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Study on thermodynamic properties of a double salt, $K_2Mg(IO_3)_4{\cdot}2H_2O$

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Abstract

The standard molar enthalpy of solution of double salts, $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$, in water has been measured by solution calorimetry. From that value, combined with auxiliary values, the standard molar formation enthalpy has been derived: $\Delta_f H_m^{\ominus}$ $(K_2Mg(IO_3)_4{\cdot}2H_2O,s,298.2\ K = -2510.69\ kJ\ mol^{-1}$. The standard free energy $\{\Delta_f G_m^{\ominus}$ $(K_2Mg(IO_3)_4{\cdot}2H_2O,s,298.2\ K) = -2061.72\ \ J\ K\ mol^{-1}\}$ and the absolute entropy $(S_m^{\ominus}(K_2Mg(IO_3)_4{\cdot}2H_2O,s,298.2\ K) = 258.36\ J\ K^{-1}\ mol^{-1}$ were also calculated.

Keywords: Double salt $K_2Mg(IO_3)_4{\cdot}2H_2O$; Solution calorimetry; Thermodynamic properties

1. Introduction

A series of double iodates are of interest in view of the fact that the compounds are expected to possess valuable electric properties [1–3]. The crystal structure and the spectral properties have been previously reported [4–7]. Recently, Rabadjieva and Maneva [8] have reported the preliminary values of the standard molar formation enthalpies of new a double salt, $K_2Mg(IO_3)_4{\cdot}2H_2O$, obtained by solubility and DSC methods. From a comparison, we have determined the standard molar formation enthalpies based on solution calorimetry.

Firstly, the dissolution enthalpies of $[K_2Mg(IO_3)_4{\cdot}2H_2O(s)]$ and $[KIO_3(s) + Mg(IO_3)_2{\cdot}4H_2O(s)]$ in water have been measured at 298.2 K. Hence, from these value, combined with auxiliary values, the standard molar formation enthalpy of $[K_2Mg(IO_3)_4{\cdot}2H_2O(s)]$ has been derived: $\Delta_f H_m^{\ominus}$ $(K_2Mg(IO_3)_4{\cdot}2H_2O,s,298.2\ K) = -2510.69\ kJ\ mol^{-1}$. The standard free energy $\{\Delta_f G_m^{\ominus}$ $(K_2Mg(IO_3)_4{\cdot}2H_2O,s,298.2\ K) = -2061.72\ KJ\ mol^{-1}\}$ and the absolute entropy $\{S_m^{\ominus}(K_2Mg(IO_3)_4{\cdot}2H_2O,s,298.2\ K) = 258.36\ J\ K^{-1}\ mol^{-1}\}$ were also calculated.

2. Experimental

2.1. Chemicals

All the chemicals (KIO_3, $Mg(IO_3)_2{\cdot}4H_2O$, KCl) used were of analytical grade.

KCl, calorimetric primary standard of purity >99.99%, was dried in a vacuum oven for 6 h at 408 K prior to use. Doubly distilled water was used throughout the experiment.

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2.2. Calorimeter

The isoperibol reaction calorimeter used for this study was constructed in this laboratory and was adapted for measuring enthalpies of solid–liquid, liquid–liquid reactions [9,10]; the volume of the reaction vessel is 100 cm^3. The precision temperature control and measurement were ±0.001 and ±0.0001 K, respectively.

The calorimeter was tested by measuring the dissolution enthalpy of THAM (NBS 742a, USA) in 0.1 mol l^{-1} HCl and KCl (calorimetric primary standard) in water at 298.2 K. The mean dissolution enthalpies were $-297\,766 \pm 16$ J mol^{-1} for THAM and $17\,597 \pm 17$ J mol^{-1} for KCl, which are in conformity with the respective published data [11,12].

2.3. Preparations

$K_2Mg(IO_3)_4{\cdot}2H_2O(s)$ was prepared by evaporating a mixture of solution of KIO_3 and $Mg(IO_3)_2{\cdot}4H_2O$ (mole ratio 2 : 1) according to the method of Rabadjieva and Maneva [8]. The water content of $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$ was identified by thermogravimetry.

3. Results

All the salts were dissolved in 100 ml of water.

Samples of 0.37 g of $KIO_3(s)$ and $Mg(IO_3)_2{\cdot}4H_2O(s)$ in a mole ratio 2 : 1 were dissolved in 100 ml water at 298.2 K. The results are shown in Table 1.

The dissolution enthalpies of $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$ in water was measured under the same conditions. The results are also tabulated in Table 1.

3.1. The standard molar formation enthalpy of $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$

The reaction scheme used to derive the standard molar formation enthalpy of $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$ is given in Table 2. The molar dissolution enthalpy of $KIO_3(s)$ and $Mg(IO_3)_2{\cdot}4H_2O(s)$ mixture in mole ratio of $n(KIO_3)/n(Mg(IO_3)_2{\cdot}4H_2O) = 2:1$ was determined in water. In the same conditions, we have measured the molar dissolution enthalpy of $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$. The dilution effect of $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$ aqueous solution diluted in 2 mol H_2O is ignored. These values were combined with auxiliary values of $\Delta_f H_m^\ominus = -501.37$ KJ mol^{-1} for $KIO_3(s)$, -285.83 KJ mol^{-1} for $H_2O(l)$ [13] and -2092.42 KJ mol^{-1} for $Mg(IO_3)_2{\cdot}4H_2O(s)$ [14] to derive the standard molar formation enthalpy of $[K_2Mg(IO_3)_4{\cdot}2H_2O(s)]$: $\Delta_f H_m^\ominus(K_2Mg(IO_3)_4{\cdot}2H_2O\text{,-s,}298.2K) = -2510.69$ KJ mol^{-1}.

Table 1
Dissolution enthalpies of $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$, $[2KIO_3(s) + Mg(IO_3)_2{\cdot}4H_2O(s)]$ in water at 298.2 K

System	No.	m [a]/g	Q [b]/J	$\Delta_s H_m^\ominus$/(kJ mol^{-1})
	$\Delta_r H_m^\ominus[K_2Mg(IO_3)_4{\cdot}2H_2O(s) = 70.530 \pm 0.056$ kJ mol^{-1}			
$K_2Mg(IO_3)_4{\cdot}2H_2O(s)$	1	0.3491	29.469	70.751
	2	0.3486	29.335	70.529
	3	0.3503	25.459	70.480
	4	0.3557	29.854	70.345
	5	0.3042	25.575	70.465
	6	0.4003	30.538	70.611
	$\Delta_s H_m^\ominus[2KIO_3(s) + Mg(IO_3)_2{\cdot}2H_2O(s)] = 83.345 \pm 0.041$ kJ mol^{-1}			
$2KIO_3(s) + Mg(IO_3)_2{\cdot}4H_2O(s)$	1	0.3650	34.796	83.335
	2	0.3654	34.810	83.277
	3	0.3642	34.675	83.222
	4	0.3650	34.836	83.428
	5	0.3642	34.712	83.311
	6	0.3580	34.485	83.495

[a] Mass of sample.
[b] Heat effect.

Table 2
Reaction scheme for the standard molar formation enthalpy of $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$ at the temperature 298.2 K. The solvent ‘s’ was water. $\Delta H_6 = \Delta H_1 - \Delta H_2 + 2\Delta H_3 + \Delta H_4 - 2\Delta H_5$

Reaction	Solution	$\Delta_s H_m^{\ominus}$/(kJ mol^{-1})
1. $\{2KIO_3(s) + Mg(IO_3)_2{\cdot}4H_2O(s)\}$ + ‘s’=	A	83.345 ± 0.041
2. $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$ + ‘s’=	B	70.530 ± 0.056
3. $K(s) + 1/2I_2(s) + 3/2O_2(g) = KIO_3(s)$		−501.37
4. $Mg(s) + I_2(s) + 5O_2(g) + 4H_2(g) = Mg(IO_3)_2{\cdot}4H_2O(s)$		−2092.42
5. $H_2(g) + 1/2O_2(g) = H_2O(l)$		−285.83
6. $2K(s) + Mg(s) + 2I_2(s) + 7O_2(g) + 2H_2(g) = K_2Mg(IO_3)_4{\cdot}2H_2O(s)$		−2510.69

3.2. The standard free energy

For the equilibrium

$$K_2Mg(IO_3)_4 \cdot 2H_2O \rightleftharpoons 2K^+ + Mg^{2+} + 4IO_3{}^- + 2H_2O$$

We can write the equilibrium as follows:

$$\begin{aligned}\Delta_f G_m{}^{\ominus}(K_2Mg(IO_3)_4 \cdot 2H_2O) &= 2\Delta_f G_m{}^{\ominus}(K^+) + \Delta_f G_m{}^{\ominus}(Mg^{2+}) \\ &\quad + 4\Delta_f G_m{}^{\ominus}(IO_3^-) + 2\Delta_f G_m{}^{\ominus}(H_2O) - \Delta_r G_m{}^{\ominus}\end{aligned}$$

The standard free energy of $\Delta_f G_m{}^{\ominus}(K^+)$, $\Delta_f G_m{}^{\ominus}(Mg^{2+})$, $\Delta_f G_m{}^{\ominus}(IO_3{}^-)$ and $\Delta_f G_m{}^{\ominus}(H_2O)$ were taken from Ref. [13]. $\Delta_r G_m{}^{\ominus} = RT \ln k$ was obtained from Ref. [8]. After combining previous data, we obtained: $\Delta_f G_m{}^{\ominus}(K_2Mg(IO_3)_4{\cdot}2H_2O,s,298.2\ K) = -2061.72$ kJ mol^{-1}.

3.3. The absolute entropy of $[K_2Mg(IO_3)_4{\cdot}2H_2O(s)]$

According to $\Delta G = \Delta H\text{-}T\Delta S$, and combining previous data ($\Delta_f G_m{}^{\ominus}$ and $\Delta_f H_m{}^{\ominus}$ values of $K_2Mg(IO_3)_4{\cdot}2H_2O$), the value $\Delta S = -1505.60$ J K^{-1} mol^{-1} was obtained. The absolute entropy of K(s), Mg(s), $I_2(s)$, $O_2(g)$ and $H_2O(l)$ were taken from available sources [13]:

$$\begin{aligned}S_m{}^{\ominus}(K_2Mg(IO_3)_4 \cdot 2H_2O, s, 298.2\,K) \\ = 258.36;\ J\,K^{-1}\,mol^{-1}\end{aligned}$$

4. Discussion

The standard enthalpies of formation in the solid state obtained in the present work for $K_2Mg(IO_3)_4{\cdot}2H_2O(s)$ differ from the values presented in Ref. [8] (see Table 2). The reason of this difference should be sought in the most probable sources of errors in calorimetric methods used. In Ref. [8], the DSC method depends on the error of the apparatus and the measurement, since the error of calculation of $\Delta_f H_m{}^{\ominus}$ is 8–10%. The data on the solubility, on the basis of which the $\Delta_f H_m{}^{\ominus}$ value has been calculated by the Van’t Hoff equation [$d \ln K/d(1/T) = \Delta H^0/R$], have been determined under the conditions of thermodynamic equilibrium. A very high accuracy over a wide temperature range is needed in the determination of K in the Van’t Hoff equation. Otherwise, the propagation of error in K to that ΔH^0 will make that latter value almost useless [15,16]. In this paper, we confirmed the thermodynamic identities of solutions A and B, and used the unique thermochemical cycle with every calorimetric solvent for double salt and $[2KIO_3(s) + Mg(IO_3)_2{\cdot}4H_2O(s)]$. Thus, we are inclined to believe that the $\Delta_f H_m{}^{\ominus}$ value determined by solution calorimeter measurements is more reliable.

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