

Thermochemistry of ulexite

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Received 26 June 1997; received in revised form 4 August 1997; accepted 19 August 1997

Abstract

The enthalpy of solution of ulexite $\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6]\cdot 5\text{H}_2\text{O}$ in $\approx 1 \text{ mol dm}^{-3}$ aqueous hydrochloric acid has been measured. From this result and the enthalpies of solution of H_3BO_3 in $\text{HCl}(\text{aq})$, of CaO in aqueous (hydrochloric acid + boric acid), and of NaCl in aqueous (hydrochloric acid + boric acid + calcium oxide), the standard molar enthalpy of formation of ulexite of $-6762.24 \pm 4.22 \text{ kJ mol}^{-1}$ has been obtained. The standard molar entropy of formation of ulexite was calculated from the thermodynamic relation with the standard molar Gibbs free energy of formation of ulexite computed from its solubility in water. © 1997 Elsevier Science B.V.

Keywords: Molar enthalpy of solution; Solution calorimetry; Standard molar enthalpy of formation; Ulexite

1. Introduction

Ulexite has been discovered in many places in the world (e.g. Qinghai – Tibetan plateau, P.R. China; Inder Lake in Turkmenistan; the north of Chile; California desert of the United State; Turkey, etc.). At present, it is commonly used for the production of fire-proof substances, insulators, and fiberglass [1]. Ulexite is a borate composed of sodium and calcium and exists in $\text{Na}_2\text{O}-\text{CaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ quaternary system [2]. The main studies about this mineral concentrated on its reaction with various media [2–6] and thermal decomposition behavior [7–9], thus there is no report on the standard molar enthalpy of formation of ulexite in literature. Thermochemical properties of hydrated borates have been studied to some extent

[10,11]. Bassett [12] calculated the standard molar Gibbs free energy of formation of ulexite from its solubility in water. In this paper, the standard molar enthalpy of formation of ulexite $\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6]\cdot 5\text{H}_2\text{O}$ has been studied by solution calorimetry, and the other thermochemical properties have been calculated.

2. Experimental

Ulexite sample was synthesized according to the improved method given in the literature [2]. The reagents used in synthesis were analytical grade (made in P.R. China). The cold saturated solution of borax (250.0 ml) were mixed with the saturated solution of CaCl_2 (200.0 ml) to form amorphous precipitate, then the solid phase was filtered, washed with water, and dried at 105°C . The pH value of the mixture of 40.0 g

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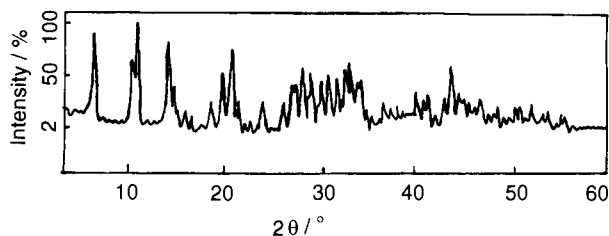


Fig. 1. The XRD of synthetic ulexite. X-axis label – 2θ in degrees; and Y-axis label — Intensity in %.

amorphous precipitate, 40.0 g boric acid and 450.0 g sodium chloride in 2.5 l water was adjusted to 9.0–9.5 with 5 M NaOH. The solid transformed from amorphous precipitate to ulexite crystal in a few days. After 15 days, the ulexite crystals were filtered and washed successively with pure water and a solution containing 50% alcohol, finally with absolute alcohol, and dried to constant weight at 40°C. The result of X-ray powder diffraction (Rigaku D/MAX-2400, Ni-filtered, Cu-radiation) and FTIR (Nicolet 170sx FTIR spectrometer, KBr pellets) showed no other phases present in the sample (Figs. 1 and 2). The sample was analyzed according to the standard methods as follows: Calcium was titrated by a standard solution of Na-EDTA in an alkaline condition by the addition of ($\text{NH}_3 + \text{H}_2\text{O} + \text{NH}_4\text{Cl}$) buffer solution, boron by a standard solution of NaOH in the presence of mannitol, and sodium was determined by spectrophotometric method [13], H_2O by thermal dehydration (TA 2100 Instrument, N_2 flow and 2.5 K min^{-1} heating rate). The composition of ulexite is given in Table 1. It is shown that the synthetic sample having a formula $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$ is suitable for the calorimetric experiment, and there was no need for impurity corrections.

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Table 1
The chemical composition of ulexite (wt %)

	Na_2O	CaO	B_2O_3	H_2O	Total
Analytical	7.60	13.86	42.96	35.50 ^a	99.92
Theoretical	7.65	13.85	42.95	35.55	100.00

^a Determined by thermal analysis method.

Table 2
The molar enthalpies of solution $\Delta_{\text{sol}}H_m$ of ulexite in $\approx 1 \text{ mol dm}^{-3}$ aqueous hydrochloric acid at $T = 298.15 \text{ K}$.^a

No.	m/mg	$\Delta_{\text{sol}}H_m / (\text{kJ mol}^{-1})$
1	407.5	46.28
2	406.8	46.39
3	405.7	46.55
4	405.8	45.97
5	409.0	46.48
	mean	46.33 ± 0.20 ^b

^a Determined with an LKB precision calorimeter; in each experiment, 100.10 cm^3 of $\text{HCl}(\text{aq})$ was used.

^b Uncertainty is twice the standard deviation of the mean.

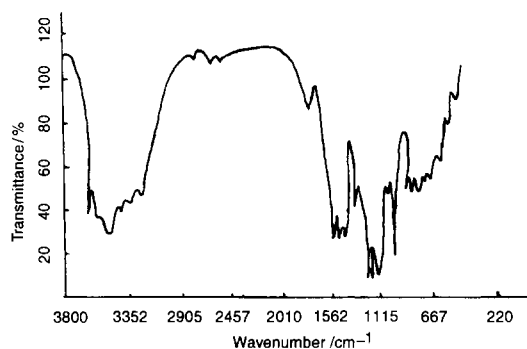


Fig. 2. The IR spectrum of synthetic ulexite: X-axis label – Wavenumber in cm^{-1} ; and Y-axis label – transmittance in %.

Table 3
The molar enthalpies of solution $\Delta_{\text{sol}}H_m$ of NaCl in aqueous (hydrochloric acid + boric acid + calcium oxide) at $T = 298.15 \text{ K}$.^a

No.	m/mg	$\Delta_{\text{sol}}H_m / (\text{kJ mol}^{-1})$
1	58.4	5.16
2	58.8	5.17
3	58.0	5.18
4	58.8	5.18
	mean	5.17 ± 0.01 ^b

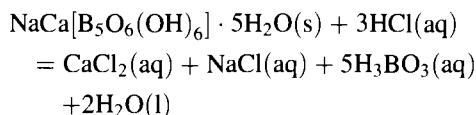
^a Determined with an LKB precision calorimeter; in each experiment, 100.10 cm^3 of $\text{HCl}(\text{aq})$ was used.

^b Uncertainty is twice the standard deviation of the mean.

Table 4
Thermochemical cycles and results for the derivation of $\Delta_f H_m^\ominus$ {NaCa[B₅O₆(OH)₆]·5H₂O, 298.15 K}

Reaction	$\Delta_f H_m^\ominus$ /(kJ mol ⁻¹)
1. NaCa[B ₅ O ₆ (OH) ₆]·5H ₂ O(s) + 100.54(HCl·54.656H ₂ O) = Na ⁺ (aq) + Ca ²⁺ (aq) + 3Cl ⁻ (aq) + 5H ₃ BO ₃ (aq) + 97.54(HCl·56.357H ₂ O)	46.33 ± 0.20
2. 5H ₃ BO ₃ (aq) + 99.54(HCl·55.225H ₂ O) = 5H ₃ BO ₃ (s) + 99.54(HCl·55.225H ₂ O)	-109.15 ± 0.4 0
3. Ca ²⁺ (aq) + 2Cl ⁻ (aq) + 5H ₃ BO ₃ (aq) + 97.54(HCl·56.357H ₂ O) = CaO(s) + 5H ₃ BO ₃ (aq) + 99.54(HCl·55.225H ₂ O)	188.63 ± 0.88
4. Na ⁺ (aq) + Ca ²⁺ (aq) + 3Cl ⁻ (aq) + 5H ₃ BO ₃ (aq) + 97.54(HCl·56.357H ₂ O) = NaCl(s) + Ca ²⁺ (aq) + 2Cl ⁻ (aq) + 5H ₃ BO ₃ (aq) + 97.54(HCl·56.357H ₂ O)	-5.17 ± 0.01
5. 100.54(HCl·55.225H ₂ O) = 100.54(HCl·54.656H ₂ O) + 57.225H ₂ O(l)	1.13 ± 0.04
6. (1/2)H ₂ (g) + (1/2)Cl ₂ (g) + 55.225H ₂ O(l) = (HCl·55.225H ₂ O)	-165.43 ± 0.0 8
7. NaCl(s) = Na(s) + (1/2)Cl ₂ (g)	411.15 ± 0.10
8. CaO(s) = Ca(s) + (1/2)O ₂ (g)	634.92 ± 0.90
9. 5H ₃ BO ₃ (s) = 5B(s) + (15/2)H ₂ (g) + (15/2)O ₂ (g)	5474.00 ± 4.0 0
10. H ₂ O(l) = H ₂ (g) + (1/2)O ₂ (g)	285.83 ± 0.04
11. NaCa[B ₅ O ₆ (OH) ₆]·5H ₂ O(s) = Na(s) + Ca(s) + 5B(s) + 8H ₂ (g) + (17/2)O ₂ (g)	6762.24 ± 4.2 2

Thermochemical reaction of ulexite with $\approx 1 \text{ mol dm}^{-3}$ HCl(aq) would be written as follows:



In addition, auxiliary determinations of the enthalpies of solution H_3BO_3 in $\approx 1 \text{ mol dm}^{-3}$ HCl(aq), of CaO in aqueous (hydrochloric acid + boric acid), and of NaCl in aqueous (hydrochloric acid + boric acid + calcium oxide) were carried out.

High-purity CaO (mass fraction > 0.9999, made in P.R. China) was heated at 1098 K for 3 h, and stored in a desiccator. The CaO was sealed in a glovebox containing P_2O_5 drying reagent. High-purity Ar gas was admitted to the glovebox to expel the air before sealing. The NaCl (mass fraction > 0.999, made in P.R. China) was heated at 623 K for 3 h, and stored in a desiccator. The H_3BO_3 (Merck, mass fraction > 0.998) was used without further purification. The HCl solvent was prepared from analytical grade hydrochloric acid and deionized water, and analyzed by titration with standard sodium carbonate.

An LKB 8700 precision calorimeter was used, and has been described in detail elsewhere [10]. The calibrations were repeated after each experiment, and the average calibration constant was used. There were no solid residues observed after reaction in any of the calorimetric experiments.

3. Results and discussion

Tables 2 and 3 present the results of the calorimetric experiments. In these tables, m is the mass of sample, $\Delta_{\text{sol}}H_m$ is the molar enthalpy of solution of solute, and the uncertainty is twice the standard deviation of the mean. Table 4 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of ulexite, the enthalpy of dilution of HCl(aq) was calculated from the NBS table [14], the molar enthalpies of solution of H_3BO_3 of $21.83 \pm 0.08 \text{ kJ mol}^{-1}$ in HCl(aq), and of CaO of $-188.83 \pm 0.88 \text{ kJ mol}^{-1}$ in the mixture of HCl and H_3BO_3 were taken from our previous works separately [10, 11]. The standard molar enthalpies of formation of $\text{H}_2\text{O}(\text{l})$, CaO(s), and $\text{H}_3\text{BO}_3(\text{s})$ were taken from the CODATA Key Values

[15], namely $-285.830 \pm 0.040 \text{ kJ mol}^{-1}$, $-634.92 \pm 0.90 \text{ kJ mol}^{-1}$, and $-1094.8 \pm 0.8 \text{ kJ mol}^{-1}$, and of NaCl from the NBS table [16], namely $-411.15 \pm 0.10 \text{ kJ mol}^{-1}$. Therefore, the standard molar enthalpy of formation of ulexite could be calculated, the result being $-6762.24 \pm 4.22 \text{ kJ mol}^{-1}$.

The standard molar Gibbs free energy of formation of ulexite has been calculated from its solubility in water [12], to be $-6045.06 \text{ kJ mol}^{-1}$. Combining the standard molar enthalpy of formation of ulexite, the standard molar entropy of formation of ulexite has been calculated at $-2045.43 \text{ J K}^{-1} \text{ mol}^{-1}$ according to following equation:

$$\Delta_f S_m^0 = (\Delta_f H_m^0 - \Delta_f G_m^0)/T$$

Finally, the standard molar entropy of ulexite has been calculated to be $864.40 \text{ J K}^{-1} \text{ mol}^{-1}$ according to Eq. (11) in Table 4. The standard molar entropies of the elements were taken from CODATA Key Values [15] as $51.30 \text{ J K}^{-1} \text{ mol}^{-1}$, $41.59 \text{ J K}^{-1} \text{ mol}^{-1}$, $5.90 \text{ J K}^{-1} \text{ mol}^{-1}$, $205.043 \text{ J K}^{-1} \text{ mol}^{-1}$, and $130.571 \text{ J K}^{-1} \text{ mol}^{-1}$ for Na(s), Ca(s), B(s), $\text{O}_2(\text{g})$, and $\text{H}_2(\text{g})$, respectively.

Acknowledgements

This project was supported by National Natural Science Foundation of China (Grant No. 29671032). Li Jun thanks financial support of the Special Foundation of the Director, The Chinese Academy of Sciences.

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