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Short communication

Thermochemistry of magnesium oxysulfate

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Abstract

The enthalpies of solution of magnesium oxysulfate compounds $MgSO_4 \cdot 5MgO \cdot 7H_2O$ and $MgSO_4 \cdot 5MgO \cdot 8H_2O$ in approximately 1 mol dm^{-3} aqueous hydrochloric acid were determined. From these results and the enthalpies of solution of $MgSO_4 \cdot 7H_2O$ and MgO in HCl(aq) respectively, the standard molar enthalpies of formation of $-(6496.00 \pm 0.73)$ kJ mol^{-1} for $MgSO_4 \cdot 5MgO \cdot 7H_2O$ and $-(6800.17 \pm 0.55)$ kJ mol^{-1} for $MgSO_4 \cdot 5MgO \cdot 8H_2O$ were obtained by using the standard molar enthalpies of formation of MgO(s), $MgSO_4 \cdot 7H_2O$(s) and H_2O(l). The standard molar entropies of formation of $MgSO_4 \cdot 5MgO \cdot 7H_2O$ and $MgSO_4 \cdot 5MgO \cdot 8H_2O$ were calculated from the thermodynamic relation with the standard molar Gibbs free energy of formation of $MgSO_4 \cdot 5MgO \cdot 7H_2O$ and $MgSO_4 \cdot 5MgO \cdot 8H_2O$ 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 oxysulfate compounds belong to a rather large group of hydrated metal sulfates which exhibit retrograde solubility upon cooling. Most of them were synthesized in the $MgO–MgSO_4–H_2O$ and $Mg(OH)_2–MgSO_4–H_2O$ ternary system [1–3]. Recently, some new members in this series of compounds, for example, $MgSO_4 \cdot 5MgO \cdot 8H_2O$ [4], $MgSO_4 \cdot (1/3)Mg(OH)_2 \cdot (1/3)H_2O$ [5] and $2MgSO_4 \cdot Mg(OH)_2$ [6], were obtained by hydrothermal reactions. These magnesium oxysulfate compounds have useful properties, for example, $MgSO_4 \cdot 5MgO \cdot 8H_2O$ is a kind of whisker which can be used for reinforcing and giving them fireproof properties in the polymers production. The main studies on these magnesium oxysulfate compounds were concentrated on their structure and thermal behavior [7–9]. There are no reports on the standard molar enthalpies of formation of magnesium oxysulfate compounds in the literature.

Thermodynamic properties play very important roles in scientific researches and industrial applications. In this paper, the standard molar enthalpies of formation of $MgSO_4 \cdot 5MgO \cdot 7H_2O$ and $MgSO_4 \cdot 5MgO \cdot 8H_2O$ were determined by solution calorimetry.

2. Experimental

$MgSO_4 \cdot 5MgO \cdot 8H_2O$ was prepared at laboratory according to method given in the literature [4]. All the reagents used in synthesis were of analytical grade (Xi'an Chemical Factory, PR China). Eighty-five

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grams NaOH solution ($10\,mol\,l^{-1}$) was dropped into 800 g of a $MgSO_4$ solution ($3.2\,mol\,l^{-1}$) to form a slurry solution after stirring. The mixture was sealed in a $2\,dm^3$ stainless steel autoclave and heated at $140 \pm 2\,°C$ during 8 h followed by quenching of the autoclave to room temperature. The solid phase was separated and washed with distilled water, alcohol and ether, respectively. Finally, it was dried at room temperature at constant weight. The compounds were characterized by chemical analysis, X-ray powder diffraction, and FT-IR spectrum, and the results were in agreement with the literature [4]. Two and a half grams of NaOH solution ($10\,mol\,l^{-1}$) was droped into 55 g of a $MgSO_4$ solution ($2.5\,mol\,l^{-1}$) to form a slurry solution after stirring, and the mixture was sealed in a $90\,cm^3$ stainless steel autoclave and heated at $160 \pm 2\,°C$ during 16 h. The preparation and characterization process of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ were similar to that of $MgSO_4{\cdot}5MgO{\cdot}8H_2O$. The composition of the compounds is given in Table 1. The compounds are pure and have the general formulas: $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$, and they are suitable for calorimetric experiments. The impurity corrections were unnecessary.

High-purity $MgSO_4{\cdot}7H_2O$ (mass fraction >0.9999, Xi'an Chemical Factory, PR China) was used without further purification. Analytical grade HCl and distilled water were used for preparation of the solvent system and its concentration was determined by titration with standard borax.

Thermochemical reaction used for the derivation of $\Delta_r H_m^\circ$ of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ was:

$$MgSO_4 \cdot 5MgO \cdot nH_2O(s) + 10HCl(aq) = MgSO_4(aq) + 5MgCl_2(aq) + (5+n)H_2O \quad (1)$$

Table 1
The chemical composition of magnesium oxysulfate compounds (mass fraction, w)

	$MgSO_4$	MgO	H_2O
$MgSO_4{\cdot}5MgO{\cdot}7H_2O$			
Analytical	0.2678	0.4495	0.2827[a]
Theoretical	0.2686	0.4500	0.2814
$MgSO_4{\cdot}5MgO{\cdot}8H_2O$			
Analytical	0.2589	0.4323	0.3088[a]
Theoretical	0.2583	0.4326	0.3091

[a] Calculated by difference.

The standard molar enthalpies of formation of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ could be obtained from the enthalpies of reaction ($\Delta_r H_m^\circ$) and the standard molar enthalpies of formation of MgO(s), $MgSO_4{\cdot}7H_2O$(s) and H_2O(l). A RD496-III precision microcalorimeter (made in Southwest Institute of Electronic Engineering, China) was used. A set of additional glass reaction cell which was put in the stainless steel cell for the microcalorimeter was used because of the corrosion by HCl(aq) of the stainless steel cell. 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 ampoule in the reaction cell was broken by a glass rod after thermal equilibrium 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

To check the performance of the RD496-III precision microcalorimeter, the enthalpy of solution of KCl (mass fraction >99.99%) was measured, and the results are listed in Table 2, the experimental value of $17.24 \pm 0.06\,kJ\,mol^{-1}$ is in agreement with that of $17.241 \pm 0.081\,kJ\,mol^{-1}$, the recommended value in the literature [10].

Tables 3–5 give the results of the calorimetric experiment. In these tables, m is the mass of the sample, $\Delta_{sol}H_m$ is the molar enthalpy of solution of solute,

Table 2
The molar enthalpies $\Delta_{sol}H_m$ of solution of KCl in water at 298.15 K[a]

No.	m (mg)	$\Delta_{sol}H_m$ ($kJ\,mol^{-1}$)
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		17.24 ± 0.06[b]

[a] Determined with a RD496-III precision microcalorimeter, in each experiment, $8\,cm^3$ of water was used.
[b] Uncertainty is twice the standard deviation of the mean.

Table 3
The molar enthalpies of solution $\Delta_{sol}H_m$ of $MgSO_4{\cdot}7H_2O$ in approximately $1\,mol\,dm^{-3}$ aqueous hydrochloric acid solution at $T = 298.15\,K$[a]

No.	m (mg)	$\Delta_{sol}H_m$ ($kJ\,mol^{-1}$)
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[b]

[a] Determined with a RD496-III precision microcalorimeter, in each experiment, $2\,cm^3$ of HCl(aq) was used.
[b] Uncertainty is twice the standard deviation of the mean.

Table 4
The molar enthalpies of solution $\Delta_{sol}H_m$ of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ in approximately $1\,mol\,dm^{-3}$ aqueous hydrochloric acid solution at $T = 298.15\,K$[a]

No.	m (mg)	$\Delta_{sol}H_m$ ($kJ\,mol^{-1}$)
1	5.02	−595.04
2	4.98	−595.60
3	4.96	−595.44
4	4.96	−595.47
5	4.96	−595.20
Mean		−(595.35 ± 0.45[b])

[a] Determined with a RD496-III precision microcalorimeter, in each experiment, $2\,cm^3$ of HCl(aq) was used.
[b] Uncertainty is twice the standard deviation of the mean.

and the uncertainty is twice the standard deviation of the mean. Tables 6 and 7 give the thermochemical cycle for the derivation of the standard molar enthalpies of formation of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$. The molar enthalpies of solution of $MgSO_4{\cdot}7H_2O$(s) of $-(36.16 \pm 0.36)\,kJ\,mol^{-1}$ in approximately $1\,mol\,dm^{-3}$ HCl(aq), and MgO(s) of $-(149.78 \pm 0.32)\,kJ\,mol^{-1}$ 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 $-(3388.71 \pm 0.04)\,kJ\,mol^{-1}$, respectively. The enthalpies of dilution of HCl(aq) were calculated from the NBS table [13]. Therefore, the standard molar enthalpies of formation of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ could be calculated and result are −(6496.00 ± 0.73) $kJ\,mol^{-1}$, $-(6800.17 \pm 0.55)\,kJ\,mol^{-1}$. Applying a group contribution method developed by Mostafa et al. [14] for the calculation of thermodynamic properties of salts, we calculated $\Delta_f H^\circ_m$ of the $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ to be $-6511.935\,kJ\,mol^{-1}$ and $-6810.868\,kJ\,mol^{-1}$. These values agree with the experimental results very well. The relative errors are 0.24 and 0.16%, respectively. Because of no experimental data on $\Delta_f G^\circ_m$ of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ available, we used a group contribution method to calculate

Table 5
The molar enthalpies of solution $\Delta_{sol}H_m$ of $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ in approximately $1\,mol\,dm^{-3}$ aqueous hydrochloric acid solution at $T = 298.15\,K$[a]

No.	m (mg)	$\Delta_{sol}H_m$ ($kJ\,mol^{-1}$)
1	4.99	−576.82
2	5.02	−576.98
3	4.98	−577.08
4	4.96	−576.99
5	4.97	−577.30
Mean		−(577.03 ± 0.35[b])

[a] Determined with a RD496-III precision microcalorimeter, in each experiment, $2\,cm^3$ of HCl(aq) was used.
[b] Uncertainty is twice the standard deviation of the mean.

Table 6
Thermochemical cycles and results for the derivation of $\Delta_f H^\circ_m$ of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$

No.	Reaction	$\Delta_r H_m$ ($kJ\,mol^{-1}$)
1	$MgSO_4{\cdot}5MgO{\cdot}7H_2O(s) + 179.144(HCl{\cdot}55.829H_2O) \rightarrow 6Mg^{2+}(aq) + SO_4{}^{2-}(aq) + 10Cl^-(aq) + 169.144(HCl{\cdot}59.201H_2O)$	−595.35 ± 0.45
2	$Mg^{2+}(aq) + SO_4{}^{2-}(aq) + 179.144(HCl{\cdot}55.868H_2O) \rightarrow MgSO_4{\cdot}7H_2O(s) + 179.144(HCl{\cdot}55.829H_2O)$	−36.16 ± 0.36
3	$5Mg^{2+}(aq) + 10Cl^-(aq) + 169.144(HCl{\cdot}59.201H_2O) \rightarrow 5MgO(s) + 179.144(HCl{\cdot}55.868H_2O)$	748.90 ± 0.32
4	$MgSO_4{\cdot}7H_2O(s) \rightarrow Mg(s) + S(s) + (11/2)O_2(g) + 7H_2(g)$	3388.71 ± 0.04
5	$5MgO(s) \rightarrow 5Mg(s) + (5/2)O_2(g)$	2989.90 ± 0.32
6	$MgSO_4{\cdot}5MgO{\cdot}7H_2O(s) \rightarrow 6Mg(s) + S(s) + 8O_2(g) + 7H_2(g)$	6496.00 ± 0.73

Table 7
Thermochemical cycles and results for the derivation of $\Delta_f H_m^\circ$ of $MgSO_4{\cdot}5MgO{\cdot}8H_2O$

No.	Reaction	$\Delta_r H_m$ ($kJ\,mol^{-1}$)
1	$MgSO_4{\cdot}5MgO{\cdot}8H_2O(s) + 181.946(HCl{\cdot}55.829H_2O)$ $\rightarrow 6Mg^{2+}(aq) + SO_4{}^{2-}(aq) + 10Cl^-(aq) + 171.946(HCl{\cdot}59.151H_2O)$	-577.03 ± 0.35
2	$Mg^{2+}(aq) + SO_4{}^{2-}(aq) + 181.946(HCl{\cdot}55.868H_2O) \rightarrow MgSO_4{\cdot}7H_2O(s) + 181.946(HCl{\cdot}55.829H_2O)$	-36.16 ± 0.36
3	$5Mg^{2+}(aq) + 10Cl^-(aq) + 171.946(HCl{\cdot}59.151H_2O) \rightarrow 5MgO(s) + 181.946(HCl{\cdot}55.873H_2O)$	748.90 ± 0.32
4	$MgSO_4{\cdot}7H_2O(s) \rightarrow Mg(s) + S(s) + (11/2)O_2(g) + 7H_2(g)$	3388.71 ± 0.04
5	$5MgO(s) \rightarrow 5Mg(s) + (5/2)O_2(g)$	2989.90 ± 0.32
6	$181.946(HCl{\cdot}55.873H_2O) \rightarrow 181.946(HCl{\cdot}55.868H_2O) + H_2O(l)$	0.02 ± 0.01
7	$H_2O(l) \rightarrow (1/2)O_2(g) + H_2(g)$	285.83 ± 0.04
8	$MgSO_4{\cdot}5MgO{\cdot}8H_2O(s) \rightarrow 6Mg(s) + S(s) + (17/2)O_2(g) + 8H_2(g)$	6800.17 ± 0.55

$\Delta_f G_m^\circ$ to be -5822.44 and $-6066.76\,kJ\,mol^{-1}$. Combining with the standard molar enthalpies of formation of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$, their standard molar entropies of formation have been calculated as -2259.13 and $-2459.87\,J\,K^{-1}\,mol^{-1}$ according to the following equation:

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

Otherwise, the standard molar entropies of $MgSO_4{\cdot}5MgO{\cdot}7H_2O$ and $MgSO_4{\cdot}5MgO{\cdot}8H_2O$ have been calculated to be 523.091 and $555.45\,J\,K^{-1}\,mol^{-1}$ according to reaction (6) in Table 6 and reaction (8) in Table 7. 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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