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Thermochemical studies on the langbeinite-type double-sulfate salts, $(NH_4)_2M_2(SO_4)_3$

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Abstract

The molar enthalpies of dissolution of $(NH_4)_2SO_4{:}2MSO_4$ and the double salts $(NH_4)_2M_2(SO_4)_3$ (where $M = Mn^{2+}$ or Cd^{2+}) in double-distilled water were determined by solution–reaction calorimetry measurements at 298.2 K. From the values obtained together with auxiliary data and by using appropriate thermochemical cycles, the standard molar enthalpies of formation of $(NH_4)_2M_2(SO_4)_3$ were hence derived:

$\Delta_f H_m^0[(NH_4)_2Cd_2(SO_4)_3(s)] = -3031.74 \pm 0.08\,\mathrm{kJ\,mol^{-1}}$

$\Delta_f H_m^0[(NH_4)_2Mn_2(SO_4)_3(s)] = -3250.16 \pm 0.09\,\mathrm{kJ\,mol^{-1}}$

Keywords: Double-sulfate salts; Solution calorimetry; Standard molar enthalpy of formation

1. Introduction

Langbeinites are double-sulfate salts which have the general formula $(M^+)_2(M^{2+})_2(XO_4)_3$, where M^+ is a monovalent and M^{2+} a divalent metal ions, X is S or Cr element. These compounds have great practical interest because of their physical and structural properties, for example, the ferroelectric and ferroelasis ones, have led to many publications [1–4].

In 1958, Von Gattow and Zemann [5] proved the possibility of synthesis of 26 such sulfate compounds by the hydrothermal method. Recently, Hikita et al. [1] and Nagaishi et al. [6] reported, respectively, new methods of prepared some langbeinites by the solid state reaction at high-heating temperatures and by the reactions between ammonium sulfate with various metal oxides.

We had already reported the standard molar formation enthalpies of $K_2M_2(SO_4)_3$ ($M = Cd^{2+}$, Zn^{2+}, Mg^{2+}) by solution–reaction calorimetry measurements [7]. In the present paper, the dissolution enthalpies of $[(NH_4)_2SO_4(s) + 2MSO_4(s)]$ and $(NH_4)_2M_2(SO_4)_3(s)$ in double-distilled water at 298.2 K were determined and hence to estimate the standard molar formation enthalpies of $(NH_4)_2Cd_2(SO_4)_3(s)$ and $(NH_4)_2Mn_2(SO_4)_3(s)$.

2. Experimental

2.1. Chemicals

K_2SO_4 (AR, Chengdu Reagent Factory) and $(NH_4)_2SO_4$ (AR, Chengdu Reagent Factory) were

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used without further purification. $CdSO_4$ and $MnSO_4$ were prepared in our laboratory from $3CdSO_4{\cdot}8H_2O$ (AR, Shanghai Reagent Factory) and $MnSO_4{\cdot}H_2O$ (AR, Beijing Reagent Factory) by dehydration at 873 and 723 K for 4 h, respectively.

KCl (SRM, Shanghai Reagent Factory) was dried before using as calorimetric primary standard, in a vacuum oven for 6 h at 408 K.

2.2. Preparations

$(NH_4)_2Cd_2(SO_4)_3(s)$ was prepared by evaporating to dryness the saturated aqueous solutions of the mixture $(NH_4)_2SO_4$:$CdSO_4$ of a molar relation of 1:2, on a hot plate at 363–368 K and was subsequently purified by means of twice recrystallization from double-distilled water [8].

$(NH_4)Mn_2(SO_4)_3(s)$ was obtained at 358 K by slow evaporation of the aqvelus solution containing 1:1 molar ratio of $(NH_4)_2SO_4$ and $MnSO_4$. It was purified by heat-treatment at 553–573 K for results of both thermal analysis and X-ray power diffraction [1].

The contents of the $(NH_4)_2Cd_2(SO_4)_3(s)$ and $(NH_4)_2Mn_2(SO_4)_3(s)$ were characterized as stated above.

2.3. Calorimeter

The dissolution enthalpies of the compounds were measured in an isoperibol reaction calorimeter, as described previously as well as was also the calorimetric procedure [9,10]. The accuracy of the calorimeter was tested by measuring the dissolving enthalpy of KCl samples in double-distilled water and that of temperature maintenance at 298 K was 10^{-3} K. The measured dissolution enthalpy of KCl was $17.569 \pm 0.017\,\mathrm{kJ\,mol^{-1}}$ in agreement with the values 17.564 ± 0.042 and $17.536 \pm 0.009\,\mathrm{kJ\,mol^{-1}}$ [11,12].

3. Results

All the sulfates with the inclusion of the double and the simple ones (or the other) were at first finely grounded in an agate mortar. The calorimetric solvent used for this study was the double-distilled water ($100\ \mathrm{cm^3}$).

3.1. Determination of the molar dissolution enthalpies ($\Delta_{\mathrm{diss}}H_{\mathrm{m}}^{\theta}$)

The mixture of mass 0.3–0.4 g of $(NH_4)_2SO_4$ and MSO_4 ($M = Cd^{2+}$, Mn^{2+}) in a molar relation of 1:2 were dissolved in $100\,\mathrm{cm^3}$ water at 298.2 K. The values obtained are shown in Table 1. The molar dissolution enthalpies of $(NH_4)_2Cd_2(SO_4)_3(s)$ and $(NH_4)_2Mn_2(SO_4)_3(s)$ in $100\ \mathrm{cm^3}$ water were measured under the same conditions. The results are also present in Table 1.

3.2. Determination of the molar reaction enthalpies ($\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\theta}$)

According to Hess's law, two thermochemical cycles were used as shown in Tables 2 and 3.

$$\{2MSO_4(s) + (NH_4)_2SO_4(s)\} + \mathrm{water} = \{\mathrm{solution\ A}\}$$

$$\{\mathrm{solution\ B}\} = (NH_4)_2M_2(SO_4)_3(s) + \mathrm{water}$$

$$\{2MSO_4(s) + (NH_4)_2SO_4(s)\} = (NH_4)_2M_2(SO_4)_3(s)$$

The reaction molar enthalpies are obtained at 298.2 K from $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\theta} = \Delta_{\mathrm{diss}}H_{\mathrm{m}}^{\theta}[2MSO_4(s) + (NH_4)_2SO_4(s)] - \Delta_{\mathrm{diss}}H_{\mathrm{m}}^{\theta}[(NH_4)_2M_2(SO_4)_3(s)]$, where M is Cd^{2+} and Mn^{2+}. The values obtained are $15.67 \pm 0.08\,\mathrm{kJ\,mol^{-1}}$ for $(NH_4)_2Cd_2(SO_4)_3(s)$ (see Table 2) and $61.19 \pm 0.09\,\mathrm{kJ\,mol^{-1}}$ for $(NH_4)_2Mn_2(SO_4)_3(s)$ (see Table 3).

3.3. Determination of the standard molar formation enthalpies of $(NH_4)_2M_2(SO_4)_3(s)$

The standard molar formation enthalpies of $(NH_4)_2Cd_2(SO_4)_3(s)$ and $(NH_4)_2Mn_2(SO_4)_3(s)$ are calculated from

$$\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\theta} = \sum \Delta_{\mathrm{f}}H_{\mathrm{m}}^{\theta}(\mathrm{products}) - \sum \Delta_{\mathrm{f}}H_{\mathrm{m}}^{\theta}(\mathrm{reactants})$$

where $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\theta}$ is a sum of dissolution enthalpies. Thus, we get (see Tables 2 and 3)

$$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\theta}[(NH_4)_2M_2(SO_4)_3(s)] = \Delta_{\mathrm{r}}H_{\mathrm{m}}^{\theta} + 2\Delta_3H_{\mathrm{m}}^{\theta} + \Delta_4H_{\mathrm{m}}^{\theta}$$

by using auxitiary data ($\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\theta}$) from Ref. [13]: $-933.28\ \mathrm{kJ\ mol^{-1}}$ for $CdSO_4(s)$, $-1065.25\ \mathrm{kJ\ mol^{-1}}$ for $MnSO_4(s)$ and $-1180.85\ \mathrm{kJ\ mol^{-1}}$ for $(NH_4)_2SO_4$ (s). The calculated enthalpies of formations at

Table 1
Dissolution enthalpies of $[2\mathrm{MSO_4} + (\mathrm{NH_4})_2\mathrm{SO_4}]$ and $(\mathrm{NH_4})_2\mathrm{M_2(SO_4)_3}$ in water at 298.2 K ($R = 996.0\,\Omega$, $I = 19.627\,\mathrm{mA}$)

	No.	m (g)[a]	$\Delta E_s/\Delta E_e$[b]	$\Delta_{\mathrm{diss}}H^{\theta}_{\mathrm{m}}$ (kJ mol^{-1})[c]
$[2\mathrm{CdSO_4(s)} + (\mathrm{NH_4})_2\mathrm{SO_4(s)}]$	1	0.3790	0.879	82.42
	2	0.3804	1.218	82.30
	3	0.3794	1.102	82.05
	4	0.3791	1.175	82.38
	5	0.3800	1.135	82.31
$\Delta_1 H^{\theta}_{\mathrm{m}}[2\mathrm{CdSO_4(s)} + (\mathrm{NH_4})_2\mathrm{SO_4(s)}] = 82.29 \pm 0.06\,\mathrm{kJ\,mol^{-1}}$				
$(\mathrm{NH_4})_2\mathrm{Cd_2(SO_4)_3(s)}$	1	0.3929	0.490	66.61
	2	0.3894	0.010	66.54
	3	0.3876	0.992	66.68
	4	0.3833	1.060	66.61
	5	0.3794	0.851	66.66
$\Delta_2 H^{\theta}_{\mathrm{m}}[(\mathrm{NH_4})_2\mathrm{Cd_2(SO_4)_3(s)}] = 66.62 \pm 0.02\,\mathrm{kJ\,mol^{-1}}$				
$[2\mathrm{MnSO_4(s)} + (\mathrm{NH_4})_2\mathrm{SO_4(s)}]$	1	0.3864	1.019	106.60
	2	0.3862	1.410	106.58
	3	0.3868	1.140	106.54
	4	0.3867	1.360	106.25
	5	0.3863	1.049	106.61
$\Delta_1 H^{\theta}_{\mathrm{m}}[2\mathrm{MnSO_4(s)} + (\mathrm{NH_4})_2\mathrm{SO_4(s)}] = 106.49 \pm 0.07\,\mathrm{kJ\,mol^{-1}}$				
$(\mathrm{NH_4})_2\mathrm{Mn_2(SO_4)_3(s)}$	1	0.3818	0.925	45.37
	2	0.3814	0.846	45.24
	3	0.3816	0.860	45.33
	4	0.3827	0.899	45.36
	5	0.3872	1.019	45.31
$\Delta_2 H^{\theta}_{\mathrm{m}}[(\mathrm{NH_4})_2\mathrm{Mn_2(SO_4)_3(s)}] = 45.30 \pm 0.02\,\mathrm{kJ\,mol^{-1}}$				

[a] Mass of the sample.

[b] The voltage change during the sample dissolution and the electrical calibration.

[c] $\Delta_{\mathrm{diss}}H^{\theta}_{\mathrm{m}} = (\Delta E_s/\Delta E_e) I^2 Rte(M/m)$.

Table 2
Reaction scheme for the determination of the standard molar formation enthalpies of $(\mathrm{NH_4})_2\mathrm{Cd_2(SO_4)_3(s)}$ at 298.2 K ($\Delta_5 H^{\theta}_{\mathrm{m}} = \Delta_1 H^{\theta}_{\mathrm{m}} - \Delta_2 H^{\theta}_{\mathrm{m}} + 2\Delta_3 H^{\theta}_{\mathrm{m}} + \Delta_4 H^{\theta}_{\mathrm{m}}$)

No.	Reactions	Solution	$\Delta_{\mathrm{diss}}H^{\theta}_{\mathrm{m}} - \Delta_{\mathrm{f}}H^{\theta}_{\mathrm{m}}$ (kJ mol^{-1})
1	$\{2\mathrm{CdSO_4(s)} + (\mathrm{NH_4})_2\mathrm{SO_4(s)}\}$ + water	A_1	82.29 ± 0.06
2	$(\mathrm{NH_4})_2\mathrm{Cd_2(SO_4)_3(s)}$ + water	B_1	66.62 ± 0.02
3	$\mathrm{Cd(s)} + \mathrm{S(s)} + 2\mathrm{O_2(g)} = \mathrm{CdSO_4(s)}$		-933.28
4	$\mathrm{N_2(g)} + 4\mathrm{H_2(g)} + \mathrm{S(s)} + 2\mathrm{O_2(g)} = (\mathrm{NH_4})_2\mathrm{SO_4(s)}$		-1180.85
5	$\mathrm{N_2(g)} + 4\mathrm{H_2(g)} + 2\mathrm{Cd(s)} + 3\mathrm{S(s)} + 6\mathrm{O_2(g)} = (\mathrm{NH_4})_2\mathrm{Cd_2(SO_4)_3(s)}$		-3031.74 ± 0.08

Table 3
Reaction scheme for the determination of the standard molar formation enthalpies of $(\mathrm{NH_4})_2\mathrm{Mn_2(SO_4)_3(s)}$ at 298.2 K ($\Delta_5 H^{\theta}_{\mathrm{m}} = \Delta_1 H^{\theta}_{\mathrm{m}} - \Delta_2 H^{\theta}_{\mathrm{m}} + 2\Delta_3 H^{\theta}_{\mathrm{m}} + \Delta_4 H^{\theta}_{\mathrm{m}}$)

No.	Reactions	Solution	$\Delta_{\mathrm{diss}}H^{\theta}_{\mathrm{m}} - \Delta_{\mathrm{f}}H^{\theta}_{\mathrm{m}}$ (kJ mol^{-1})
1	$\{2\mathrm{MnSO_4(s)} + (\mathrm{NH_4})_2\mathrm{SO_4(s)}\}$ + water	A_2	106.49 ± 0.07
2	$(\mathrm{NH_4})_2\mathrm{Mn_2(SO_4)_3(s)}$ + water	B_2	45.30 ± 0.02
3	$\mathrm{Mn(s)} + \mathrm{S(s)} + 2\mathrm{O_2(g)} = \mathrm{MnSO_4(s)}$		-1065.25
4	$\mathrm{N_2(g)} + 4\mathrm{H_2(g)} + \mathrm{S(s)} + 2\mathrm{O_2(g)} = (\mathrm{NH_4})_2\mathrm{SO_4(s)}$		-1180.85
5	$\mathrm{N_2(g)} + 4\mathrm{H_2(g)} + 2\mathrm{Mn(s)} + 3\mathrm{S(s)} + 6\mathrm{O_2(g)} = (\mathrm{NH_4})_2\mathrm{Mn_2(SO_4)_3(s)}$		-3250.16 ± 0.09

298.2 K are

$$\Delta_f H_m^\theta[(NH_4)_2Cd_2(SO_4)_3(s)] = -3031.74 \pm 0.08\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\theta[(NH_4)_2Mn_2(SO_4)_3(s)] = -3250.16 \pm 0.09\,kJ\,mol^{-1}$$

4. Discussion

In the present study, we designed a reasonable thermochemical cycle and verified the thermodynanic identity of A and B solutions, by using the same thermochemical cycle and the same calorimetric solvent to measure the enthalpies of dissolution of each separate salt. The error of the measurements is the mean-square error of the heat value evolved, which was obtained by averaging the partial mean-square error for each solution–reaction from the sequence. For comparison, the $\Delta_f H_m^\theta$ values of some solid salts determined by the solubility, the combustion, the DSC and the solution–reaction calorimetric methods, which the final result is more reliable in Ref. [14]. Nevertheless, the main problem of this kind of work is found to be difficult to prepare single crystals.

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