# Standard Molar Enthalpies of Formation for the Two Alkali Metal Borates, $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$

**Ping Li and Zhi-Hong Liu***

Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, People's Republic of China

Two pure hydrated alkali borates, $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$, have been synthesized under mild hydrothermal conditions and characterized by single X-ray diffraction, infrared spectra, thermogravimetric analysis, differential thermal analysis, and chemical analysis. The enthalpies of solution of $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$ in 1 $mol \cdot L^{-1}$ HCl(aq) were measured to be (53.37 ± 0.09) $kJ \cdot mol^{-1}$ and (46.61 ± 0.15) $kJ \cdot mol^{-1}$. With the incorporation of the previously determined enthalpies of solution of $H_3BO_3$(s) in 1 $mol \cdot L^{-1}$ HCl(aq) and of NaCl(s) and KCl(s) in ($HCl + H_3BO_3$) aqueous solution, together with the standard molar enthalpies of formation of NaCl(s), KCl(s), $H_3BO_3$(s), HCl(aq), and $H_2O$(l), the standard molar enthalpies of formation were found to be $-(14093.0 \pm 9.7)$ $kJ \cdot mol^{-1}$ for $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and $-(8651.0 \pm 8.1)$ $kJ \cdot mol^{-1}$ for $K_4[B_{10}O_{15}(OH)_4]$ by solution calorimetry.

## Introduction

Studies of alkali borates have attracted much interest in recent years because some of these compounds show interesting physical properties, such as nonlinear optical behavior for $CsLiB_6O_{10}$, $CsB_3O_5$, and $KB_5O_8 \cdot 4H_2O$.[1] So far, several phases have been obtained in the $Na_2O-B_2O_3-H_2O$ and $K_2O-B_2O_3-H_2O$ systems under hydrothermal conditions, such as $Na_6[B_4O_5(OH)_4)]_3 \cdot 8H_2O$[2] and $K_4[B_{10}O_{15}(OH)_4]$.[3] Thermodynamic properties play very important roles in scientific research and industrial applications. Until now, the standard molar enthalpies of formation of some hydrated sodium and potassium borates have been reported.[4−7] As part of a continuing study of the thermochemistry of hydrated alkali borates, this paper reports the determination of the standard molar enthalpies of formation of these two alkali borates, $Na_6[B_4O_5(OH)_4)]_3 \cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$, using a heat conduction microcalorimeter.

## Experimental Section

***Synthesis and Characterization of Samples.*** All reagents used in the synthesis of the compounds were of analytical grade. Single crystals of $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ were synthesized from a mixture of $H_3BO_3$ (2.4728 g), $CH_3COONa \cdot 3H_2O$ (1.3608 g), triethylenetriamine (2.98 mL), and $H_2O$ (4.32 mL) in the molar ratio of 4:1:2:24 sealed in a Teflon-lined stainless steel vessel, heated at 160 °C for about 7 days under autogenous pressure, then cooled to room temperature. Single crystals of $K_4[B_{10}O_{15}(OH)_4]$ were synthesized by referring to the literature.[3] The resulting colorless crystals were collected and dried in air at ambient temperature. The samples were characterized by FT-IR spectroscopy (recorded over the (400 to 4000) $cm^{-1}$ region on a Nicolet NEXUS 670 spectrometer with KBr pellets at room temperature), single X-ray diffraction (the X-ray diffraction intensities were recorded by a Bruker Smart-1000 CCD diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.071073$ nm)), chemical analysis, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (performed on a SDT Q600 simultaneous thermal analyzer under $N_2$ atmosphere with a heating rate of 10 $°C \cdot min^{-1}$). The $B_2O_3$ content was determined by NaOH titration in the presence of mannitol. The $H_2O$ content was determined by the wetght loss in the TG curve.

***Calorimetric Experiment.*** The thermochemical cycles designed for the derivation of the $\Delta_f H_m^o$ of $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$ are shown in Figure 1. The 1 $mol \cdot L^{-1}$ HCl(aq) solvent can dissolve all components of the designed reaction (5), and its concentration was determined by titration with standard sodium carbonate. The standard molar enthalpies of formation of $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of NaCl(s), KCl(s), $H_3BO_3$(s), HCl(aq), and $H_2O$(l).

The RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) used was described in detail previously.[8,9] Calorimetric experiments were performed five times at 298.15 K as previously described.[9] No solid residues were observed after the reactions.

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) $kJ \cdot mol^{-1}$, which is in agreement with that of (17.524 ± 0.028) $kJ \cdot mol^{-1}$ reported in the literature.[10] This shows that the device used for measuring the enthalpy of solution in this work is reliable.

## Results and Discussion

***Characterization of the Synthetic Samples.*** The sample of $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ crystallized in the trigonal system, space group *R*3(2), $a = 11.153(12)$ Å, $c = 21.22(2)$ Å, and $\gamma = 120°$, which are consistent with the reported unit cell in the literature.[2] The sample of $K_4[B_{10}O_{15}(OH)_4]$ crystallized in the monoclinic system, space group *C*2/*c*, $a = 17.99(6)$ Å, $b = 6.83(3)$ Å, $c =$

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* Corresponding author. Tel.: +86 29 8530 7765. Fax: +86 29 8530 7774. E-mail: liuzh@snnu.edu.cn.

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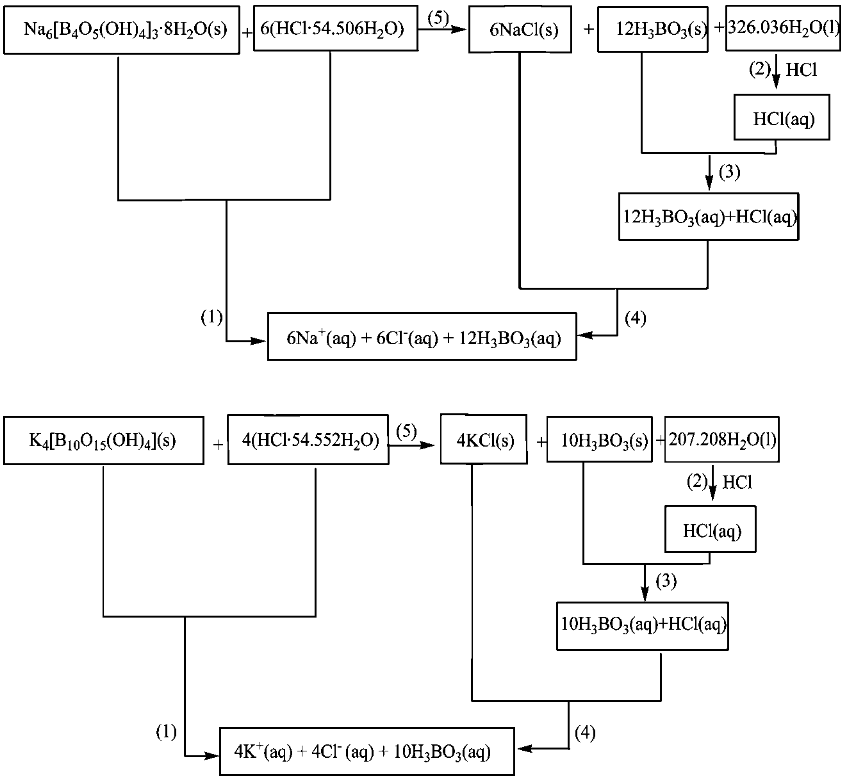

**Figure 1.** Designed thermochemical cycles.

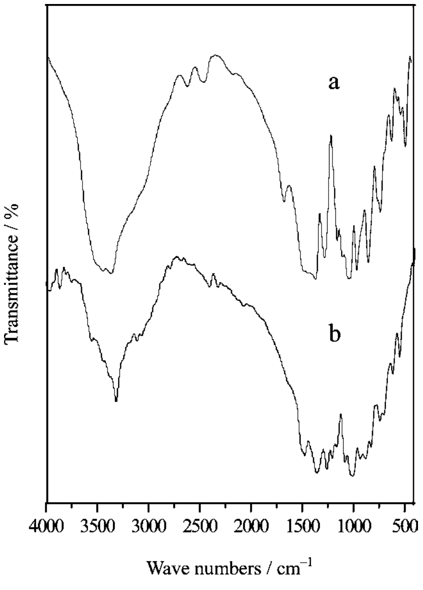

**Figure 2.** FT-IR spectra of the samples. (a) $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and (b) $K_4[B_{10}O_{15}(OH)_4]$.

13.15(4) Å, and $\beta = 94.84(5)$ °, which are consistent with the reported unit cell in the literature.[3]

The FT-IR spectra (Figure 2) of samples exhibited the following absorption bands and they were assigned referring to the literature.[11] For sample $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$: The bands at (3452 and 3368) $cm^{-1}$ were the stretching modes of O−H. The bands at (2614 and 2449) $cm^{-1}$ might be the stretching modes of O−H because of hydrogen bonds. The band at 1659 $cm^{-1}$ was H−O−H bending because of lattice water. The bands at (1348 and 940) $cm^{-1}$ might be the asymmetric and symmetric stretching modes of B−O in $BO_3$, respectively. The bands at (1132, 1023 and 826) $cm^{-1}$ were assigned as the asymmetric and symmetric stretching modes of B−O in $BO_4$, respectively. The band at 707 $cm^{-1}$ might be out-of-plane bending of B−O in $BO_3$. The band at 595 $cm^{-1}$ might be symmetric pulse vibration of tetraborate anion, $[B_4O_5(OH)_4]^{2-}$. The bands at (507 and 460) $cm^{-1}$ might be the bending of B−O. For sample $K_4[B_{10}O_{15}(OH)_4]$: The band at 3301 $cm^{-1}$ was the stretching mode of O−H. The bands at (1473, 1355 and 933) $cm^{-1}$ might be the asymmetric and symmetric stretching modes of B−O in $BO_3$, respectively. The band at 1258 $cm^{-1}$ might be the in-plane bending of B−O−H. The bands at (1005 and 741) $cm^{-1}$ were assigned as the asymmetric and symmetric stretching modes of B−O in $BO_4$, respectively. The band at 547 $cm^{-1}$ might be the bending of B−O.

The simultaneous TG-DTA curves of the synthetic sample $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ (Figure 3) indicate that the total weight loss is 29.55 % from (50 to 750) °C, which might correspond to the continuous loss of 14 water molecules and can be compared with the calculated value of 29.44 %. In the DTA curve, the endothermic peak appearing at 201 °C is related to the dehydration and formation of the amorphous phase $Na_2B_4O_7$. This amorphous phase recrystallizes as proven by the exothermic peak at 681 °C. The simultaneous TG-DTA curves of the synthetic sample $K_4[B_{10}O_{15}(OH)_4]$ (Figure 4) indicate that the total weight loss is 6.67 % from (130 to 580) °C, which might correspond to the loss of two water molecules, which can be compared with calculated value of 6.29 %. In the DTA curve, the endothermic peak at 467 °C is related to the dehydration and formation of the amorphous phase, this amorphous phase recrystallizes as proven by the exothermic peaks at 562 °C.

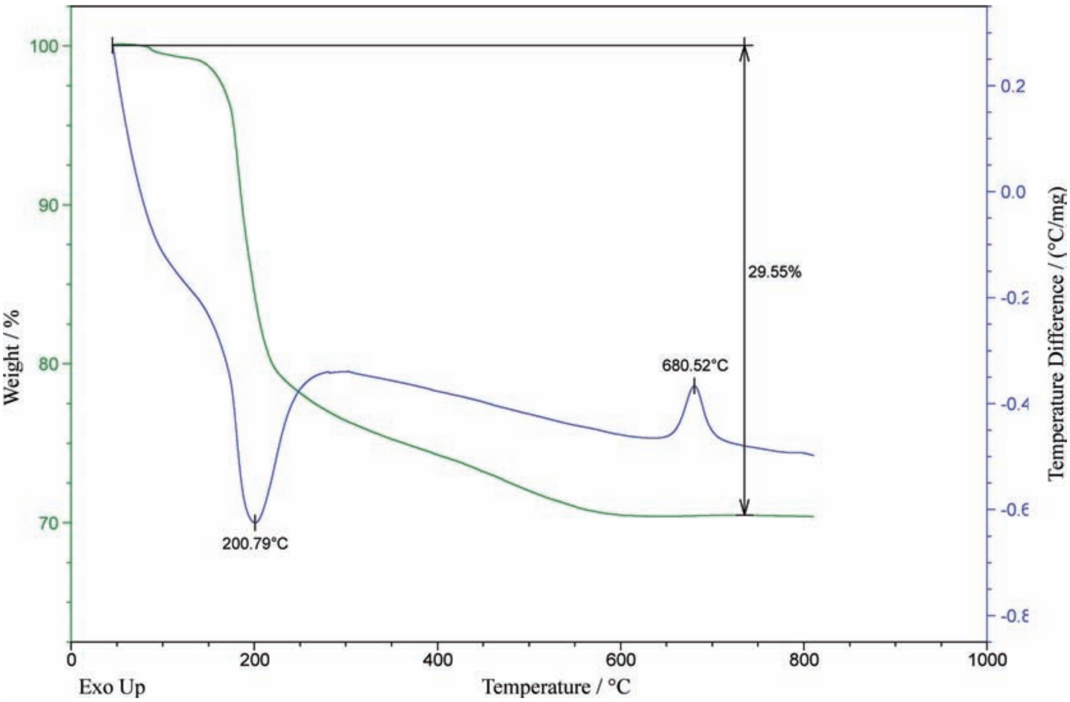

**Figure 3.** Simultaneous TG-DTA curves of the $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ sample.

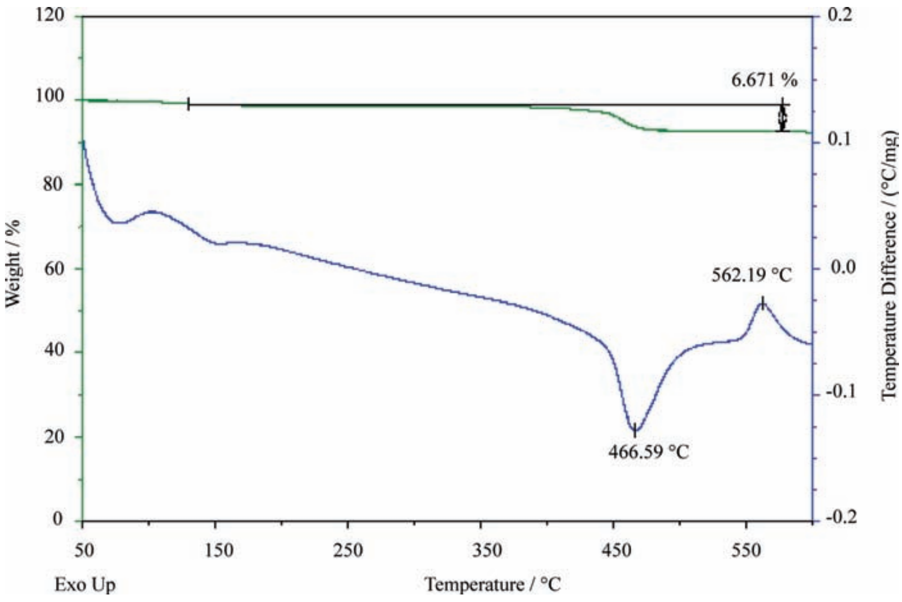

**Figure 4.** Simultaneous TG-DTA curves of the $K_4[B_{10}O_{15}(OH)_4]$ sample.

The chemical analytical data of the synthetic samples are (found/calcd, %), $B_2O_3$ (49.32/48.81), $H_2O$ (29.55/29.44) for $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and $B_2O_3$ (58.48/58.26), $H_2O$ (6.67/6.29) for $K_4[B_{10}O_{15}(OH)_4]$. The chemical analytical results are consistent with the theoretical values.

As above stated, the synthetic single crystals samples are pure and suitable for the calorimetric experiments.

***Results of Calorimetric Experiment.*** The molar enthalpies of solution of $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$ in 1 $\text{mol} \cdot \text{L}^{-1}$ HCl(aq) at 298.15 K are listed in Table 1, in which $m$ is the mass of sample, $\Delta_{\text{sol}}H_{\text{m}}$ is the molar enthalpy of solution of the solute, and the uncertainty is estimated as twice the standard deviation of the mean.

Tables 2 and 3 give the thermochemical cycles for the derivation of the standard molar enthalpies of formation of $Na_6[B_4O_5(OH)_4]_3 \cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$, respectively. The molar enthalpy of solution of $H_3BO_3$(s) of (21.83 ± 0.08) $\text{kJ} \cdot \text{mol}^{-1}$ in 1 $\text{mol} \cdot \text{L}^{-1}$ HCl(aq) was taken from the literature.[12] The molar enthalpy of solution of NaCl(s) of (5.14 ± 0.02) $\text{kJ} \cdot \text{mol}^{-1}$ and KCl(s) of (17.63 ± 0.11) in (1 $\text{mol} \cdot \text{L}^{-1}$ HCl + $H_3BO_3$) (aq) was taken from the literature.[5] The standard molar enthalpies of formation of NaCl(s) and KCl(s) were taken from the NBS tables,[4] namely −(411.15 ± 0.10) $\text{kJ} \cdot \text{mol}^{-1}$ and −(436.75 ± 0.10) $\text{kJ} \cdot \text{mol}^{-1}$. The standard molar enthalpy of formation of HCl(aq) and the enthalpy of dilution of HCl(aq) were calculated from the NBS tables.[4]

**Table 1. Molar Enthalpies of Solution of $Na_6[B_4O_5(OH)_4]_3\cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$ in 1 mol·L$^{-1}$ HCl(aq) at 298.15 K**[a]

| no. | $m$/mg | $\Delta_r H$/mJ | $\Delta_{sol}H_m$/kJ mol$^{-1}$ |
|---|---|---|---|
| | $Na_6[B_4O_5(OH)_4]_3\cdot 8H_2O$ | | |
| 1 | 3.88 | 241.455 | 53.26 |
| 2 | 3.81 | 238.097 | 53.49 |
| 3 | 3.95 | 246.059 | 53.32 |
| 4 | 3.90 | 243.768 | 53.32 |
| 5 | 3.96 | 247.237 | 53.44 |
| mean | | | 53.37 ± 0.09[b] |
| | $K_4[B_{10}O_{15}(OH)_4]$ | | |
| 1 | 5.88 | 478.648 | 46.60 |
| 2 | 5.69 | 463.483 | 46.64 |
| 3 | 6.05 | 493.882 | 46.74 |
| 4 | 6.04 | 493.109 | 46.74 |
| 5 | 6.28 | 508.056 | 46.32 |
| mean | | | 46.61 ± 0.15[b] |

[a] In each experiment, 2.00 mL of HCl(aq) was used. [b] Uncertainty is estimated as twice the standard deviation of the mean, namely, $\delta = 2[\sum(x_i - x)^2/n(n-1)]^{1/2}$, in which $n$ is the number of experimentals ($n = 5$); $x_i$ is the experimental value of each repeated measurement; and $\bar{x}$ is the mean value.

**Table 2. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^o$ ($Na_6[B_4O_5(OH)_4]_3\cdot 8H_2O$, 298.15 K)**

| no. | reaction | $\Delta_r H_m^o$/(kJ mol$^{-1}$) |
|---|---|---|
| (1) | $Na_6[B_4O_5(OH)_4]_3\cdot 8H_2O(s) + 438.739(HCl\cdot 54.506H_2O) = 6Na^+(aq) + 6Cl^-(aq) + 12H_3BO_3(aq) + 432.739(HCl\cdot 55.259H_2O)$ | 53.37 ± 0.09 |
| (2) | $432.739(HCl\cdot 55.259H_2O) = 432.739(HCl\cdot 54.506H_2O) + 326.036H_2O(l)$ | 6.49 ± 0.24 |
| (3) | $12H_3BO_3(aq) + 432.739(HCl\cdot 55.259H_2O) = 12H_3BO_3(s) + 432.739(HCl\cdot 55.259H_2O)$ | −261.96 ± 0.96 |
| (4) | $6Na^+(aq) + 6Cl^-(aq) + 12H_3BO_3(aq) + 432.739(HCl\cdot 55.259H_2O) = 6NaCl(s) + 12H_3BO_3(aq) + 432.739(HCl\cdot 55.259H_2O)$ | −30.84 ± 0.12 |
| (5) | $3H_2(g) + 3Cl_2(g) + 327.036H_2O(l) = 6(HCl\cdot 54.506H_2O)$ | −992.73 ± 0.60 |
| (6) | $6NaCl(s) = 6Na(s) + 3Cl_2(g)$ | 2466.90 ± 0.60 |
| (7) | $12H_3BO_3(s) = 12B(s) + 18H_2(g) + 18O_2(g)$ | 13137.6 ± 9.6 |
| (8) | $H_2(g) + (1/2)O_2(g) = H_2O(l)$ | −285.83 ± 0.04 |
| (9) | $Na_6[B_4O_5(OH)_4]_3\cdot 8H_2O(s) = 6Na(s) + 12B(s) + 14H_2(g) + (35/2)O_2(g)$ | 14093.0 ± 9.7[a] |

[a] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

The standard molar enthalpies of formation of $H_3BO_3$(s) and $H_2O$(l) were taken from the CODATA Key Values,[13] namely −(1094.8 ± 0.8) and −(285.830 ± 0.040) kJ·mol$^{-1}$, respectively. From these data, the standard molar enthalpies of formation of $Na_6[B_4O_5(OH)_4]_3\cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$ were calculated to be −(14093.0 ± 9.7) kJ·mol$^{-1}$ and −(8651.0 ± 8.1) kJ·mol$^{-1}$, respectively.

## Conclusions

Through two appropriate thermochemical cycles, the standard molar enthalpies of formation of $Na_6[B_4O_5(OH)_4]_3\cdot 8H_2O$ and $K_4[B_{10}O_{15}(OH)_4]$ have been obtained from measured enthalpies of solution, together with the standard molar enthalpies of formation of NaCl(s), KCl(s), $H_3BO_3$(s), HCl(aq), and $H_2O$(l).

**Table 3. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^o$ ($K_4[B_{10}O_{15}(OH)_4]$, 298.15 K)**

| no. | reaction | $\Delta_r H_m^o$/(kJ mol$^{-1}$) |
|---|---|---|
| (1) | $K_4[B_{10}O_{15}(OH)_4](s) + 191.37(HCl\cdot 54.552H_2O) = 4K^+(aq) + 4Cl^-(aq) + 10H_3BO_3(aq) + 187.37(HCl\cdot 55.658H_2O)$ | 46.61 ± 0.15 |
| (2) | $187.37(HCl\cdot 55.658H_2O) = 187.37(HCl\cdot 54.552H_2O) + 207.208H_2O(l)$ | 4.14 ± 0.18 |
| (3) | $10H_3BO_3(aq) + 187.37(HCl\cdot 55.658H_2O) = 10H_3BO_3(s) + 187.37(HCl\cdot 55.658H_2O)$ | −218.30 ± 0.80 |
| (4) | $4K^+(aq) + 4Cl^-(aq) + 10H_3BO_3(aq) + 187.37(HCl\cdot 55.658H_2O) = 4KCl(s) + 10H_3BO_3(aq) + 187.37(HCl\cdot 55.658H_2O)$ | −70.52 ± 0.44 |
| (5) | $2H_2(g) + 2Cl_2(g) + 218.208H_2O(l) = 4(HCl\cdot 54.552H_2O)$ | −661.82 ± 0.40 |
| (6) | $4KCl(s) = 4K(s) + 2Cl_2(g)$ | 1747.00 ± 0.40 |
| (7) | $10H_3BO_3(s) = 10B(s) + 15H_2(g) + 15O_2(g)$ | 10948.0 ± 8.0 |
| (8) | $11H_2(g) + (11/2)O_2(g) = 11H_2O(l)$ | −3144.13 ± 0.44 |
| (9) | $K_4[B_{10}O_{15}(OH)_4](s) = 4K(s) + 10B(s) + 2H_2(g) + (19/2)O_2(g)$ | 8651.0 ± 8.1[a] |

[a] 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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