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Thermochemistry of teepleite

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Abstract

The enthalpy of solution of teepleite, $Na_2B(OH)_4Cl$, in approximately 1 mol dm^{-3} aqueous hydrochloric acid was determined. Together with the previously determined enthalpies of solution of H_3BO_3 in approximately 1 mol dm^{-3} HCl(aq), and of NaCl in aqueous (hydrochloric acid + boric acid), the standard molar enthalpy of formation of -2007.98 ± 0.84 J K^{-1} mol^{-1} for $Na_2B(OH)_4Cl$ was obtained from the standard molar enthalpies of formation NaCl(s), H_3BO_3(s), and H_2O(l). The standard molar entropy of formation of -700.59 J K^{-1} mol^{-1} and standard molar entropy of 190.62 J K^{-1} mol^{-1} for $Na_2B(OH)_4Cl$ were calculated from the thermodynamic relations. The group contribution method by Li is applicable to teepleite.

Keywords: $Na_2B(OH)_4Cl$; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy of solution; Aqueous hydrochloric acid solution

1. Introduction

Teepleite, being of structural formula $Na_2B(OH)_4Cl$ [1], is an important borate mineral found at several boron deposits around the world [2]. In former series papers on the thermochemistry of hydrated borates [3–10], we reported the standard molar enthalpies of hydrated magnesium, calcium, potassium, sodium, and lithium borates, as well as ulexite ($NaCa[B_5O_6(OH)_6]\cdot 5H_2O$) and $K_2O\cdot CaO\cdot 4B_2O_3\cdot 12H_2O$, and proposed a group contribution method to correlate and predict thermodynamic properties of hydrated borates. With group contribution method, once the structure of a hydrated borate is known, the unknown standard molar enthalpy of formation and standard molar Gibbs free energy of formation of this borate can be calculated from that of metal ions in aqueous solution, borate anions, and water molecules. The method can also be applied to double metal borates such as ulexite and $K_2O\cdot CaO\cdot 4B_2O_3\cdot 12H_2O$. But the applicability of group contribution method is not tested to other complicated borates consisted of multiple anions such as teepleite, because no experimental data are available. Here, we present the standard molar enthalpy of formation $\Delta_f H^0_m$ of teepleite and check if the group contribution method can apply. There is no report on the standard molar enthalpy of formation of teepleite in the literature.

2. Experimental

The $Na_2B(OH)_4Cl$ was synthesized at laboratory according to the isotherm of system $NaBO_2$–NaCl–H_2O at 20°C [11]. The synthetic sample was characterized by chemical analysis (Table 1), X-ray powder

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Table 1
The chemical composition of $Na_2B(OH)_4Cl$ (mass%)

	NaCl	$NaBO_2$	H_2O
Expected	36.12	40.59	22.96
Calculated	36.46	41.06	22.48

diffraction (Fig. 1), FT-IR spectrum (Fig. 2), FT-Raman spectrum (Fig. 3), and thermal analysis. The FT-IR spectrum was recorded on a Nicolet 170SX FT-IR spectrometer with KBr pellets; X-ray powder diffraction on a Rigaku D/MAX-B with Ni-filtered and Cu-radiation; FT-Raman spectrum on a Nicolet Raman 910; thermal analysis on a TA Instrument 2100 with the heating rate of 0.17 K s^{-1} at the N_2 flow rate of 2.5 cm^3 s^{-1}. All spectra are being of high quality and match existed data. The results show the sample is a pure compound being of formula of $Na_2B(OH)_4Cl$, and suitable for calorimetric experiment. The impurity corrections were unnecessary.

Thermochemical reaction designed for the derivation of $\Delta_f H^0_m$ of $Na_2B(OH)_4Cl$ as follows:

$$Na_2B(OH)_4Cl(s) + HCl(aq) = 2NaCl(s) + H_3BO_3(aq) + H_2O(l) \quad (1)$$

The standard molar enthalpy of formation of $Na_2B(OH)_4Cl$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of NaCl(s), H_3BO_3(s), and H_2O(l). The solution calorimetric procedure used here is similar to that used in our previous paper [7]. The H_3BO_3 and $Na_2B(OH)_4Cl$ were dissolved in approximately 1 mol dm^{-3} aqueous hydrochloric acid, respectively, then, the stoichiometric amount of substance of NaCl was dissolved in aqueous (hydrochloric acid + boric acid) which consisted of approximately 1 mol dm^{-3} HCl(aq) and the calculated amount of substance of H_3BO_3. The temperature of the calorimetric experiments was 298.15 ± 0.02 K.

In the previous paper, we have carried out the determination on the enthalpy of solution of H_3BO_3 in HCl(aq) [3], and NaCl(s) in aqueous (hydrochloric acid + boric acid) [5]. In this paper, we only determine $\Delta_{sol}H_m$ of $Na_2B(OH)_4Cl$ in HCl(aq). The aqueous HCl solution was prepared from analytical grade hydrochloric acid and deionized water, and its concentration was determined by titration with standard sodium carbonate.

An LKB 8700 precision calorimeter was used, and has been described in detail previously [3]. The calibrations were repeated after each experiment. There were no solid residues observed after the reactions in each calorimetric experiment.

3. Results and discussion

Table 2 presents the results of the calorimetric experiments. In this table, m is the mass of sample, $\Delta_{sol}H_m$ the molar enthalpy of solution of solute, and the uncertainty twice the standard deviation of the mean. Table 3 gives detailed thermochemical derivation of the standard molar enthalpy of formation of $Na_2B(OH)_4Cl$. The molar enthalpies of solution of H_3BO_3(s) of 21.83 ± 0.08 kJ mol^{-1} [3] in approximately 1 mol dm^{-3} HCl(aq), and of NaCl(s) of 5.14 ± 0.02 kJ mol^{-1} [5] in the mixture of HCl and H_3BO_3 were taken from our previous works separately. The enthalpy of dilution of HCl(aq) was calculated from NBS tables [12]. The standard molar enthalpies of formation of $-(285.830 \pm 0.040)$ kJ mol^{-1} for H_2O(l) and of $-(1094.8 \pm 0.8)$ kJ mol^{-1} for H_3BO_3(s) were taken from the CODATA key values [13], and of $-(411.153 \pm 0.100)$ kJ mol^{-1} for NaCl(s) from NBS Tables [14]. The standard molar enthalpy of formation of HCl(aq) was calculated from the NBS tables [14]. Therefore, the standard molar enthalpy of formation of $Na_2B(OH)_4Cl$ could be calculated and the result is $-(2007.98 \pm 0.84)$ kJ mol^{-1}.

Table 2
The molar enthalpies of solution $\Delta_{sol}H_m$ of $Na_2B(OH)_4Cl$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid at $T = 298.15$ K[a]

No.	m (mg)	$\Delta_{sol}H_m$ (kJ mol^{-1})
1	807.6	1.48
2	800.8	1.44
3	802.0	1.50
4	802.0	1.48
5	800.6	1.51
	Mean	1.48 ± 0.02[b]

[a] Determined with an LKB precision calorimeter; in each experiment, 100.10 cm^3 of HCl(aq) was used.
[b] Uncertainty is twice the standard derivation of the mean.

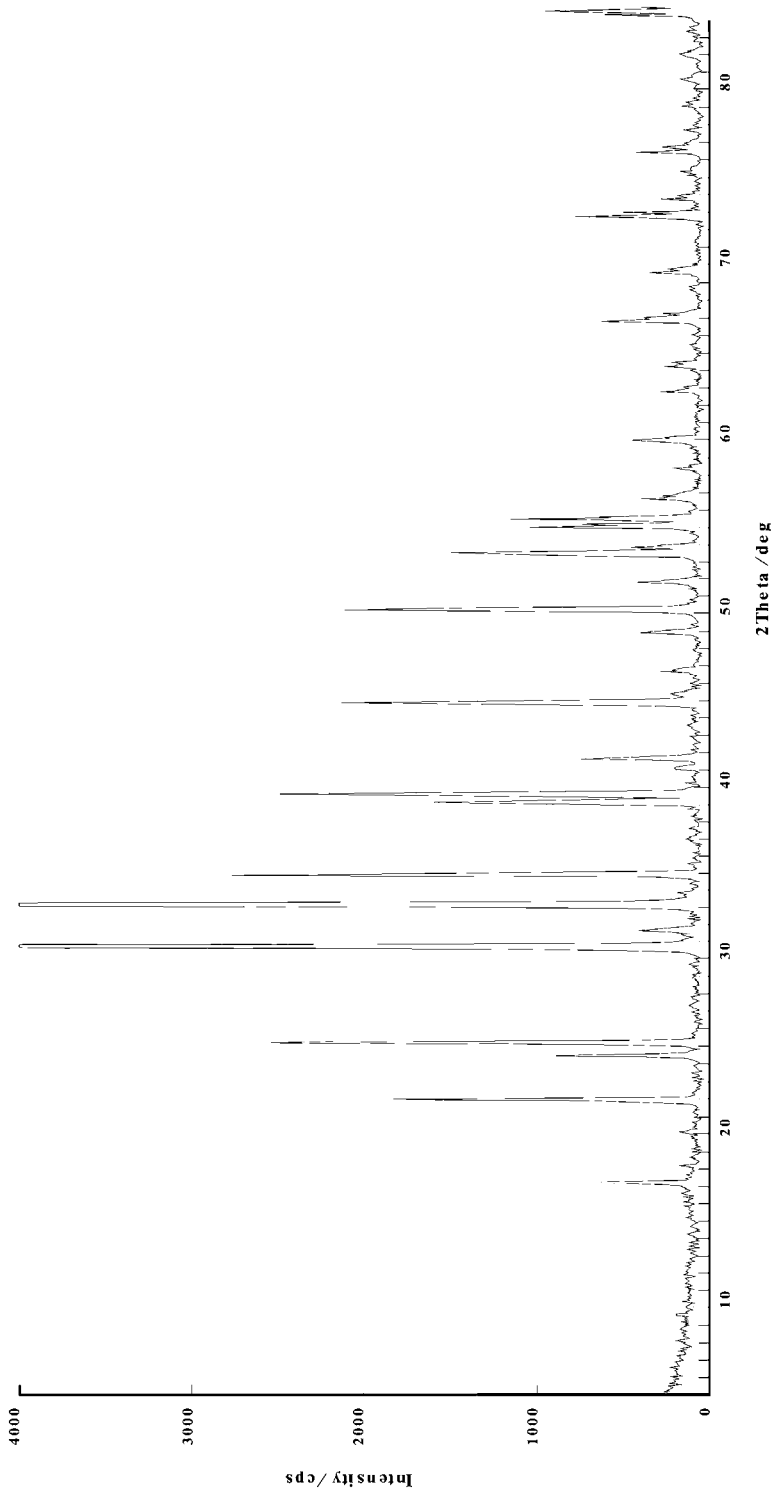

Fig. 1. The XRD of synthetic $Na_2B(OH)_4Cl$.

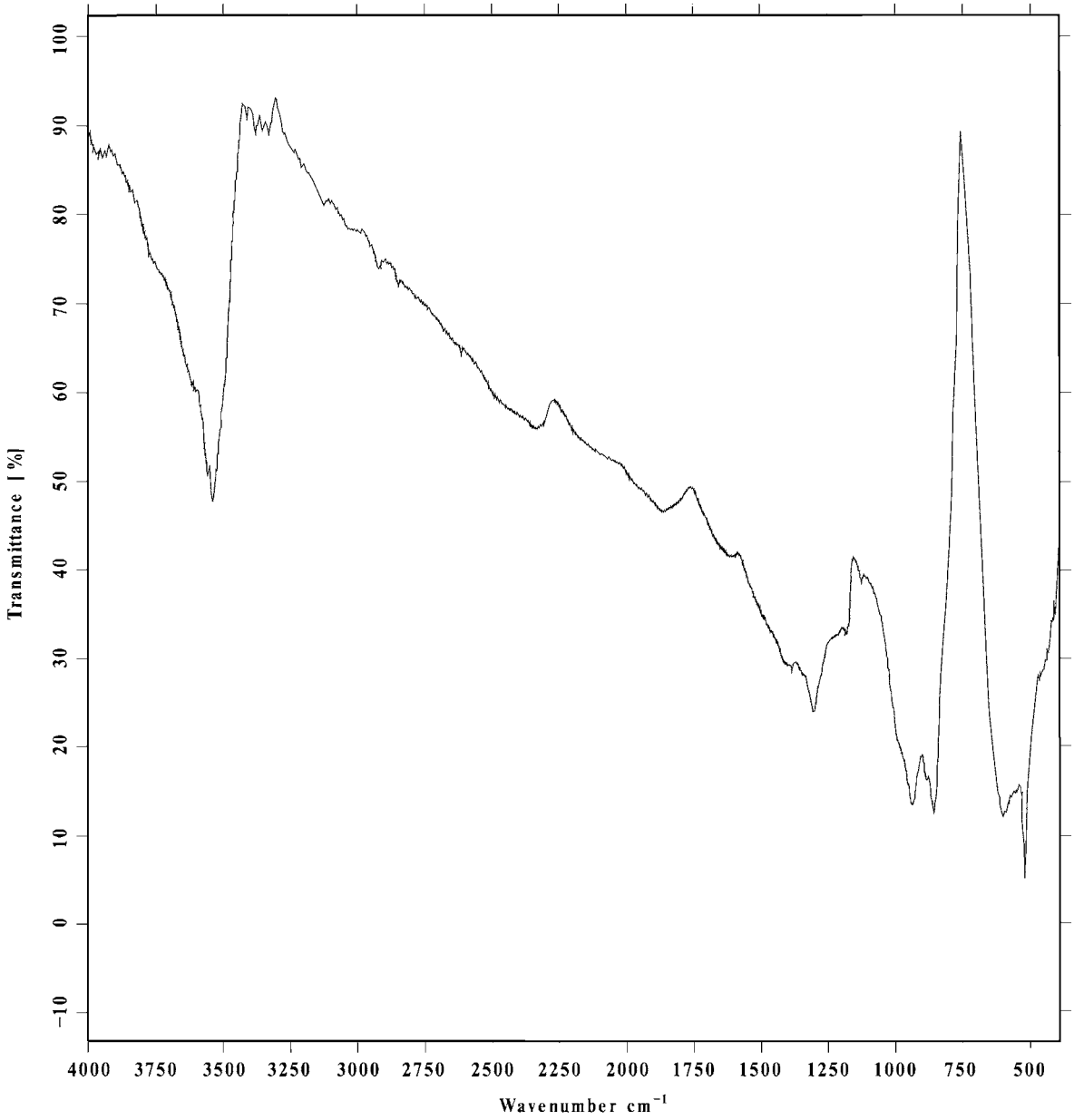

Fig. 2. The FT-IR spectrum of synthetic $Na_2B(OH)_4Cl$.

Combining with the $\Delta_f G^0_m$ of -1799.1 kJ mol^{-1} calculated from solubility data by Felmy and Weare [15], the standard molar entropy of formation of $Na_2B(OH)_4Cl$ was calculated to be -700.59 J K^{-1} mol^{-1}. Applying the group contribution method developed by Li [10] for the calculation of thermodynamic properties of hydrated borates, we calculated the $\Delta_f H^0_m$ and $\Delta_f G^0_m$ of $Na_2B(OH)_4Cl$ to be -1992.86 and -1814.88 kJ mol^{-1}, respectively, these two values agree with the experimental results quite well.

Finally, the standard molar entropy of $Na_2B(OH)_4Cl$ of 190.62 J K^{-1} mol^{-1} was obtained according to

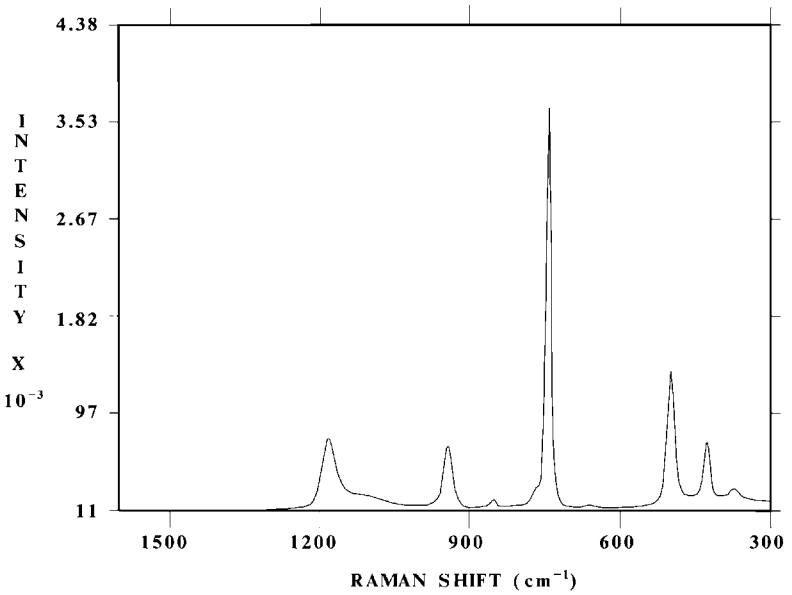

Fig. 3. The Raman spectrum of synthetic $Na_2B(OH)_4Cl$.

Table 3
Thermochemical derivation of $\Delta_f H^0_m$ ($Na_2B(OH)_4Cl$, 298.15 K)

No.	Reaction	$\Delta_f H_m$ (kJ mol^{-1})
1	$Na_2B(OH)_4Cl(s) + 20.96(HCl{\cdot}51.878H_2O) = 2Na^+(aq) + 2Cl^-(aq) + H_3BO_3(aq) + 19.96(HCl{\cdot}54.527H_2O)$	1.48 ± 0.02
2	$H_3BO_3(aq) + 19.96(HCl{\cdot}54.527H_2O) = H_3BO_3(s) + 19.96(HCl{\cdot}54.527H_2O)$	−21.83 ± 0.08
3	$2Na^+(aq) + 2Cl^-(aq) + H_3BO_3(aq) + 19.96(HCl{\cdot}54.527H_2O) = 2NaCl(s) + H_3BO_3(aq) + 19.96(HCl{\cdot}54.527H_2O)$	−10.28 ± 0.04
4	$20.96(HCl{\cdot}54.527H_2O) = 20.96(HCl{\cdot}51.878H_2O) + 55.527H_2O(l)$	1.10 ± 0.04
5	$0.5H_2(g) + 0.5Cl_2(g) + 54.527H_2O(l) = (HCl{\cdot}54.527H_2O)$	−165.42 ± 0.10
6	$2NaCl(s) = 2Na(s) + Cl_2(g)$	822.30 ± 0.20
7	$H_3BO_3(s) = B(s) + 1.5H_2(g) + 1.5O_2(g)$	1094.8 ± 0.8
8	$H_2O(l) = H_2(g) + 0.5O_2(g)$	285.83 ± 0.04
9	$Na_2B(OH)_4Cl(s) = 2Na(s) + 0.5Cl_2(g) + B(s) + 2H_2(g) + 2O_2(g)$	2007.98 ± 0.84

reaction (9) in Table 3. The standard molar entropies of the elements were taken from the CODATA key values [13] as 51.30, 222.972, 5.90, 130.571, and 205.043 J K^{-1} mol^{-1} for Na(s), Cl_2(g), B(s), H_2(g), and O_2(g), respectively.

References

[1] H. Effenberger, Acta Crystallogr. B 38 (1982) 82.
[2] X.D. Xie, M.P. Zheng, L.B. Liu, Borate Minerals, Science Press, Beijing, 1965.
[3] J. Li, Sh.Y. Gao, Sh.P. Xia, B. Li, R.Z. Hu, J. Chem. Thermodyn. 29 (1997) 491.
[4] J. Li, Sh.Y. Gao, Sh.P. Xia, B. Li, R.Z. Hu, J. Chem. Thermodyn. 29 (1997) 1071.
[5] J. Li, B. Li, Sh.Y. Gao, J. Chem. Thermodyn. 30 (1998) 425.
[6] J. Li, B. Li, Sh.Y. Gao, J. Chem. Thermodyn. 30 (1998) 681.
[7] R.Y. Chen, J. Li, Sh.P. Xia, Sh.Y. Gao, Thermochim. Acta 306 (1997) 1.
[8] Y.Zh. Jia, J. Li, Sh.Y. Gao, Sh.P. Xia, Thermochim. Acta 335 (1999) 1.

[9] Y.Zh. Jia, J. Li, Sh.Y. Gao, Sh.P. Xia, J. Chem. Thermodyn. 31 (1999) 1605.
[10] J. Li, B. Li, Sh.Y. Gao, J. Phys. Chem. Mineral. 27 (2000) 342.
[11] V.G. Skvortsov, R.S. Tsekhanskii, A.M. Gavrilov, Russ. J. Inorg. Chem. 21 (2) (1976) 315.
[12] V.B. Parker, Thermal Properties of Aqueous Uni-univalent Electrolytes, Natl. Stand. Ref. Data Ser.-NSRDS-NBS 2, 1965.
[13] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.
[14] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, R.L. Nuttall, J. Phys. Chem. Ref. Data, Suppl. 2 (1982) 11.
[15] A.R. Felmy, J.H. Weare, Geochim. Cosmochim. Acta 50 (1986) 2771.