at 1412 cm^{-1} and 982 cm^{-1} are the asymmetric and symmetric stretching of B(3)–O, respectively. The bands at 1088 cm^{-1} and 758 cm^{-1} are the asymmetric and symmetric stretching of B(4)–O, respectively. The band at 670 cm^{-1} is assigned to out-of-plane bending of B(3)–O. The band at 550 cm^{-1} is assigned bending of B(3)–O and B(4)–O. In 1972, Smirnova proposed that the polyborate anion of $[B_5O_9(OH)]^{4-}$ existed in this compound through IR spectrum [8]. The present assignments are consistent with that result.

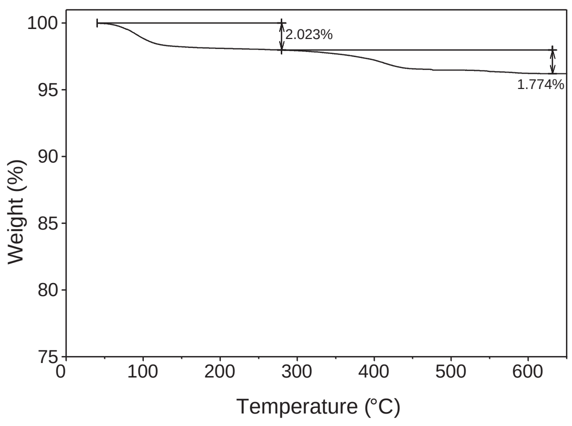

Fig. 4. TG curve of $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ sample.

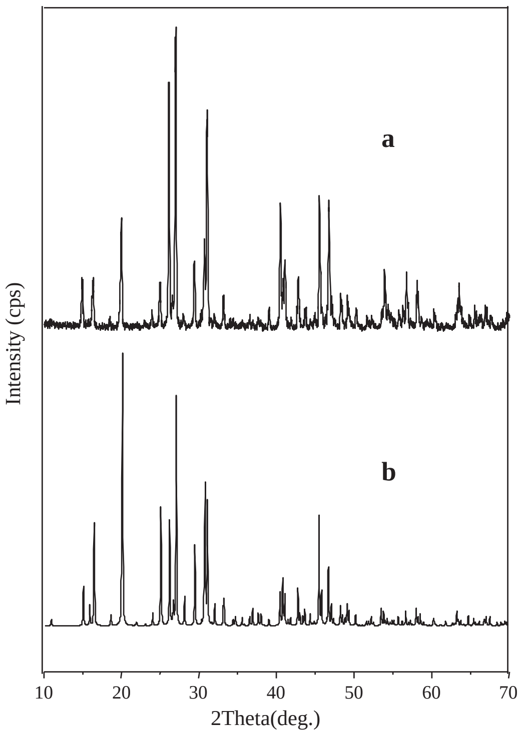

Fig. 5. Powder X-ray diffraction patterns for $Pb_6B_{11}O_{18}(OH)_9$: (a) experimental, (b) simulated on the basis of the single-crystal structure.

The thermal behavior of $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ is shown in Fig. 4. The TG curve shows that $Pb_4B_{10}O_{19}\cdot 2.5H_2O$ has a two-step weight loss from 313 K to 873 K, and the total mass loss is 3.79%, which corresponds to the loss of 2.5 water molecules and agrees with the calculated value of 3.49%. The first mass loss (2.02%) at 313–540 K corresponds to the loss of 1.5 crystal water molecules and is in good agreement with the calculated value of 2.10%. In the second step, the mass loss (1.77%) at 540–873 K corresponds to the loss of one water molecule and can be compared with the calculated value of 1.40%. This two-step weight loss result is consistent with its structure of $Pb_4\ [B_5O_9(OH)]_2\cdot 1.5H_2O$ [8].

3.2. Characterization of synthetic $Pb_6B_{11}O_{18}(OH)_9$ sample

The chemical analytical data of $Pb_6B_{11}O_{18}(OH)_9$ are (calcd/found, %), PbO (74.27/73.61), B_2O_3 (21.24/21.42), H_2O (4.49/3.93), which are consistent with the theoretical values.

Fig. 5 shows the powder XRD pattern of as-synthesized compound and the simulated pattern on the basis of single-crystal structure of $Pb_6B_{11}O_{18}(OH)_9$. The diffraction peaks on patterns corresponded well in position, indicating the phase purity of the as-synthesized samples.

The FT-IR spectrum of synthesized $Pb_6B_{11}O_{18}(OH)_9$ sample (Fig. 3b) is the same as the one in literature [6], which exhibited the following absorption bands and they were assigned referring to the literature [6,11]. The band at 3435 cm^{-1} is the stretching vibration of the O–H group. The band at 2319 cm^{-1} is the O–H stretching because of hydrogen bond. The bands at 1382 and 1306 cm^{-1} and 897 cm^{-1} are the asymmetric and symmetric stretching of B(3)–O, respectively. The bands at 1032 cm^{-1} and 737 cm^{-1} might be the asymmetric and symmetric stretching modes of B(4)–O, respectively. The band at 645 cm^{-1} is assigned to out-of-plane bending of B(3)–O. The band at 565 cm^{-1} is the bending of B(3)–O and B(4)–O. These assignments are consistent with its structure of $Pb_6B_{11}O_{18}(OH)_9$, in which the polyborate anion contains BO_3 and BO_4 groups.

Table 1
Molar enthalpies of solution of $Pb_4B_{10}O_{19}\cdot2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$ in 1 mol dm^{-3} HNO_3(aq) at 298.15 K[a].

No.	m (mg)	$\Delta_r H$ (mJ)	$\Delta_{sol} H_m$ (kJ mol^{-1})
$Pb_4B_{10}O_{19}\cdot2.5H_2O$			
1	5.04	−202.33	−51.63
2	5.11	−204.84	−51.55
3	5.10	−202.66	−51.10
4	5.17	−206.85	−51.45
5	5.10	−204.20	−51.49
Mean			−51.44 ± 0.18[b]
$Pb_6B_{11}O_{18}(OH)_9$			
1	6.73	−342.75	−91.84
2	6.71	−340.80	−91.59
3	6.59	−335.02	−91.67
4	6.55	−332.08	−91.43
5	6.66	−339.75	−91.99
Mean			−91.70 ± 0.19[b]

[a] In each experiment, 2.00 cm^3 of HNO_3(aq) was used.
[b] Uncertainty is estimated as twice the standard deviation of the mean.

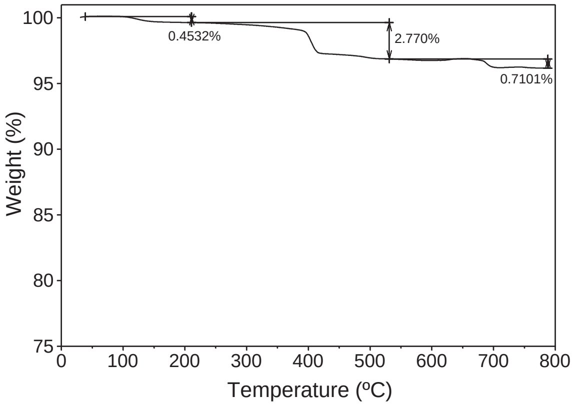

Fig. 6. TG curve of $Pb_6B_{11}O_{18}(OH)_9$ sample.

The thermal behavior of $Pb_6B_{11}O_{18}(OH)_9$ is shown in Fig. 6. The TG curve shows that $Pb_6B_{11}O_{18}(OH)_9$ has a three-step weight loss from 373 K to 1073 K, and the total mass loss is 3.93%, which corresponds to the loss of 4.5 water molecules and agrees with the calculated value of 4.49%. The first mass loss (0.45%) at 373–473 K corresponds to the loss of 0.5 water molecule and is in good agreement with the calculated value of 0.50%. In the second step, the mass loss (2.77%) at 473–823 K corresponds to the loss of 3 water molecules and can be compared with the calculated value of 2.99%. In the third step, the mass loss (0.71%) at 823–1073 K corresponds to the loss of 1 water molecules and can be compared with the calculated value of 0.99%.

All of above results indicate that the two synthetic samples are pure and suitable for the calorimetric experiments.

3.3. Results of calorimetric experiment

The molar enthalpy of solution of H_3BO_3(s) of 21.19 ± 0.18 kJ mol^{-1} and PbO(s) of −61.84 ± 0.10 kJ mol^{-1} in 2.00 cm^3 of 1 mol dm^{-3} HNO_3(aq) at 298.15 K were taken from our previous work [7]. The molar enthalpies of solution of $Pb_4B_{10}O_{19}\cdot2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$ in 2.00 cm^3 of 1 mol dm^{-3} HNO_3(aq) at 298.15 K are listed in Table 1, in which m is the mass of samples, $\Delta_{sol}H_m$ is the molar enthalpy of solution of solute, and the uncertainty is estimated as twice the standard deviation of the mean with $n = 5$.

Tables 2 and 3 give the thermochemical cycles used for the derivation of the standard molar enthalpy of formation of $Pb_4B_{10}O_{19}\cdot2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$, respectively. The enthalpy of dilution of HNO_3(aq) was calculated according to the standard molar enthalpy of formation of HNO_3(aq) from the NBS tables [12], which was near 0. The enthalpies change of 31.96 ± 3.70 kJ mol^{-1} for the formation of $Pb_4B_{10}O_{19}\cdot2.5H_2O$ and −46.25 ± 2.08 kJ mol^{-1} for the formation of $Pb_6B_{11}O_{18}(OH)_9$ from the reagents in the solid phase (reactions (5)) were calculated on the basis of the thermochemical cycles. The standard molar enthalpy of formation of PbO(s) of −218.06 ± 0.63 kJ mol^{-1} was taken from the JANAF Thermochemical Tables [13]. The standard molar enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values[14], namely −1094.8 ± 0.8 kJ mol^{-1} and −285.830 ± 0.040 kJ mol^{-1}, respectively. From these data, the standard molar enthalpies of formation of $Pb_4B_{10}O_{19}\cdot2.5H_2O$ and $Pb_6B_{11}O_{18}(OH)_9$ were calculated to be −8231.4 ± 8.6 kJ mol^{-1} and −9967.5 ± 9.8 kJ mol^{-1}, respectively.

Acknowledgments

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Table 2
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($Pb_4B_{10}O_{19}\cdot2.5H_2O$, 298.15 K)[a].

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$20H_3BO_3(s) + 506.30\ (HNO_3\cdot53.59H_2O) = 20H_3BO_3(aq) + 506.30(HNO_3\cdot53.59H_2O)$	423.80 ± 3.60
2	$8PbO(s) + 20H_3BO_3(aq) + 506.30(HNO_3\cdot53.59H_2O) = 8Pb(NO_3)_2(aq) + 20H_3BO_3(aq) + 490.30(HNO_3\cdot55.36H_2O)$	−494.72 ± 0.80
3	$506.30\ (HNO_3\cdot53.59\ H_2O) + 25H_2O(l) = 506.30\ (HNO_3\cdot53.64H_2O)$	0
4	$2Pb_4B_{10}O_{19}\cdot2.5H_2O(s) + 506.30\ (HNO_3\cdot53.64H_2O) = 8Pb(NO_3)_2(aq) + 20H_3BO_3(aq) + 490.30(HNO_3\cdot55.36H_2O)$	−102.88 ± 0.36
5	$8PbO(s) + 20H_3BO_3(s) = 2Pb_4B_{10}O_{19}\cdot2.5H_2O(s) + 25H_2O(l)$	31.96 ± 3.70[b]

[a] $\Delta_f H_m^\circ$ ($Pb_4B_{10}O_{19}\cdot2.5H_2O$, s) = $0.5\Delta_r H_m^\circ(5) + 4\Delta_f H_m^\circ(PbO, s) + 10\Delta_f H_m^\circ(H_3BO_3, s) - 12.5\Delta_f H_m^\circ(H_2O, l)$.
[b] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

Table 3
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($Pb_6B_{11}O_{18}(OH)_9$, 298.15 K)[a].

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$11H_3BO_3(s) + 544.62(HNO_3\cdot53.59H_2O) = 11H_3BO_3(aq) + 544.62\ (HNO_3\cdot53.59H_2O)$	233.09 ± 1.98
2	$6PbO(s) + 11H_3BO_3(aq) + 544.62\ (HNO_3\cdot53.59H_2O) = 6Pb(NO_3)_2(aq) + 11H_3BO_3(aq) + 532.62(HNO_3\cdot54.81H_2O)$	−371.04 ± 0.60
3	$544.62\ (HNO_3\cdot53.59H_2O) + 12H_2O(l) = 544.62\ (HNO_3\cdot53.61H_2O)$	0
4	$Pb_6B_{11}O_{18}(OH)_9(s) + 544.62(HNO_3\cdot53.61H_2O) = 6Pb(NO_3)_2(aq) + 11H_3BO_3(aq) + 532.62(HNO_3\cdot54.81H_2O)$	−91.70 ± 0.19
5	$6PbO(s) + 11H_3BO_3(s) = Pb_6B_{11}O_{18}(OH)_9(s) + 12H_2O(l)$	−46.25 ± 2.08[b]

[a] $\Delta_f H_m^\circ((Pb_6B_{11}O_{18}(OH)_9, s) = \Delta_r H_m^\circ(5) + 6\Delta_f H_m^\circ(PbO, s) + 11\Delta_f H_m^\circ(H_3BO_3, s) - 12\Delta_f H_m^\circ(H_2O, l)$.
[b] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

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