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Dissolution Enthalpy and Thermodynamic Properties of $NaB_5O_8 \cdot 5H_2O$

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Abstract: Thermodynamic parameters of different borates, such as the dissolution enthalpy (ΔH_s), the standard enthalpy of formation (ΔH_f^θ), the standard entropy of formation (ΔS_f^θ) and the standard Gibbs free energy (ΔG_f^θ) are essential to enrich and develop the boron chemistry theory of salt lakes. In the present work, the dissolution enthalpy (ΔH_s) of sodium pentaborate pentahydrate ($NaB_5O_8 \cdot 5H_2O$) at 298.15 K and 101.325 kPa was measured using microcalorimeter. Based on the designed thermochemical cycles and the basic formulae of thermodynamics, the standard enthalpy of formation (ΔH_f^θ), the standard entropy of forma1tion (ΔS_f^θ) and the standard Gibbs free energy (ΔG_f^θ) of $NaB_5O_8 \cdot 5H_2O$ were obtained for the first time, and the results are in order with $-5\,189.482\,0$ kJ·mol^{-1}, $701.272\,8$ J·mol^{-1}·K^{-1}, $-5\,398.566\,5$ kJ·mol^{-1}, respectively. These basic thermodynamic parameters obtained in this work are of great significance in enriching the thermodynamic data of inorganic salts and promoting the comprehensive utilization of salt lake resources.

Key words: Dissolution enthalpies; Sodium borates; Standard enthalpy of formation; Standard entropy of formation; Standard Gibbs free energy

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1 Introduction

In the Qinghai-Tibet Plateau, China, over 700 salt lakes with an area of larger than 1 km^2 hold high boron reverse[1-2]. The exploitation of boron resources is mainly distributed in Turkey, the United States, Argentina, and other countries. Although boron resources are abundant in China, 70% of boron is obtained by the evaporation method, which is faced with the dilemma of high storage, low production, and low utilization rate[3]. Boron and its com-

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pounds are widely used in glass technology, ceramic technology, detergent production and agricultural fertilizer, accounting for about 75% of the global consumption of boron resources each year[4]. The study of thermodynamic properties is conducive to the comprehensive utilization of boron in salt lake brine. Remarkably, the enthalpy of the inorganic salt solution containing borate ions is not only of great significance for understanding the thermodynamic behavior of borates in natural systems, including the ionic interaction between solutes and solvents and the influence of ionic strength, but also provides basic data for predicting the crystallization and evaporation behavior of these salts[5]. At the same time, sodium pentaborate crystal has unique physical and chemical properties[6], and it is also commonly used in medicine, biology and the chemical industry[7-8].

In the present work, the dissolution enthalpies of $NaB_5O_8 \cdot 5H_2O$ were determined, and their thermodynamic parameters, including the standard enthalpy of formation (ΔH_f^θ), the standard entropy of formation (ΔS_f^θ) and the standard Gibbs free energy (ΔG_f^θ) were systematically studied, which have been reported for the first time.

2 Experimental section

2.1 Materials

The purity and purification methods of the chemicals used in this work show in Table 1.

Table 1 Chemicals used in the study

Chemicals	CAS Reg. No.	Purity in mass fraction	Purification method	Final mass fraction purity	Analysis method
[a] KCl	7447-40-7	0.999 9	No furtherpurification	0.999 9	Titration for Cl^-
[b] $NaB_4O_7 \cdot 10H_2O$	1303-96-4	0.995	Re-crystallization	0.999	Gravimetric method for boron
[b] H_3BO_3	52869-79-1	0.99	Re-crystallization	0.996	Gravimetric method for boron
[c] $NaB_5O_8 \cdot 5H_2O$	-	0.99	Re-crystallization	0.997	Gravimetric method for boron

[a] A. R. from Aladdin Industrial Corporation

[b] A. R. from Sinopharm Chemical Reagent Co. Ltd

[c] Synthesized in our laboratory

KCl is from Aladdin Industrial Corporation, and $NaB_5O_8 \cdot 5H_2O$ was synthesized using H_3BO_3 and $NaB_4O_7 \cdot 10H_2O$ according to previous work[6]. Briefly, a certain amount of $NaB_4O_7 \cdot 10H_2O$, H_3BO_3, and CO_2-free deionized distilled water were added into the beaker and stirred evenly at 298.15 K. Then, the solution was transferred to the reactor and reacted for 7 days at 333.15 K under stirring. Finally, $NaB_5O_8 \cdot 5H_2O$ was obtained by separation, re-crystallization, filtration, washing, and drying at 308.15 K. The chemical synthesized was identified by X-ray diffraction (PERSEE XD-3 polycrystalline X-ray diffractometer with Cu-Kα radiation at 4°/min), and the results were shown in Fig. 1. The purity of $NaB_5O_8 \cdot 5H_2O$ is 0.996 by chemical analysis, theoretical and experimental values of Na_2O, B_2O_3 and H_2O in mass fraction with the ratio values of $Na_2O:B_2O_3:H_2O$ were shown in Table 2. Double deionized water (DDW) for experiments, which was produced by ULUP-II-10T (Chongqing Jiuyang Co. Lt., China) with a conductivity below 1×10^{-4} S·m^{-1}.

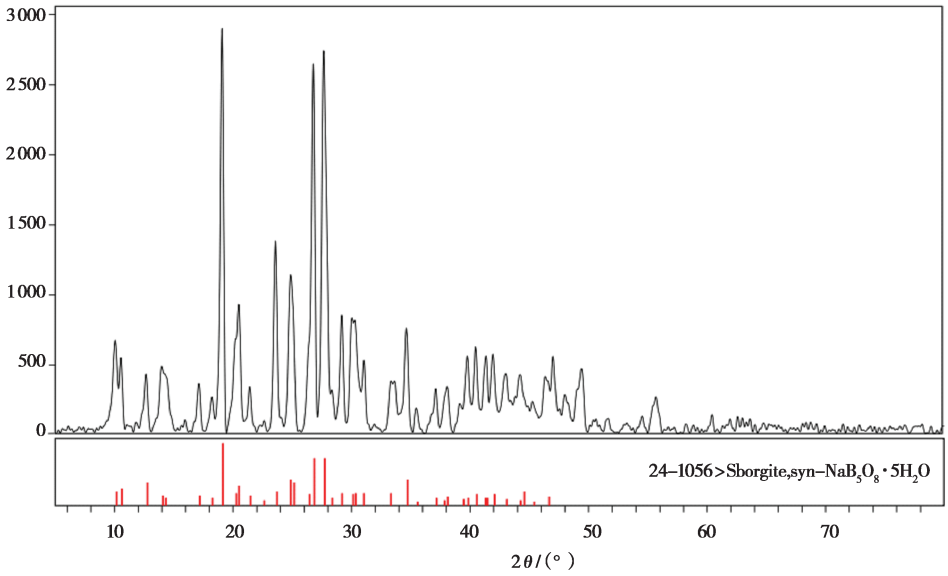

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Fig. 1　The X – ray diffraction pattern of $NaB_5O_8 \cdot 5H_2O$

Table 2　Chemical analytical result of sodium pentaborate pentahydrate in a mass fraction [a]

$NaB_5O_8 \cdot 5H_2O$	Mass fraction purity [b]	Na_2O	B_2O_3	H_2O	$n(Na_2O:B_2O_3:H_2O)$
Experimental	0.996	0.104 7	0.590 0	0.306 0	1:4.99:10.03
Theoretical	1	0.105 1	0.590 2	0.305 2	1:5:10

[a] Standard uncertainties are $u(Na_2O) = 0.008\ 5$, $u(B_2O_3) = 0.001\ 9$, $u(H_2O) = 0.006\ 1$ in mass fraction

[b] Purity in mass fraction

2.2　Instruments and measurements

The dissolution enthalpy of $NaB_5O_8 \cdot 5H_2O$ at 298.15 K was determined by the calorimetry method. The instrument used in this study was a microcalorimeter TAM IV (T. A. Instruments Company, New Castle, Delaware, USA), with an operating temperature range of 277.15 to 423.15 K, and the temperature control accuracy can reach $\pm 10^{-6}$ K[9]. Its unparalleled temperature stability can ensure the accurate measurement of the heat flow signal. The structure is shown in Fig. 2. The calorimeter has good stability and accuracy, and short – range noise is 100 nW, accuracy is 2%, precision is 100 nW. Before the experiment, calibration experiments are needed to verify the accuracy of the calorimeter. The dissolution enthalpy of KCl was measured at 298.15 K. The results showed that the average value measured by the calorimeter was consistent with that reported in the literature[10]. The results are shown in Table 3, and the error was less than 0.1%, indicating that the instrument and measurement were reliable.

The concentration of boron was determined by the gravimetric methods with standard uncertainty ±0.000 5 in mass fraction. The concentration of Na^+ was determined by the ICP – OES (Prodigy, Leman Corporation, USA) method with the uncertainty of ±0.5%[11].

Before the experiment, the adjusted instrument kept the temperature stable at 298.15 K. Quantitative $NaB_5O_8 \cdot 5H_2O$ was weighed by analytical balance (METTLER TOLEDO, New Classic MS105) and added into the sample cell, quantitative DDW was added into the reaction cell, and then the instrument was assembled. Adjust the speed of 120 r/min until the heat flow signal is stable, let the sample cell into the reaction cell, and the heat flow signal will cause mutation until the heat flow signal is stable for adequate time, the end of the experiment. Data analysis was performed using TAM IV analysis software on the computer. Seven parallel experiments were performed,

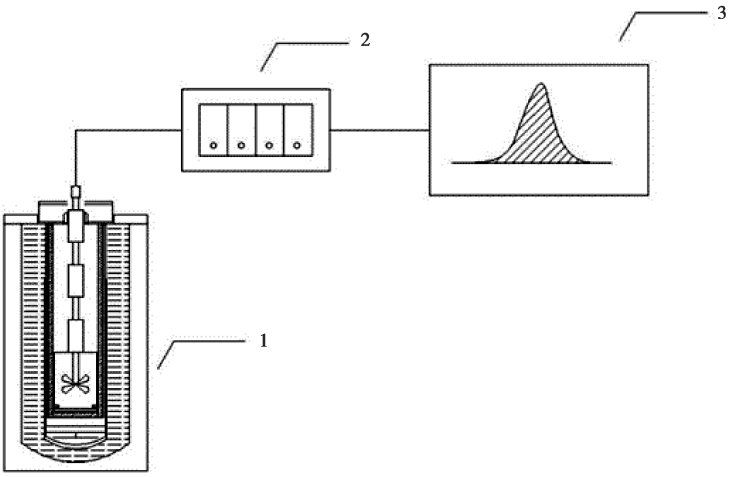

Fig. 2 Schematic diagram of microcalorimeter TAM IV

(1. Host; 2. Control system; 3. Signal sampling and processing system)

Table 3 The dissolution enthalpy for KCl(s) at 298.15 K and 101.325 kPa [a]

No.	1	2	3	4	5
m / mg	131.64	33.92	32.42	28.28	20.32
ΔH / (kJ·mol^{-1}) [b]	17.533	17.580	17.581	17.609	17.558
Ave / (kJ·mol^{-1})			17.572 ± 0.021		
Ref. [10] / (kJ·mol^{-1})			17.586 ± 0.017		

[a] Standard uncertainties u are $u(m)$ = 0.002 mg, $u(T)$ = ±0.01 K, $u(p)$ = ±5 kPa

[b] $u(\Delta H)$ = 0.021 kJ·mol^{-1}

and the relative error is needed to be within 0.2%.

3 Results and discussion

3.1 Dissolution enthalpies

The results of dissolution enthalpy for $NaB_5O_8 \cdot 5H_2O$ at 298.15 K and the heat flow diagrams of the dissolution process are shown in Table 4 and Fig. 3, respectively. The average values of dissolution enthalpies were calculated by the data of seven parallel experiments with a relative error of less than 0.65%. According to Table 4, $NaB_5O_8 \cdot 5H_2O$ has a more significant positive dissolution enthalpy, which is not conducive to the dissolution of $NaB_5O_8 \cdot 5H_2O$ in water, so the solubility is significantly low also, which is consistent with the data in the literature[12-13]. As shown in Fig. 3, the curves indicate that $NaB_5O_8 \cdot 5H_2O$ in water are endothermic for the macroscopic analysis.

Table 4 Dissolution enthalpies of $NaB_5O_8 \cdot 5H_2O$ at 298.15 K and 101.325 kPa [a]

No.	n / (mol × 10^{-5})	m / (mmol · kg^{-1})	ΔH_s / (kJ·mol^{-1}) [b]
1	4.993	2.930 9	−80.119
2	7.491	4.671 7	−80.475
3	6.701	4.179 2	−80.579
4	8.656	5.297 3	−80.633
5	5.084	2.984 7	−80.634
6	4.460	2.781 9	−80.710
7	6.779	3.979 6	−81.136
ΔH_{ave} / (kJ·mol^{-1})		−80.612	

[a] Standard uncertainties u are $u(m)$ = 0.009 mmol·kg^{-1}, $u(T)$ = 0.01 K, $u(p)$ = 5 kPa

[b] $u(\Delta H)$ = 0.302 kJ·mol^{-1}

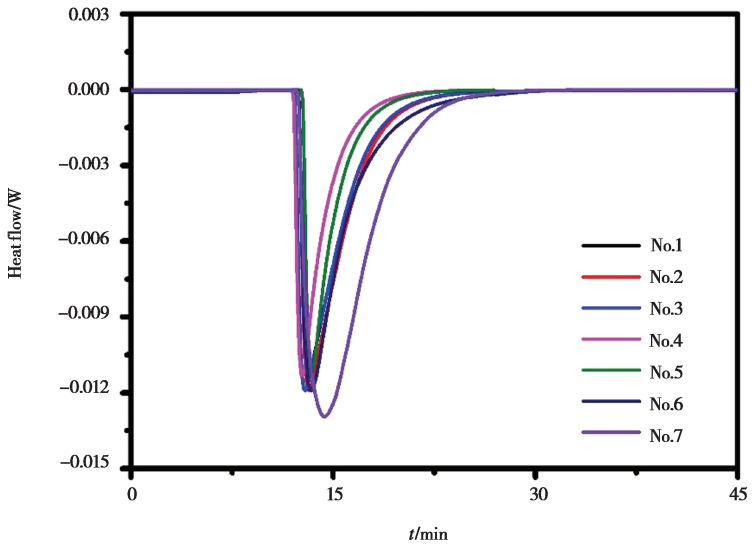

Fig. 3　Heat flow diagram of dissolution process for $NaB_5O_8 \cdot 5H_2O$ of seven parallel experiments

3.2　Thermodynamic functions

According to the principles of thermochemistry, the thermochemical cycles of $NaB_5O_8 \cdot 5H_2O$ were designed and shown in Fig. 4. Then the Eqs. 1 to 3 can be obtained based on the thermochemical cycles in Fig. 4.

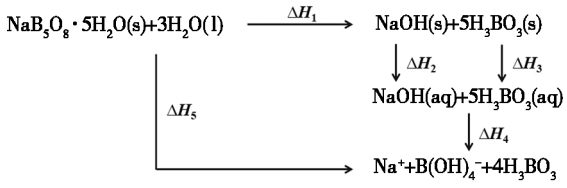

Fig. 4　Thermochemical cycle of $NaB_5O_8 \cdot 5H_2O(s)$

$$\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 \quad (1)$$

$$\Delta H_1 = \Delta H_5 - \Delta H_2 - \Delta H_3 - \Delta H_4 \quad (2)$$

$$\Delta H_1 = \Delta H^{\theta}_{f,NaOH} + 5\Delta H^{\theta}_{f,H_3BO_3} - \Delta H^{\theta}_{f,NaB_5O_8 \cdot 5H_2O} - 3\Delta H^{\theta}_{f,H_2O} \quad (3)$$

The dissolution enthalpies of NaOH and H_3BO_3 are -44.5 kJ·mol^{-1} (ΔH_2) and 20.92 kJ·mol^{-1} (ΔH_3), respectively[14]. The mean value of the neutralization heat for the reaction of NaOH(aq) and H_3BO_3(aq) is 1.803 mJ·mol^{-1}, which is the average of five parallel experiments. The values of $\Delta H^{\theta}_{f,NaOH}$, $\Delta H^{\theta}_{f,H_3BO_3}$ and $\Delta H^{\theta}_{f,H_2O}$ are -470.11 kJ·mol^{-1}, $-1\,094.534$ kJ·mol^{-1} and -285.83 kJ·mol^{-1}[10,14]. Combining Eqs. 1 to 3, $\Delta H^{\theta}_{f,NaB_5O_8 \cdot 5H_2O}$ can be obtained with $-5\,189.482\,0$ kJ·mol^{-1}.

The van't Hoff equation reflects the relationship between the equilibrium constant of a reaction and the temperature in a real solution, which is expressed as Eq. 4[15]:

$$\ln k = \frac{\Delta H^{\theta}_s}{R.\,T} + \frac{\Delta S^{\theta}_s}{R} \quad (4)$$

Where R is the ideal gas constant for 8.314 J·mol^{-1}·K^{-1}; T is temperature with 298.15 K; k is the equilibrium constant; ΔH^{θ}_s is the dissolution enthalpy and ΔS^{θ}_s is the dissolution entropy.

Due to the low solubility of NaB_5O_8, the activity of NaB_5O_8(aq) can be approximately expressed with its solution concentration. The solubility of NaB_5O_8 at 298.15 K is 0.413 3 mol·L^{-1}[13], so the equilibrium constant (k) can be calculated according to the dissolution equilibrium equation. Therefore, the dissolution entropy of $NaB_5O_8 \cdot 5H_2O$ could be calculated with $-32.097\,8$ kJ·mol^{-1}·K^{-1} according to Eq. 4.

According to the data in the literature[16], the standard molar formation entropies of Na^+, $B(OH)_4^-$, H_3BO_3 and H_2O are 69.76, 159.665, 162.4 and 69.95 J·mol^{-1}·K^{-1}, respectively. Based on the principle of thermochemical cycles and Eq. 5, the entro-

py of formation of $NaB_5O_8 \cdot 5H_2O$ could be calculated with 701.272 8 J·mol^{-1}·K^{-1}. Finally, the standard Gibbs free energy of $NaB_5O_8 \cdot 5H_2O$ was obtained with −5 398.566 5 kJ·mol^{-1} using Eq. 6.

$$\Delta S^{\theta}_{S,NaB_5O_8 \cdot 5H_2O} = \Delta S^{\theta}_{f,Na^+} + \Delta S^{\theta}_{f,B(OH)_4^-} + 4\Delta S^{\theta}_{f,H_3BO_3} - \Delta S^{\theta}_{S,NaB_5O_8 \cdot 5H_2O} - 3\Delta S^{\theta}_{f,H_2O} \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

4 Conclusions

The dissolution enthalpy, the standard enthalpy of formation, the entropy of formation, and the standard Gibbs free energy of $NaB_5O_8 \cdot 5H_2O$ at 298.15 K were obtained for the first time. The phenomenon and mechanism of dissolving processes are helpful to study the thermal behavior of inorganic salts and find proper methods for new chemical material synthesis. These thermodynamic properties are worth understanding the ion − interaction between solute − solvent and the effects of ion strength and temperature against excess free energy to provide fundamental data in predicting the crystallizing and evaporating behaviors of salt lake brine.

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Research Progress on the Adaptation of Halophytes to Salt Stress in Germination Stage

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Abstract: At present, the area of saline land in our country is relatively large, especially on the Qinghai-Tibet Plateau, which is often accompanied by arid and semi-arid habitats, making it difficult for plants to grow and the ecological environment is getting worse. This ecological status quo needs to be resolved urgently. Halophytes have a certain degree of salt tolerance and drought tolerance. They are the preferred plants to improve saline soil. The vigor of seeds determines the germination of seeds. Most researchers studied on introduction of halophytes in order to improve the severe ecological environment. There are direct methods and indirect methods to determine seed vigor. Most researchers use direct methods, that is, simulating certain conditions in the laboratory to directly determine the germination rate. This paper briefly describes the general situation of halophytes, the main methods for producing stress, and the indicators for detecting seed vigor, and summarizes the opinions on 22 typical halophytes such as salt claw and *Nitraria* during seed germination. The study on salt tolerance and drought resistance provides a theoretical basis for improving the ecological environment of saline land and increasing the production of saline land.

Key words: Halophytes; Seed; Salt stress; Drought stress

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五水合五硼酸钠溶解热测定及其热力学性质

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摘 要: 不同形态硼酸盐焓、熵、吉布斯自由能等热力学参数极为缺乏, 其准确测定对丰富和发展盐湖硼酸盐化学理论至关重要。采用微量热计测定了五水合五硼酸钠($NaB_5O_8 \cdot 5H_2O$)溶解热。根据设计的热化学循环和热力学基本公式, 获得了 $NaB_5O_8 \cdot 5H_2O$ 在 298.15 K 下标准生成焓($\Delta H^{\theta}_{f,NaB_5O_8 \cdot 5H_2O}$, −5 189.482 0 kJ·mol^{-1})、标准生成熵($\Delta S^{\theta}_{f,NaB_5O_8 \cdot 5H_2O}$, 701.272 8 J·mol^{-1}·K^{-1})、标准生成吉布斯自由能($\Delta G^{\theta}_{f,NaB_5O_8 \cdot 5H_2O}$, −5 398.566 5 kJ·mol^{-1})等热力学参数。这些基础热力学参数的获得对丰富无机盐热力学数据和促进盐湖资源综合利用具有重要意义。

关键词: 溶解焓; 硼酸钠; 标准生成焓; 标准生成熵; 标准吉布斯自由能