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A thermochemical study of $K_2M(IO_3)_4{\cdot}2H_2O$(M=Mg^{2+}, Ni^{2+}, Zn^{2+})

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Abstract

The following reactions:

$$2KIO_3 + M(IO_3)_2 \cdot nH_2O \xrightarrow{\Delta_r H_m^\theta} K_2M(IO_3)_4 \cdot 2H_2O + (n-2)H_2O\,(M{=}Mg^{2+}, Ni^{2+}, Zn^{2+}) \quad (1)$$

were used for the calculation of the enthalpies of the formation of double salts. From the enthalpies of dissolution of iodates and double salts in a calorimetric solvent (water or 3 mol l^{-1} aqueous HNO_3), measured by classical solution calorimetry using an isoperibol reaction calorimeter at 298.2 K. From these values, auxiliary data and by using appropriate thermochemical cycles, the standard molar enthalpy of formation of $K_2M(IO_3)_4{\cdot}2H_2O$ (M=Mg^{2+}, Ni^{2+}, Zn^{2+}) have been obtained:

$$\Delta_f H_m^\theta(K_2Mg(IO_3)_4 \cdot 2H_2O, s, 298.2\,K) = -2510.68 \pm 0.10\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\theta(K_2Zn(IO_3)_4 \cdot 2H_2O, s, 298.2\,K) = -2198.35 \pm 0.10\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\theta(K_2Ni(IO_3)_4 \cdot 2H_2O, s, 298.2\,K) = -2114.88 \pm 0.26\,kJ\,mol^{-1}$$

Keywords: Double salts; Iodates; Calorimetry; Standard molar enthalpy of formation

1. Introduction

Iodates and double iodates have valuable electric and nonlinear optic properties [1]. Since the 1970s decade, many papers dealing with the KIO_3–$M(IO_3)_2$–H_2O system have been published and double iodates have been synthesized [2,3]. Only in the last few years, new methods were applied in the synthesis of double salt iodates of the type $K_2M(IO_3)_4{\cdot}2H_2O$ (M=Mg^{2+}, Ni^{2+}, Zn^{2+}) and their thermal and calorimetric behavior were investigated by DTA, TG and DSC [4,5].

The purpose of this study is to determine the dissolution enthalpies of the iodates and double iodates and by using reactions(1), auxiliary data and appropriate thermochemical cycles, the standard molar

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formation enthalpies of these double iodates were determined.

2. Experimental

2.1. Chemicals

All the chemicals used were of A.R. grade. KCl (obtained from Shanghai Reagent Factory),with purity higher than 99.99%, was dried in a vacuum oven for 6 h at 408 K prior to use.

2.2. Preparations

According to the method given in [4,5], $K_2M(IO_3)_4{\cdot}2H_2O$ (M=Mg^{2+}, Ni^{2+}, Zn^{2+}) were prepared.

2.3. Calorimeter and calibration

The enthalpy of solution was measured in an isoperibol calorimeter, as described previously as well as it was the calorimetric procedure [6]. The solution enthalpies of KCl in water and THAM (NBS 742a, USA) in 0.1000 mol l^{-1}HCl were determined to check the precision of the calorimetric system. The measured dissolution enthalpy of KCl(s) in water at 298.2 K was 17597±17 J mol^{-1} and the enthalpy of reaction of THAM in 0.1000 mol l^{-1} HCl was −29776±16 J mol^{-1}, which agree with the corresponding published data [7,8].

3. Results and discussion

3.1. Determination of the molar dissolution enthalpies of the mixture $2KIO_3+M(IO_3)_2{\cdot}nH_2O$

The results of dissolution enthalpies measurements of these reactants are shown in Tables 1–3.

3.2. Determination of the molar dissolution enthalpies of double iodates

The results of dissolution enthalpies measurements of these products are shown in Table 4.

3.3. Evaluation of the standard molar formation enthalpy of $Zn(IO_3)_2{\cdot}2H_2O(s)$

The standard molar formation enthalpy of $Zn(IO_3)_2{\cdot}2H_2O$(s) has not been reported. To obtain the value, the enthalpy of dissolution of $Zn(IO_3)_2{\cdot}2H_2O$(s) in 100 ml 1 mol l^{-1} HNO_3 was measured and presented in Table 5.

The dissolution process of the $Zn(IO_3)_2{\cdot}2H_2O$ in 1 mol $l^{-1}HNO_3$(aq) is

$$Zn(IO_3)_2 \cdot 2H_2O(s) \overset{\Delta_s H_m^\theta}{\rightarrow} Zn^{2+}(aq) + 2IO_3^-(aq) + 2H_2O(l)$$

$$\Delta_s H_m^\theta = \Delta_f H_m^\theta(Zn^{2+}, aq) + 2\Delta_f H_m^\theta(IO_3^-, aq) + 2\Delta_f H_m^\theta(H_2O, l) - \Delta_f H_m^\theta(Zn(IO_3)_2 \cdot 2H_2O, s)$$

According to [9]

$$\Delta_f H_m^\theta(Zn^{2+}, aq) = -151.69\,kJ\,mol^{-1}$$

Table 1
Dissolution enthalpies of the mixture $2KIO_3 + Mg(IO_3)_2{\cdot}4H_2O$ in water at 298.2 K

No	m_{KIO_3}(g)	$m_{Mg(IO_3)_2\cdot 4H_2O}$(g)	Q (J)	$\Delta_s H_m^\theta$ (kJ mol^{-1})
1	0.1787	0.1863	34.796	83.335
2	0.1789	0.1865	34.810	83.277
3	0.1783	0.1859	34.675	83.222
4	0.1787	0.1863	34.836	83.428
5	0.1783	0.1859	34.712	83.311
6	0.1753	0.1827	34.485	83.495

$\Delta_s H_m^\theta(2KIO_{3(s)} + Mg(IO_3)_2 \cdot 4H_2O_{(s)}, 298.2\,K) = \Delta_1 H_m^\theta = 83.35 \pm 0.04\,kJ\,mol^{-1}$

m–mass of samples; *Q*–heat effect.

Table 2
Dissolution enthalpies of the mixture $2KIO_3 + Zn(IO_3)_2{\cdot}4H_2O$ in 3 mol l^{-1} aqueous HNO_3 solvent at 298.2 K

No	m_{KIO_3}(g)	$m_{Zn(IO_3)_2\cdot 4H_2O}$(g)	Q (J)	$\Delta_s H_m^\theta$ (kJ mol^{-1})
1	0.1457	0.1543	21.162	62.145
2	0.1457	0.1543	21.223	62.324
3	0.1457	0.1543	21.204	62.267
4	0.1457	0.1543	21.175	62.182
5	0.1457	0.1543	21.172	62.174
6	0.1457	0.1543	21.196	62.243

$\Delta_s H_m^\theta(2KIO_{3(s)} + Zn(IO_3)_2 \cdot 4H_2O_{(s)},\ 298.2\,K) = \Delta_4 H_m^\theta = 62.22 \pm 0.03\,kJ\,mol^{-1}$

$$\Delta_f H_m^\theta(IO_3^-, aq) = -221.12\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\theta(H_2O, l) = -285.83\,kJ\,mol^{-1}$$

and $\Delta_s H_m^\theta$ ($Zn(IO_3)_2{\cdot}2H_2O_{(s)}$,298.2 K)=17.99± 0.02 kJ mol^{-1}, measured above, so that $\Delta_f H_m^\theta$ ($Zn(IO_3)_2{\cdot}2H_2O$, s)=−1183.58±0.02 kJ mol^{-1}.

3.4. Determination of the standard molar reaction enthalpy of the reactions (1)

According to Hess's law, three thermochemical cycles were used as shown in Table 6. So, the reaction molar enthalpies are:

$$2KIO_3 + Mg(IO_3)_2 \cdot 4H_2O \overset{\Delta_r H_m^\theta}{\rightarrow} K_2Mg(IO_3)_4 \cdot 2H_2O + 2H_2O$$

$$\Delta_r H_m^\theta = \Delta_3 H_m^\theta = \Delta_2 H_m^\theta - \Delta_1 H_m^\theta = 12.82 \pm 0.10\,kJ\,mol^{-1}$$

$$2KIO_3 + Zn(IO_3)_2 \cdot 2H_2O \overset{\Delta_r H_m^\theta}{\rightarrow} K_2Zn(IO_3)_4 \cdot 2H_2O$$

$$\Delta_r H_m^\theta = \Delta_6 H_m^\theta = \Delta_5 H_m^\theta - \Delta_4 H_m^\theta = -12.03 \pm 0.08\,kJ\,mol^{-1}$$

$$2KIO_3 + Ni(IO_3)_2 + 2H_2O \overset{\Delta_r H_m^\theta}{\rightarrow} K_2Ni(IO_3)_4 \cdot 2H_2O$$

$$\Delta_r H_m^\theta = \Delta_9 H_m^\theta = \Delta_8 H_m^\theta - \Delta_7 H_m^\theta = -51.84 \pm 0.26\,kJ\,mol^{-1}$$

3.5. Determination of the standard molar formation enthalpies of $K_2M(IO_3)_4{\cdot}2H_2O$ ($M=Mg^{2+}$, Ni^{2+}, Zn^{2+})

From reaction(1):

$$\Delta_3 H_m^\theta = \Delta_f H_m^\theta(K_2Mg(IO_3)_4 \cdot 2H_2O,\ s,\ 298.2\,K) + 2\Delta_f H_m^\theta(H_2O,\ l) - \Delta_f H_m^\theta(Mg(IO_3)_2 \cdot 4H_2O,\ s) - 2\Delta_f H_m^\theta(KIO_3,\ s)$$

$$\Delta_6 H_m^\theta = \Delta_f H_m^\theta(K_2Zn(IO_3)_4 \cdot 2H_2O,\ s,\ 298.2\,K) - \Delta_f H_m^\theta(Zn(IO_3)_2 \cdot 2H_2O,\ s) - 2\Delta_f H_m^\theta(KIO_3,\ s)$$

$$\Delta_9 H_m^\theta = \Delta_f H_m^\theta(K_2Ni(IO_3)_4 \cdot 2H_2O,\ s,\ 298.2\,K) - \Delta_f H_m^\theta(Ni(IO_3)_2,\ s) - 2\Delta_f H_m^\theta(KIO_3, s) - 2\Delta_f H_m^\theta(H_2O,\ l)$$

Table 3
Dissolution enthalpies of the mixture $2KIO_3 + Ni(IO_3)_2$ in water at 298.2 K

No	m_{KIO_3}(g)	$m_{Ni(IO_3)_2}$(g)	Q (J)	$\Delta_s H_m^\theta$ (kJ mol^{-1})
1	0.1543	0.1466	20.278	56.577
2	0.1543	0.1466	20.239	56.468
3	0.1543	0.1466	20.346	56.765
4	0.1543	0.1466	20.399	56.914
5	0.1543	0.1466	20.162	56.252
6	0.1543	0.1466	20.381	56.863

$\Delta_s H_m^\theta(2KIO_{3(s)} + Ni(IO_3)_{2(s)}, 298.2\,K) = \Delta_7 H_m^\theta = 56.64 \pm 0.10\,kJ\,mol^{-1}$

Table 4
Dissolution enthalpies of the double iodates in the solvent at 298.2 K

System	Solvent	No.	m (g)	Q_r (J)	$\Delta_s H_m^\theta$ (kJ mol^{-1})
$K_2Mg(IO_3)_4{\cdot}2H_2O$	H_2O	1	0.3491	29.469	70.751
		2	0.3486	29.335	70.529
		3	0.3503	29.459	70.480
		4	0.3557	29.854	70.345
		5	0.3042	25.575	70.465
		6	0.4003	30.538	70.611
$\Delta_s H_m^\theta(K_2Mg(IO_3)_4 \cdot 2H_2O_{(s)}, 298.2\,K) = \Delta_2 H_m^\theta = 70.53 \pm 0.06\,kJ\,mol^{-1}$					
$K_2Zn(IO_3)_4{\cdot}2H_2O$	3 mol l^{-1} O_3(aq)	1	0.3051	25.678	74.147
		2	0.3042	25.644	74.268
		3	0.3039	25.672	74.425
		4	0.2952	24.921	74.374
		5	0.3034	25.542	74.169
		6	0.3065	25.798	74.154
$\Delta_s H_m^\theta(K_2Zn(IO_3)_4 \cdot 2H_2O_{(s)}, 298.2\,K) = \Delta_5 H_m^\theta = 74.26 \pm 0.05\,kJ\,mol^{-1}$					
$K_2Ni(IO_3)_4{\cdot}2H_2O$	H_2O	1	0.3049	37.755	108.102
		2	0.3041	37.858	108.647
		3	0.3177	39.315	108.034
		4	0.3084	38.272	108.339
		5	0.3068	38.243	108.821
		6	0.3096	38.635	108.943
$\Delta_s H_m^\theta(K_2Ni(IO_3)_4 \cdot 2H_2O_{(s)}, 298.2\,K) = \Delta_8 H_m^\theta = 108.48 \pm 0.16\,kJ\,mol^{-1}$					

Table 5
Dissolution enthalpies of $Zn(IO_3)_2{\cdot}2H_2O$ in 1 mol l^{-1} aqueous HNO_3(aq) solvent at 298.2 K

No.	m (g)	Q_r (J)	$\Delta_s H_m^\theta$ (kJ mol^{-1})
1	0.3051	11.997	17.985
2	0.3059	12.156	17.962
3	0.3064	12.237	18.052
4	0.3073	12.195	17.938
5	0.3087	12.297	18.005
6	0.3043	12.123	18.013
$\Delta_s H_m^\theta(Zn(IO_3)_2 \cdot 2H_2O_{(s)}, 298.2\,K) = 17.99 \pm 0.02\,kJ\,mol^{-1}$			

according to [9,10]:

$$\Delta_f H_m^\theta(H_2O, l) = -285.83\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\theta(Mg(IO_3)_2{\cdot}4H_2O, s) = -2092.42\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\theta(KIO_3, s) = -501.37\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\theta(Ni(IO_3)_2, s = -488.64\,kJ\,mol^{-1}$$

as well as the determined enthalpy values:

$$\Delta_f H_m^\theta(Zn(IO_3)_2 \cdot 2H_2O, s) = -1183.58 \pm 0.02\,kJ\,mol^{-1}$$

Table 6
Reactions scheme for the calculation of the standard molar reaction enthalpies of the reactions at 298.2 K

i	Reaction	$\Delta_i H_m^\theta$ (kJ mol^{-1})
1	$2KIO_3+Mg(IO_3)_2{\cdot}4H_2O=2K^+ +4IO_3^- +Mg^{2+}+4H_2O$ (sln in water)	83.35±0.04
2	$K_2Mg(IO_3)_2{\cdot}2H_2O=2K^+ +4IO_3^- +Mg^{2+}+2H_2O$ (sln in water)	70.53±0.06
3	$2KIO_3+Mg(IO_3)_2{\cdot}4H_2O=K_2Mg(IO_3)_4{\cdot}2H_2O+2H_2O$	12.82±0.10
4	$2KIO_3+Zn(IO_3)_2{\cdot}2H_2O=2K^+ +4IO_3^- +Zn^{2+}+2H_2O$ (sln in 3 mol l^{-1} HNO_3)	62.22±0.03
5	$K_2Zn(IO_3)_2{\cdot}2H_2O=2K^+ +4IO_3^- +Zn^{2+}+2H_2O$ (sln in 3 mol l^{-1} HNO_3)	74.26±0.05
6	$2KIO_3+Zn(IO_3)_2{\cdot}2H_2O=K_2Zn(IO_3)_4{\cdot}2H_2O$	−12.03±0.08
7	$2KIO_3+Ni(IO_3)_2=2K^+ +4IO_3^- +Ni^{2+}$ (sln in water)	56.64±0.10
8	$K_2Ni(IO_3)_2{\cdot}2H_2O = 2K^+ +4IO_3^- +Ni^{2+}+2H_2O$ (sln in water)	108.48±0.16
9	$2KIO_3+Ni(IO_3)_2+2H_2O=K_2Ni(IO_3)_4{\cdot}2H_2O$	−51.84±0.26

So that

$$\Delta_f H_m^\theta(K_2Mg(IO_3)_4 \cdot 2H_2O, \text{ s, } 298.2\,K) = -2510.68 \pm 0.10\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\theta(K_2Zn(IO_3)_4 \cdot 2H_2O, \text{ s, } 298.2\,K) = -2198.35 \pm 0.10\,kJ\,mol^{-1}$$

$$\Delta_f H_m^\theta(K_2Ni(IO_3)_4 \cdot 2H_2O, \text{ s, } 298.2\,K) = -2114.88 \pm 0.26\,kJ\,mol^{-1}$$

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