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Short communication

Thermodynamic properties of $K_2Sr[B_4O_5(OH)_4]_2·10H_2O$

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Abstract

A pure hydrated double strontium borates, $K_2Sr[B_4O_5(OH)_4]_2·10H_2O$, has been synthesized and characterized by XRD, FT-IR, DTA–TG and chemical analysis. The enthalpies of solution of $K_2Sr[B_4O_5(OH)_4]_2·10H_2O$ in $1\,mol\,dm^{-3}$ HCl(aq) and KCl(s) in mixed solvent [$1\,mol\,dm^{-3}$ HCl + $Sr(OH)_2·8H_2O + H_3BO_3$](aq) were determined. With the incorporation of the previously determined enthalpies of solution of $Sr(OH)_2·8H_2O$(s) in [$1\,mol\,dm^{-3}$ HCl + H_3BO_3](aq), H_3BO_3(s) in $1\,mol\,dm^{-3}$ HCl(aq) and the standard molar enthalpies of formation of HCl(aq), H_2O(l), $Sr(OH)_2·8H_2O$(s), H_3BO_3(s) and KCl(s), the standard molar enthalpy of formation of $K_2Sr[B_4O_5(OH)_4]_2·10H_2O$ was found to be $-(10882.0 \pm 6.5)\,kJ\,mol^{-1}$. Thermodynamic properties of the compound were also estimated by a group contribution method. The standard molar free energy of formation ($\Delta_f G_m^\circ$) was estimated to be $-9690.80\,kJ\,mol^{-1}$. From these values, the standard molar entropy of formation ($\Delta_f S_m^\circ$) was estimated to be $-3995.3\,J\,mol^{-1}\,K^{-1}$. The standard molar entropy (S_m°) was estimated to be $933.8\,J\,mol^{-1}\,K^{-1}$.

Keywords: $K_2Sr[B_4O_5(OH)_4]_2·10H_2O$; Solution calorimetry; Thermodynamic properties

1. Introduction

We have determined the standard molar enthalpies of formation of strontium borates $SrB_2O_4·4H_2O$ and SrB_2O_4 by solution calorimetry [1]. As part of the continuing study of the thermochemistry of the strontium borates, this paper reports the determination of the standard molar enthalpy of formation of the hydrated double strontium borate $K_2Sr[B_4O_5(OH)_4]_2·10H_2O$ [2] and an estimate of the $\Delta_f G_m^\circ$ and S_m° of this double borate by a group contribution method.

2. Experimental

2.1. Preparation of $K_2Sr[B_4O_5(OH)_4]_2·10H_2O$

All reagents used in the synthesis were analytic grade (made in Xi'an Chemical Factory, China). A solution of 1.3 g of $SrCl_2·2H_2O$ in 20 ml of water was added to a solution of 7.1 g of $K_2B_4O_7·4H_2O$ in 50 ml of water. Crystallization began in a few days at room temperature. The resulting solids were separated and washed thoroughly with distilled water, and then with alcohol and ether, and finally dried at room temperature to constant mass. The synthetic sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target at $8^\circ\,min^{-1}$), FT-IR spectroscopy (Nicolet NEXUS 670 FT-IR spectrometer with KBr pellets at room temperature) and TG–DTA (TA-SDT Q600 simultaneous thermal analyzer at a heating rate of $10\,K\,min^{-1}$ in flowing N_2). The chemical composition of the sample was determined by EDTA titration for Sr^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by the mass lost in the TG curve for H_2O, and by difference for K_2O.

2.2. Calorimetric experiment

Thermochemical reaction designed for the derivation of $\Delta_r H_m^\circ$ of $K_2Sr[B_4O_5(OH)_4]_2·10H_2O$ is

$$K_2Sr[B_4O_5(OH)_4]_2·10H_2O(s) + 201.345(HCl·54.506H_2O) = 2KCl(s) + Sr(OH)_2·8H_2O(s) + 8H_3BO_3(s) + 199.345(HCl·54.506H_2O) + 103.012H_2O(l) \quad (1)$$

The $1\,mol\,dm^{-3}$ HCl(aq) solvent rapidly dissolves all components of reaction (1).

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The RD496 – III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) used was described in detail previously [3]. Calorimetric experiment was performed five times at 298.15 K as previously described [1].

3. Results and discussion

3.1. Characterization of the synthetic sample

The chemical analytical data of synthetic samples are (found/calcd., %), K_2O (12.34/12.93), SrO (14.19/14.22), B_2O_3 (38.27/38.23), and H_2O (35.20/34.62).

The XRD pattern of synthetic sample is given in Fig. S1 in Supplementary data files. All the diffraction peaks can be exactly indexed with those of $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$ (JCPDS File no. 87-0443) and shows absence of other crystalline forms in the synthetic sample. FT-IR spectrum is given in Fig. S2 in Supplementary data files.

The simultaneous TG–DTA curves of synthetic sample (Fig. S3 in Supplementary data files) indicate that the total mass loss is 35.20% from 303 to 1073 K, which corresponds to the loss of 14 water molecules and is near to the calculated value of 34.62%.

3.2. Results of calorimetric experiment

The molar enthalpy of solution of KCl(s) is (19.90 ± 0.18, n = 5, kJ mol^{-1}) in the mixed solvent of [1 mol dm^{-3} HCl + $SrCl_2$ + H_3BO_3](aq), and that of $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$ is (104.40 ± 0.28, n = 5, kJ mol^{-1}) in 1 mol dm^{-3} HCl(aq) at 298.15 K (Tables S1 and S2 in Supplementary data files).

Table 1 gives the thermochemical cycle for derivation of the standard molar enthalpy of formation of $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$.

3.3. Estimate thermodynamic properties by a group contribution method

The enthalpy of formation of $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$ can also be estimated by a group contribution method [7], which can be expressed in the following equation:

$$\Delta_f H_m^\circ(K_2Sr[B_4O_5(OH)_4]_2 \cdot 10H_2O, s) = 2\Delta_f H_m^\circ(K^+, aq) + \Delta_f H_m^\circ(Sr^{2+}, aq) + 2\Delta_f H_m^\circ([B_4O_5(OH)_4]^{2-}, aq) + 10\Delta_f H_m^\circ(H_2O, l)$$

in which the $\Delta_f H_m^\circ$ of −3464.46 kJ mol^{-1} of $[B_4O_5(OH)_4]^{2-}$ and −290.42 kJ mol^{-1} of structural H_2O were taken from [7], the $\Delta_f H_m^\circ$ of −252.38 kJ mol^{-1} of K^+ and −545.80 kJ mol^{-1} of Sr^{2+} were taken from the NBS tables [5]. Using this scheme, the standard molar enthalpy of formation is −10883.69 kJ mol^{-1}.

We also used a group contribution method to calculate $\Delta_f G_m^\circ$ of $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$ to be −9690.80 kJ mol^{-1} accord-

Table 1
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$(s), 298.15 K)

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$K_2O{\cdot}SrO{\cdot}4B_2O_3{\cdot}14H_2O + 201.345(HCl{\cdot}54.506H_2O) = 2K^+(aq) + Sr^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 197.345(HCl{\cdot}55.631H_2O)$	104.40 ± 0.28
2	$2K^+(aq) + Sr^{2+}(aq) + 4Cl^-(aq) + 8H_3BO_3(aq) + 197.345(HCl{\cdot}55.631H_2O) = 2KCl(s) + Sr^{2+}(aq) + 2Cl^-(aq) + 8H_3BO_3(aq) + 197.345(HCl{\cdot}55.631H_2O)$	−39.80 ± 0.36
3	$Sr^{2+}(aq) + 2Cl^- + 8H_3BO_3(aq) + 197.345(HCl{\cdot}55.631H_2O) = Sr(OH)_2{\cdot}8H_2O(s) + 8H_3BO_3(aq) + 199.345(HCl{\cdot}55.023H_2O)$	51.69 ± 0.15 [1]
4	$8H_3BO_3(aq) + 199.345(HCl{\cdot}55.023H_2O) = 8H_3BO_3(s) + 199.345(HCl{\cdot}55.023H_2O)$	−174.64 ± 0.64 [4]
5	$199.345(HCl{\cdot}55.023H_2O) = 199.345(HCl{\cdot}54.506H_2O) + 103.012H_2O(l)$	2.06 ± 0.08 [5]
6	$H_2(g) + Cl_2(g) + 109.012H_2O(l) = 2(HCl{\cdot}54.506H_2O)$	−330.84 ± 0.20 [5]
7	$2KCl(s) = 2K(s) + Cl_2(g)$	873.49 ± 0.20 [5]
8	$Sr(OH)_2{\cdot}8H_2O(s) = Sr(s) + 5O_2(g) + 9H_2(g)$	3352.2 ± 0.40 [5]
9	$8H_3BO_3(s) = 8B(s) + 12H_2(g) + 12O_2(g)$	8758.4 ± 6.4 [6]
10	$6H_2(g) + 3O_2(g) = 6H_2O(l)$	−1714.98 ± 0.24 [6]
11	$K_2O{\cdot}SrO{\cdot}4B_2O_3{\cdot}14H_2O(s) = 2K(s) + Sr(s) + 8B(s) + 14H_2(g) + 14O_2(g)$	10882.0 ± 6.5[a]

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

ing to the following equation:

$$\Delta_f G_m^\circ(K_2Sr[B_4O_5(OH)_4]_2 \cdot 10H_2O, s) = 2\Delta_f G_m^\circ(K^+, aq) + \Delta_f G_m^\circ(Sr^{2+}, aq) + 2\Delta_f G_m^\circ([B_4O_5(OH)_4]^{2-}, aq) + 10\Delta_f G_m^\circ(H_2O, l)$$

in which the $\Delta_f G_m^\circ$ of $-3095.99\,kJ\,mol^{-1}$ of $[B_4O_5(OH)_4]^{2-}$ and $-237.28\,kJ\,mol^{-1}$ of structural H_2O were taken from [7], and the $\Delta_f G_m^\circ$ of $-283.27\,kJ\,mol^{-1}$ of K^+ and $-559.48\,kJ\,mol^{-1}$ of Sr^{2+} were taken from the NBS tables [5].

Combining the $\Delta_f H_m^\circ$ of $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$, the standard molar entropy of formation of $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$ has been calculated at $-3995.3\,J\,mol^{-1}\,K^{-1}$ according to following equation:

$$\Delta_f S_m^\circ = \frac{\Delta_f H_m^\circ - \Delta_f G_m^\circ}{T}$$

Finally, the standard molar entropy of $K_2Sr[B_4O_5(OH)_4]_2{\cdot}10H_2O$ has been calculated to be $933.8\,J\,mol^{-1}\,K^{-1}$ according to following reaction (2) and equation:

$$2K(s) + Sr(s) + 8B(s) + 14H_2(g) + 14O_2(g) = K_2O{\cdot}SrO{\cdot}4B_2O_3{\cdot}14H_2O(s) \qquad (2)$$

$$S_m^\circ(K_2Sr[B_4O_5(OH)_4]_2 \cdot 10H_2O, s) = [2S_m^\circ(K, s) + S_m^\circ(Sr, s) + 8S_m^\circ(B, s) + 14S_m^\circ(H_2, g) + 14S_m^\circ(O_2, g)] + \Delta_f S_m^\circ$$

The standard molar entropies of the elements were taken from the NBS tables [5].

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.03.007.

References

[1] Z.H. Liu, H.S. Huang, Thermochim. Acta 448 (2006) 59.
[2] N.P. Ivchenko, E.N. Kurkutova, Kristallographiya 20 (1975) 533.
[3] M. Ji, M.Y. Liu, Sh.L. Gao, Q.Zh. Shi, Instrum. Sci. Technol. 29 (1) (2001) 53.
[4] J. Li, Sh.Y. Gao, Sh.P. Xia, B. Li, R.Z. Hu, J. Chem. Thermodyn. 29 (1997) 491.
[5] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Chumey, R.L. Nuttall, The NBS tables of chemical thermodynamic properties, J. Phys. Chem. Ref. Data 11 (Suppl. 2) (1982).
[6] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.
[7] J. Li, B. Li, S.Y. Gao, Phys. Chem. Minerals 27 (2000) 342.