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Thermochemical studies on langbeinite-type double sulphate salts, $K_2M_2(SO_4)_3$

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Abstract

The standard molar enthalpies of dissolution of mixtures $K_2SO_4{:}2MSO_4$ and double salts $K_2M_2(SO_4)_3$ (where $M = Cd^{2+}$, Zn^{2+} or Mg^{2+}) in aqueous 3 M HNO_3 have been measured by using an isoperibol reaction calorimeter 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 $K_2M_2(SO_4)_3$ at 298.2 K were hence derived.

$$\Delta_f H^\theta_m[K_2Cd_2(SO_4)_{3(s)}] = -3305.52 \pm 0.17\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H^\theta_m[K_2Zn_2(SO_4)_{3(s)}] = -3406.85 \pm 0.23\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H^\theta_m(K_2Mg_2(SO_4)_{3(s)}] = -3953.07 \pm 0.25\,\mathrm{kJ\,mol^{-1}}$$

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

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1. Introduction

The double sulphate salts with langbeinite-type structure, of chemical formula $(M^+)_2(M^{2+})_2(SO_4)_3$, are interesting mainly because their ferroelectric activity, an extrinsically induced ferroelectric activity and a strong first-order phase transition. There are a large number of this kind of compounds with $M^+ = NH_4$, K, Rb, Tl, Cs and M^{2+} = Mn, Ca, Mg, Fe, Co, Ni, Zn, Cd [1–5]. They have the space group symmetry $T^4 - P2_13$ [6]. Gattow and Zemann [7] mention the possibility of the synthesis of 26 double sulphates. A ferroelectric phase transition in this kind of compounds was first found in $(NH_4)_2Cd_2(SO_4)_3$, in 1956 [8]. This langbeinite also displays triboluminescence, an optical property discovered for this compound in 1980 [9].

The aim of the present article is to measure the dissolution enthalpies of $[K_2SO_{4(s)} + 2MSO_{4(s)}]$ and $[K_2M_2(SO_4)_{3(s)}]$ in aqueous 3 M HNO_3 at 298.2 K. The values obtained together with auxiliary data and by using appropriate thermochemical cycles, the standard molar formation enthalpies of $K_2Cd_2(SO_4)_3$, $K_2Zn_2(SO_4)_3$ and $K_2Mg_2(SO_4)_3$ were determined.

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2. Experimental

2.1. Chemicals

K_2SO_4 (AR, Chengdu Reagent Factory) and $MgSO_4$ (AR, Chengdu Reagent Factory) were used without further purification. $CdSO_4$ and $ZnSO_4$ were prepared in our laboratory from the dehydration of $3CdSO_4 \cdot 8H_2O$ (AR, Shanghai Reagent Factory) and $ZnSO_4 \cdot 7H_2O$ (AR, Shanghai Reagent Factory) during 4 h at 873 and 793 K, respectively.

KCl (SRM, Shanghai Reagent Factory) and THAM (NBS 742_a, USA) were dried before using as calorimetric primary standards in a vacuum oven during 6 h at 408 K.

2.2. Preparations

$K_2Cd_2(SO_4)_3$, $K_2Zn_2(SO_4)_3$ and $K_2Mg_2(SO_4)_3$ are polycrystalline samples. They are not soluble in water [7]. After finely grinding the mixture M_2SO_4:MSO_4 of a molar relation of 1:2 was put into a crucible and heating in an electric furnace at 1023 K for 1 h. The furnace was gradually cooled to room temperature during 15 h. The polycrystals of $K_2Cd_2(SO_4)_3$ and $K_2Zn_2(SO_4)_3$ were obtained in the form of semitransparent, milky colored boules. However, $K_2Mg_2(SO_4)_3$ was obtained in the form of white powder-like crystalline. The polycrystalline samples were annealed at 673 K for 10 h according to the method of Hikita et al. [6]. All the compounds obtained were characterized by both X-ray powder diffraction and chemical analysis of metallic and sulphate ions contents.

2.3. Calorimeter and calibration

The enthalpies of dissolution of the compounds were measured in an isoperibol calorimeter as described previously as well as it was also the calorimetric procedure [10,11]. The solution enthalpy of KCl in water and that of THAM in 0.1 $\mathrm{mol\,dm^{-3}}$ HCl at 298.2 K were determined to check the precision of the calorimetric system. The measured dissolution enthalpy of $KCl_{(s)}$ was $17597 \pm 17\ \mathrm{J\,mol^{-1}}$ and the enthalpy of reaction of THAM was $-29776 \pm 16\ \mathrm{J\,mol^{-1}}$, which agree with the corresponding published data [12,13].

3. Results and discussion

Since $K_2Cd_2(SO_4)_3$, $K_2Zn_2(SO_4)_3$ and $K_2Mg_2(SO_4)_3$ hardly dissolve in water, all the double salts, as well as, the simple sulphates (or the other salts) were at first finely grounded in an agate mortar. After this, they were dissolved in 100 ml of the calorimetric solvent.

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

The mixture of 0.3–0.4 g of $K_2SO_{4(s)}$ and $MSO_{4(s)}$ ($M = Cd^{2+}, Zn^{2+}, Mg^{2+}$) in a molar relation of 1:2 were dissolved in 100 ml aqueous 3 M HNO_3 at 298.2 K. The values obtained are shown in Table 1.

The molar dissolution enthalpies of $K_2Cd_2(SO_4)_3$, $K_2Zn_2(SO_4)_3$ or $K_2Mg_2(SO_4)_3$ in the same calorimetric solvent 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, three thermochemical cycles were used as shown in Tables 2–4. The reaction molar enthalpies are obtained at 298.2 K from

$$\begin{array}{c} \{K_2SO_{4(s)} + 2MSO_{4(s)}\} + 3\,\mathrm{M}\,HNO_3 = \{\text{solution A}\} \\ \{\text{solution B}\} = K_2M_2(SO_4)_{3(s)} + 3\,\mathrm{M}\,HNO_3 \\ \hline \{K_2SO_{4(s)} + 2MSO_{4(s)}\} = K_2M_2(SO_4)_{3(s)} \end{array}$$

$\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\theta} = \Delta_{\mathrm{diss}}H_{\mathrm{m}}^{\theta}[K_2SO_4 + 2MSO_4] - \Delta_{\mathrm{diss}}H_{\mathrm{m}}^{\theta}[K_2M_2(SO_4)_{3(s)}]$, where $M = Cd^{2+}, Zn^{2+}$ or Mg^{2+}. The values obtained are $5.27 \pm 0.17\ \mathrm{kJ\,mol^{-1}}$ for $K_2Cd_2(SO_4)_{3(s)}$ (Table 2), $-7.52 \pm 0.23\ \mathrm{kJ\,mol^{-1}}$ for $K_2Zn_2(SO_4)_{3(s)}$ (Table 3) and $37.04 \pm 0.25\ \mathrm{kJ\,mol^{-1}}$ for $K_2Mg_2(SO_4)_{3(s)}$ (Table 4).

3.3. Determination of the standard molar formation enthalpies of $K_2M_2(SO_4)_3$

The standard molar formation enthalpies of $K_2M_2(SO_4)_3$ ($M = Cd^{2+}, Zn^{2+}, Mg^{2+}$) are calculated from

$$\begin{aligned} &\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\theta}[K_2M_2(SO_4)_{3(s)}] \\ &\quad = \Delta_{\mathrm{r}}H_{\mathrm{m}}^{\theta} + \Delta_{\mathrm{f}}H_{\mathrm{m}}^{\theta}[K_2SO_{4(s)}] + 2\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\theta}[M(SO_4)_{3(s)}] \end{aligned}$$

Table 1
Dissolution enthalpies of $[2MSO_{4(s)} + K_2SO_{4(s)}]$ and $K_2M_2(SO_4)_3$ in aqueous 3 M HNO_3 at 298.2 K ($R = 996.0\,\Omega$, $I = 19.627\,mA$)

	No.	m(g)	$\Delta E_s/\Delta E_e$ [a]	$\Delta_{diss}H^{\theta}_{m}$(kJ mol^{-1}) [b]
$[2CdSO_{4(s)} + K_2SO_{4(s)}]$	1	0.3562	0.610	11.06
	2	0.3566	0.640	10.62
	3	0.3564	0.556	10.72
	4	0.3565	0.590	10.27
	5	0.3565	0.490	10.54
$\Delta_1H^{\theta}_{m}[2CdSO_{4(s)} + K_2SO_{4(s)}] = 10.64 \pm 0.13\,kJ\,mol^{-1}$				
$K_2Cd_2(SO_4)_{3(s)}$	1	0.3558	0.386	15.78
	2	0.3578	0.716	15.84
	3	0.3604	0.671	15.90
	4	0.3625	0.881	16.04
	5	0.3624	0.453	15.94
$\Delta_2H^{\theta}_{m}[K_2Cd_2(SO_4)_{3,s}] = 15.91 \pm 0.04\,kJ\,mol^{-1}$				
$[2ZnSO_{4(s)} + K_2SO_{4(s)}]$	1	0.3610	0.865	59.74
	2	0.3590	0.860	59.88
	3	0.3587	0.796	59.70
	4	0.3590	0.781	60.02
	5	0.3589	0.850	60.47
$\Delta_1H^{\theta}_{m}[2ZnSO_{4(s)} + K_2SO_{4(s)}] = 59.96 \pm 0.14\,kJ\,mol^{-1}$				
$K_2Zn_2(SO_4)_{3(s)}$	1	0.3470	0.930	67.22
	2	0.3450	0.986	68.12
	3	0.3460	0.655	67.29
	4	0.3461	0.986	67.39
	5	0.3450	0.970	67.40
$\Delta_2H^{\theta}_{m}[K_2Zn_2(SO_4)_{3,s}] = 67.48 \pm 0.09\,kJ\,mol^{-1}$				
$[2MgSO_{4(s)} + K_2SO_{4(s)}]$	1	0.3610	0.962	73.07
	2	0.3610	0.999	73.85
	3	0.3610	0.962	73.27
	4	0.3610	0.964	73.36
	5	0.3610	0.962	73.21
$\Delta_1H^{\theta}_{m}[2MgSO_{4(s)} + K_2SO_{4(s)}] = 73.35 \pm 0.13\,kJ\,mol^{-1}$				
$K_2Mg_2(SO_4)_{3(s)}$	1	0.3500	0.750	36.11
	2	0.3500	0.790	36.58
	3	0.3500	0.785	36.59
	4	0.3500	0.791	36.25
	5	0.3500	0.765	36.04
$\Delta_2H^{\theta}_{m}[k_2Zn_2(SO_4)_{3,s}] = 36.31 \pm 0.12\,kJ\,mol^{-1}$				

[a] ΔE_s(mV) and ΔE_e(mV) are the voltage change during the sample dissolution and the electrical calibration, respectively.

[b] $\Delta_sH^{\theta}_{m} = (\Delta E_s/\Delta E_e)I^2Rte(M/m)$.

Table 2
Reaction scheme for the determination of the standard molar formation enthalpies of $K_2Cd_2(SO_4)_{3(s)}$ at 298.2 K ($\Delta_5H^{\theta}_{m} = \Delta_1H^{\theta}_{m} - \Delta_2H^{\theta}_{m} + 2\Delta_3H^{\theta}_{m} + \Delta_4H^{\theta}_{m}$)

i	Reaction	Solution	$\Delta_{diss}H^{\theta}_{m} - \Delta_fH^{\theta}_{m}$(kJ mol^{-1})
1	$\{2CdSO_{4(s)} + K_2SO_{4(s)}\} + 3\,M\,HNO_3$	A_1	10.64 ± 0.13
2	$K_2Cd_2(SO_4)_{3(s)} + 3\,M\,HNO_3$	B_1	15.91 ± 0.04
3	$Cd_{(s)} + S_{(s)} + 2O_{2(g)} = CdSO_{4(s)}$		-933.28
4	$2K_{(s)} + S_{(s)} + 2O_{2(g)} = K_2SO_{4(s)}$		-1433.69
5	$2K_{(s)} + 2Cd_{(s)} + 3S_{(s)} + 6O_{2(g)} = K_2Cd_2(SO_4)_{3(s)}$		-3305.52 ± 0.17

Table 3
Reaction scheme for the determination of the standard molar formation enthalpies of $K_2Zn_2(SO_4)_{3(s)}$ at 298.2 K ($\Delta_5 H^\theta_m = \Delta_1 H^\theta_m - \Delta_2 H^\theta_m + 2\Delta_3 H^\theta_m + \Delta_4 H^\theta_m$)

i	Reaction	Solution	$\Delta_{diss}H^\theta_m - \Delta_f H^\theta_m$ (kJ mol^{-1})
1	$\{2ZnSO_{4(s)} + K_2SO_{4(s)}\} + 3\,M\,HNO_3$	A_2	59.96 ± 0.14
2	$K_2Zn_2(SO_4)_{3(s)} + 3\,M\,HNO_3$	B_2	67.48 ± 0.09
3	$Zn_{(s)} + S_{(s)} + 2O_{2(g)} = ZnSO_{4(s)}$		-982.82
4	$2K_{(s)} + S_{(s)} + 2O_{2(g)} = K_2SO_{4(s)}$		-1433.69
5	$2K_{(s)} + 2Zn_{(s)} + 3S_{(s)} + 6O_{2(g)} = K_2Zn_2(SO_4)_{3(s)}$		-3406.85 ± 0.23

Table 4
Reaction scheme for the determination of the standard molar formation enthalpies of $K_2Mg_2(SO_4)_{3(s)}$ at 298.2 K ($\Delta_5 H^\theta_m = \Delta_1 H^\theta_m - \Delta_2 H^\theta_m + 2\Delta_3 H^\theta_m + \Delta_4 H^\theta_m$)

i	Reaction	Solution	$\Delta_{diss}H^\theta_m - \Delta_f H^\theta_m$ (kJ mol^{-1})
1	$\{2MgSO_{4(s)} + K_2SO_{4(s)}\} + 3\,M\,HNO_3$	A_3	73.35 ± 0.13
2	$K_2Mg_2(SO_4)_{3(s)} + 3\,M\,HNO_3$	B_3	36.31 ± 0.12
3	$Mg_{(s)} + S_{(s)} + 2O_{2(g)} = MgSO_{4(s)}$		-1278.21
4	$2K_{(s)} + S_{(s)} + 2O_{2(g)} = K_2SO_{4(s)}$		-1433.69
5	$2K_{(s)} + 2Mg_{(s)} + 3S_{(s)} + 6O_{2(g)} = K_2Mg_2(SO_4)_{3(s)}$		-3953.07 ± 0.25

Thus, we get (Tables 2–4)

$$\Delta_f H^\theta_m[K_2M_2(SO_4)_{3(s)}] = \Delta_r H^\theta_m + 2\Delta_3 H^\theta_m + \Delta_4 H^\theta_m$$

by using auxiliary data ($\Delta_f H^\theta_m$) from Ref. [14]: -1433.69 kJ mol^{-1} for $K_2SO_{4(s)}$, -933.28 kJ mol^{-1} for $CdSO_{4(s)}$, -982.82 kJ mol^{-1} for $ZnSO_{4(s)}$ and -1278.21 kJ mol^{-1} for $MgSO_{4(s)}$.

The calculated enthalpies of formation at 298.2 K are:

$$\Delta_f H^\theta_m[K_2Cd_2(SO_4)_{3(s)}] = -3305.52 \pm 0.17\,\text{kJ mol}^{-1}$$

$$\Delta_f H^\theta_m[K_2Zn_2(SO_4)_{3(s)}] = -3406.85 \pm 0.23\,\text{kJ mol}^{-1}$$

$$\Delta_f H^\theta_m[K_2Mg_2(SO_4)_{3(s)}] = -3953.07 \pm 0.25\,\text{kJ mol}^{-1}$$

In the present study, we verified the thermodynamic 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 measurements was estimated according to the equation $\sigma_x = \sqrt{\sum (x_i - x)^2/(n(n-1))}$, where $n \geq 5, x$ is the mean value of the molar dissolution enthalpies and σ_x the mean-square error.

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