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Thermochemistry of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$

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Abstract

The enthalpy of dissolution of magnesium oxysulfate compound $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid was determined. From this result and the enthalpies of dissolution of $MgSO_4{\cdot}7H_2O$ and MgO in the same solvent and the standard molar enthalpies of formation of MgO(s), $MgSO_4{\cdot}7H_2O$(s) and H_2O(l), the standard molar enthalpy of formation of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ (-4132.07 ± 0.57 kJ mol^{-1}) was calculated. The standard molar entropy of formation of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ was calculated from the thermodynamic relation with the standard molar Gibbs free energy of formation of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ that was computed from a group contribution methods.

Keywords: Magnesium oxysulfate; Standard molar enthalpy of formation; Solution calorimetry; Molar enthalpy; Aqueous hydrochloric acid solution

1. Introduction

Magnesium hydroxide sulfate hydrate ($2MgSO_4{\cdot}x$Mg$(OH)_2{\cdot}(2–2x)H_2O$, x = 0.5–1.0) was discovered by Bischoff and Seyfried [1] in their studies on the hydrothermal chemistry of sea water at elevated temperatures and pressures. Recently some new members in this series of compounds, for example $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ [2], $MgSO_4{\cdot}1/3Mg(OH)_2{\cdot}1/3H_2O$[3] and $2MgSO_4{\cdot}Mg(OH)_2$ [4], were prepared by hydrothermal reaction. These magnesium oxysulfate compounds have useful properties, for example, $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ is a kind of material which can be used for reinforced and fire-proof substances in the polymer productions. The main studies about these magnesium oxysulfate compounds have concentrated on their structure and thermal decomposition behavior [5–7].

Thermodynamic properties play very important roles in scientific researches and industrial applications. In our previous paper [8], the standard molar enthalpies of formation of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ have been reported. In this paper, the standard molar enthalpies of formation of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ is determined by solution calorimetry.

2. Experimental

$2MgSO_4{\cdot}MgO{\cdot}3H_2O$ sample was prepared in laboratory according to method given in the literature [9]. All the reagents used in synthesis were of analytical grade (Xi'an Chemical Factory, PR China). NaOH (3 g) solution (10 mol L^{-1}) was dropped into 20 g $MgSO_4$ solution(3.2 mol L^{-1}) to form a slurry solution without stirring. The mixture was sealed in a 90 cm^{-3} stainless steel autoclave and heated at 160 ± 2 °C for 21days, then quenched the autoclave to room temperature, the solid phase was separated and washed with distilled water, alcohol and ether, respectively. It was finally dried at room temperature to constant weight. The product was analyzed according to the methods outline in the literature as follows: magnesium content was determined by titration with a standard solution of EDTA; sulphate content was determined by a gravimetric method by using Ba^{2+} to precipitate $BaSO_4$ and H_2O content was calculated by dif-

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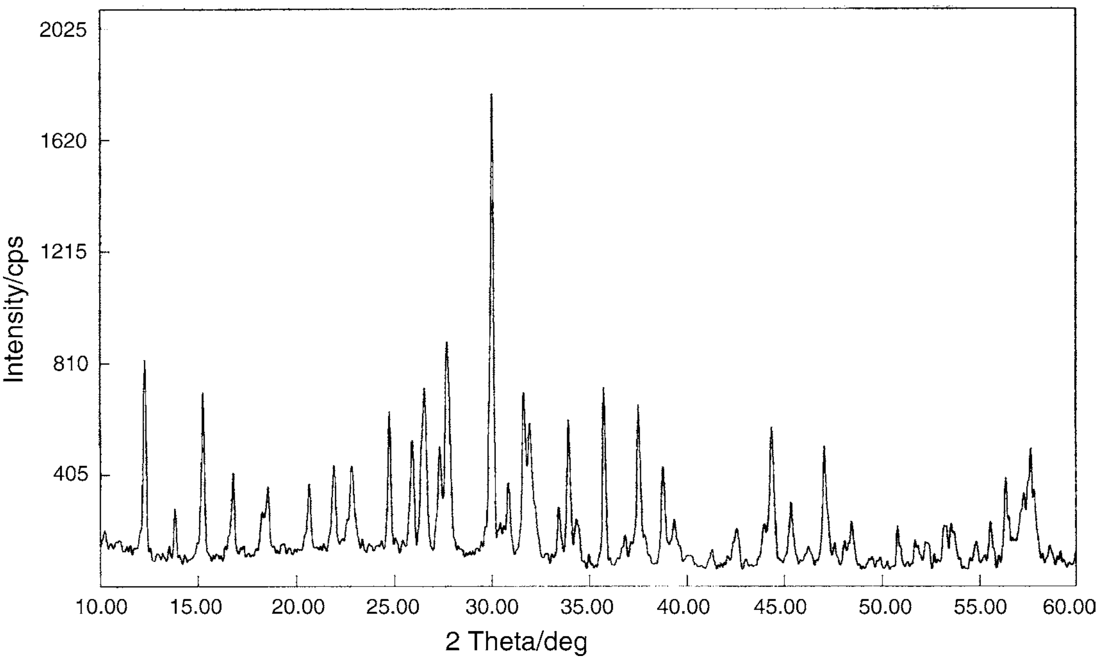

Fig. 1. The XRD pattern of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$.

ference. The powder X-ray diffraction data (Fig. 1) of the synthesized sample were obtained by using Rigaku D/MAX-III with Cu Kα radiation (λ = 1.5418 Å). Thermogravimetric analysis (TGA) and DSC were conducted on a NETZSCH-Geratebau STA 449c, current of N_2 with a heating rate of 10 °C min^{-1}. FT-IR spectrum (Fig. 2) was recorded within the 4000–400 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer using KBr pellets. The composition of samples is given in Table 1. It is shown the compound that was obtained is a pure one of general formula $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ and it is suitable for calorimetric measurements. The impurity corrections were unnecessary.

High-purity $MgSO_4{\cdot}7H_2O$ (mass fraction > 0.9999, made in the PR China) was used without further purification. An-

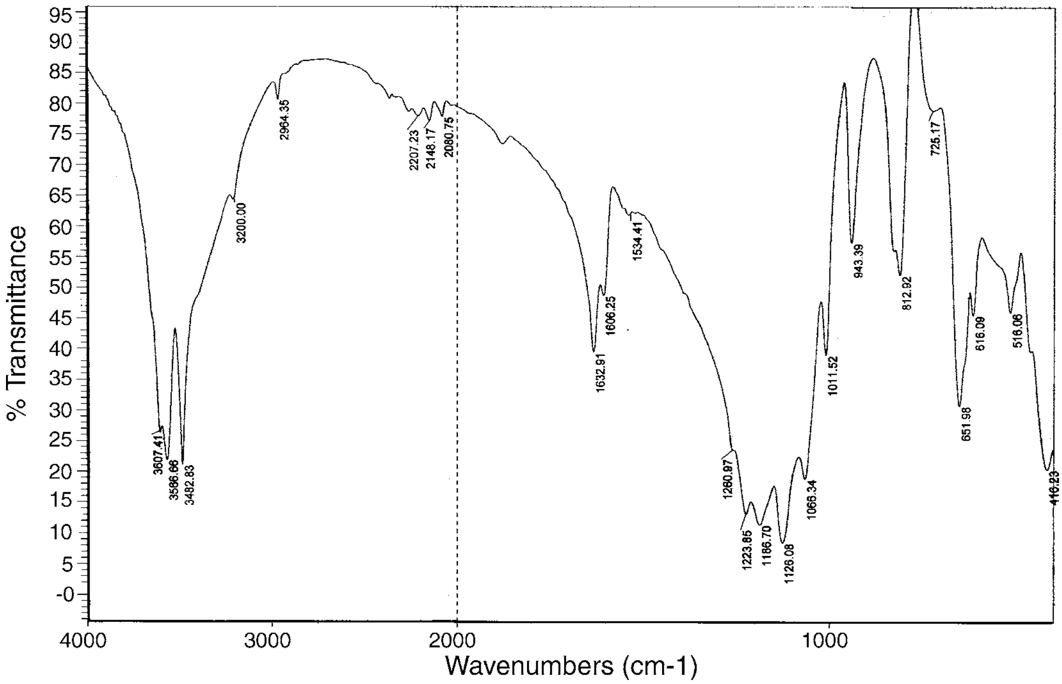

Fig. 2. The FT-IR spectrum of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$.

Table 1
The chemical composition of magnesium oxysulfate compound ($2MgSO_4{\cdot}MgO{\cdot}3H_2O$, mass fraction)

	$MgSO_4$	MgO	H_2O[a]
Analytical	0.2678	0.1195	0.1070
Theoretical	0.2686	0.1203	0.1074

[a] Calculated by difference.

alytical grade HCl and distilled water were used for preparation of the calorimetric solvent and its concentration was determined by titration with standard sodium carbonate.

Thermochemical reaction used for obtaining $\Delta_r H_m^o$ of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ is as follows:

$$\begin{aligned}&2MgSO_4 \cdot MgO \cdot 3H_2O(s) + 2HCl(aq)\\&\quad = 2MgSO_4(aq) + MgCl_2(aq) + 4H_2O(l) \qquad (1)\end{aligned}$$

The standard molar enthalpy of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of MgO(s), $MgSO_4{\cdot}7H_2O(s)$ and $H_2O(l)$. A RD496-III precision microcalorimeter was used. An additional glass reaction cell which was put in the stainless steel cell of the microcalorimeter was used due to the corrosion of the stainless steel cell by the HCl solution. The RD496-III precision microcalorimeter was calibrated for the Joule effect; the calibration was repeated after each experiment, and the average calibration constant was used. The glass tube containing the sample in the reaction cell was broken by a glass rod after thermal equilibration for at least 2 h, and thermal effect was recorded. Total time required for the complete reaction was about 1 h, depending on the samples. There was no solid residue observed after reaction in any of the calorimetric experiments.

3. Results and discussion

Table 2
Enthalpies of dissolution, $\Delta_{diss} H_m^o$ in water, of KCl at 298.15 K[a]

No.	m/mg	$\Delta_{diss} H_m^o$ (kJ mol^{-1})
1	8.01	17.23
2	12.02	17.29
3	13.32	17.25
4	15.00	17.21
5	15.02	17.24
		Mean $\Delta_{diss} H_m^o$ = 17.24 ± 0.06[b]

[a] In each experiment 8.00 cm^{-3} of water was used.

[b] Uncertainty is twice the standard deviation of the mean.

Table 3
Enthalpies of solution $\Delta_{diss} H_m^o$ of $MgSO_4{\cdot}7H_2O$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid solution at T = 298.15 K

No.	m/mg	$\Delta_{diss} H_m^o$ (kJ mol^{-1})
1	2.72	36.30
2	2.73	35.93
3	2.74	36.04
4	2.76	36.15
5	2.80	36.37
		Mean = 36.16 ± 0.36

In each experiment 2.00 cm^{-3} of HCl(aq) was used.

To check the performance of the RD496-III precision microcalorimeter, calorimetric measurements of the enthalpy of dissolution of standard KCl was made, and the results are listed in Table 2. From Table 2, it can be seen that the average experimental result of 17.24 ± 0.06 kJ mol^{-1} agrees very well with the recommended value of 17.241 ± 0.081 kJ mol^{-1}[10].

Tables 3 and 4 give the results of the calorimetric experiment. In these tables, m is the mass of the sample, $\Delta_{diss} H_m^o$ is the molar enthalpy of dissolution of the referring compound, and the uncertainty are twice the deviation of the means of five replicate measurement. Table 5 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$. The molar enthalpies of dissolution of $MgSO_4{\cdot}7H_2O(s)$ of −36.16 ± 0.16 kJ mol^{-1} in approximately 1 mol dm^{-3} HCl(aq), and MgO(s) of −149.78 ± 0.32 kJ mol^{-1} in approximately 1 mol dm^{-3} HCl(aq) were taken from literature [11]. The standard molar enthalpies of formation of $H_2O(l)$, MgO(s), $MgSO_4{\cdot}7H_2O(s)$ were taken from the CODATA Key Values [12], namely −285.83 ± 0.04, −597.98 ± 0.32 and −3388.71 ± 0.04 kJ mol^{-1}, respectively. The enthalpies of dilution of HCl(aq) were calculated from the NBS table [13]. Therefore, the standard molar enthalpy of formation of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ could be calculated and result is −4132.07 ± 0.47 kJ mol^{-1}. Applying the group contribution method developed by A.T.M.G. Mostafa et al. [14] for the calculation of thermodynamic properties of salts, we calculated $\Delta_f H_m^o$ of the $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ to be −4078.868 kJ mol^{-1}. This value agrees with our experimental result. The relative error is 1.29%. Because of no available experimental data on $\Delta_f G_m^o$ of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$, we used the group contribution method to calculate $\Delta_f G_m^o$ to be –3656.824 kJ mol^{-1}. Combining the standard molar enthalpy of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$, the standard molar entropy of formation has been calculated at −1593.98 J K^{-1} mol^{-1}

Table 4
Enthalpies of solution $\Delta_{diss} H_m^o$ of $2MgSO_4{\cdot}MgO{\cdot}3H_2O$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid solution at T = 298.15 K

No.	m/mg	$\Delta_{diss} H_m^o$ (kJ mol^{-1})
1	3.97	−176.53
2	3.98	−176.45
3	3.95	−176.39
4	4.02	−176.38
5	3.96	−176.43
		Mean = −176.44 ± 0.12

In each experiment 2.00 cm^{-3} of HCl(aq) was used.

Table 5
Thermochemical cycle for the derivation of $\Delta_{\mathrm{diss}}H_m^{\mathrm{o}}$ of $2MgSO_4 \cdot MgO \cdot 3H_2O$

Reaction	$\Delta_{\mathrm{diss}}H_m^{\mathrm{o}}$ (kJ mol^{-1})[a]
1. $2MgSO_4 \cdot MgO \cdot 3H_2O(s) + 2HCl \cdot 55.829H_2O \rightarrow 3Mg^{2+}(aq) + 2SO_4{}^{2-}(aq) + 2Cl^{-}(aq) + 4\{H_2O\}_{\mathrm{in\,sol}} + 111.658H_2O$	-176.44 ± 0.12
2. $2Mg^{2+}(aq) + 2SO_4{}^{2-}(aq) + 2Cl^{-}(aq) + 14\{H_2O\}_{\mathrm{in\,sol}} + 111.658H_2O \rightarrow 2MgSO_4 \cdot 7H_2O(s) + 2\,HCl \cdot 55.829H_2O$	-72.32 ± 0.32
3. $Mg^{2+}(aq) + 2Cl^{-}(aq) + \{H_2O\}_{\mathrm{in\,sol}} + 111.658H_2O \rightarrow MgO(s) + 2HCl \cdot 55.829H_2O$	149.78 ± 0.32
4. $2MgSO_4 \cdot 7H_2O(s) \rightarrow 2Mg(s) + 2S(s) + 11O_2(g) + 14H_2(g)$	6777.42 ± 0.04
5. $MgO(s) \rightarrow Mg(s) + 1/2O_2(g)$	597.98 ± 0.32
6. $2HCl \cdot 55.829H_2O + 11H_2O(l) \rightarrow 2Cl^{-}(aq) + 11\{H_2O\}_{\mathrm{in\,sol}} + 111.658H_2O$	-0.22 ± 0.01
7. $11/2O_2(g) + 11H_2(g) \rightarrow 11H_2O(l)$	-3144.13 ± 0.04
8. $2MgSO_4 \cdot MgO \cdot 3H_2O(s) \rightarrow 3Mg(s) + 2S(s) + 6O_2(g) + 3H_2(g)$	4132.07 ± 0.47

[a] Reactions 1, 2, 3 and 6 are enthalpies of dissolution; reactions 4, 5, 7 and 8 are enthalpies of formation.

according to the following equation:

$$\Delta_{\mathrm{f}}S_m^{\mathrm{o}} = \frac{\Delta_{\mathrm{f}}H_m^{\mathrm{o}} - \Delta_{\mathrm{f}}G_m^{\mathrm{o}}}{T}$$

Finally, the standard molar entropy of $2MgSO_4 \cdot MgO \cdot 3H_2O$ has been calculated to be 191.953 J K^{-1} mol^{-1} according to reaction (8) in Table 5. The standard molar entropies of the elements were taken from CODATA. Key Values as 32.68, 31.80, 205.43 and 130.571 J K^{-1} mol^{-1} for Mg(s), S(s), O_2(g) and H_2(g), respectively.

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