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Synthesis, thermal investigations and solubility of a new double salt $K_2Mg(IO_3)_4 \cdot 2H_2O$

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Abstract

A new double salt $K_2Mg(IO_3)_4 \cdot 2H_2O$ has been synthesized. Its thermal and calorimetric behaviors were investigated by the DTA, TG and DSC methods. A mechanism of thermal decomposition has been suggested. The $\Delta_f H^0_{298}$ was calculated from the recorded ΔH^0 of the DSC curve. The data from the TG curves were processed by the methods of formal kinetics involving the calculation of the kinetic parameters E^* and Z, and the type of the kinetic equation determined. The solubility of $K_2Mg(IO_3)_4 \cdot 2H_2O$ in water was investigated in the 20–50°C temperature interval. The value of $\Delta_{dissol} H^0_{298}$ was calculated on the basis of the solubility data, whence the value of $\Delta_f H^0_{298}$ of the double salt was calculated. The values of $\Delta_f H^0_{298}$, determined by the two methods, were compared. © 1997 Elsevier Science B.V.

Keywords: Double salts; Iodates; Solubility; Thermal investigations; Thermodynamic properties

1. Introduction

The study undertaken is a continuation of our research [1,2] on establishing the conditions of synthesis of double iodates and on determining their thermal and calorimetric properties. The problem is of interest in view of the fact that the newly synthesized compounds are expected to possess valuable electric properties [3].

There is little information in available literature on the double iodates of the $K_2Me(IO_3)_4 \cdot 2H_2O$ type. The ternary KIO_3–$Mg(IO_3)_2$–H_2O system has been investigated at 50°C [4]. The solubility diagram only exhibits a crystallization field of the double salt $K_2Mg(IO_3)_4 \cdot 4H_2O$. The compound has been isolated and described by X-ray analysis and the method of differential thermal analysis.

There are no data in the literature available about the existence of $K_2Mg(IO_3)_4 \cdot 2H_2O$. The aim of this study is to determine the conditions for obtaining the new double salt $K_2Mg(IO_3)_4 \cdot 2H_2O$ under non-equilibrium conditions. The aim is also to study its thermal and calorimetric properties and to use the data obtained to calculate certain kinetic (E^* and Z) and thermodynamic (ΔH^0) parameters for the dehydration process. Another aim is to study its solubility in the 20–50°C interval and, from the data obtained, to calculate the enthalpy of dissolution ($\Delta_{dissol} H^0_{298}$). The values thus obtained for ΔH^0 and $\Delta_{dissol} H^0_{298}$ are to be used for calculating the change of the standard enthalpy of formation ($\Delta_f H^0_{298}$) of $K_2Mg(IO_3)_4 \cdot 2H_2O$ by the two methods.

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2. Experimental

The investigations carried out show that $K_2Mg(IO_3)_4{\cdot}2H_2O$ can be obtained by two methods, namely:

- by the addition, in the stoichiometric proportion, of solid $Mg(IO_3)_2{\cdot}4H_2O$ to a saturated solution of KIO_3 at 40°C, under continuous stirring in a magnetic stirrer for 8 h (Method I); and
- by desalination with ethanol of a solution obtained as a result of mixing 1% $Mg(IO_3)_2$ and 3% KIO_3 solutions at room temperature (Method II).

The compounds obtained by these methods were identified spectroscopically and by X-ray and quantitative analysis as follows:

- Mg^{2+} – complexometrically [5];
- K^+ – by weight, through precipitation with sodium tetraphenyl borate [6];
- iodine – iodometrically [7]; and
- water by Fisher's method and thermogravimetrically.

X-ray powder diffraction patterns were taken on a diffractometer type TUR M-62 with FeK_α irradiation, while the IR spectra were taken on a spectrophotometer Philips PU-9700 as tablets with KBr. Our thermal investigations were carried out on a derivatograph Paulik–Paulik–Erdey MOM-OD-102 at a heating rate of 10°C min^{-1} up to 900°C, while the calorimetric investigations were made on a DSC-4 Perkin–Elmer apparatus, in the 20–500°C range in standard crucibles. The kinetic analysis was made using TG curves obtained on heating up to 500°C at a rate of 5°C min^{-1}.

The investigations for determining salt solubility were carried out in the 20–50°C interval in sealed glass containers under continuous stirring at ~400 rpm. The temperature was maintained by an ultrathermostat UT-4 with an accuracy of ±0.05°C. At each one of the temperatures investigated, the equilibrium was achieved after 48 h. The constant composition of the liquid and solid phases, respectively, of the two successive samples obtained within different times of treatment while maintaining T=const. is the criterion for the presence of equilibrium. The compositions of the liquid and solid phases were determined. The solid phase has been identified by the methods of quantitative and X-ray analyses and infrared spectroscopy for each of the temperatures investigated.

3. Results and discussion

The data from the quantitative analysis are shown in Table 1. They confirm the preparation of a compound with composition $K_2Mg(IO_3)_4{\cdot}2H_2O$.

Its X-ray data were also obtained and we established that its reflection differed from those shown in [4] for $K_2Mg(IO_3)_4{\cdot}4H_2O$ (Fig. 1).

The compound has also been identified by its IR spectrum, obtained in the region of normal vibrations (1000–200 cm^{-1}) of the iodate group, which has been compared with the IR spectra of the initial compounds, KIO_3 and $Mg(IO_3)_2{\cdot}4H_2O$ (Fig. 2). The spectrum of the newly obtained compound is characterized by an absorption band different in its nature with a maximum at 765 cm^{-1} and arms at 805 cm^{-1} and 705 cm^{-1}. They are attributed to the oscillations of the I–O bond [8,9]. The bending vibrations (ν_2 and ν_4) of the IO_3^- group appear at 385 and 325 cm^{-1} and are displaced toward the lower frequencies compared to those of the initial compounds.

The DTA and TG curves of the investigated compound are shown in Fig. 3, while DSC curve can be seen in Fig. 4.

The DTA curve shows initially a strong endothermic effect with T_{max}=330°C (Fig. 3) which corre-

Table 1
Data from the quantitative analysis for $K_2Mg(IO_3)_4{\cdot}2H_2O$ obtained by the two methods

Method	K^+ (mass %)		Mg^{2+} (mass %)		IO_3^- (mass %)		H_2O (mass %)	
	Theoretical	Experiment	Theoretical	Experiment	Theoretical	Experiment	Theoretical	Experiment
I	9.3	9.6±0.5	2.9	3.2±0.5	83.5	82.9±0.5	4.3	4.2±0.5
II		8.9±0.5		3.1±0.5		82.9±0.5		4.5±0.5

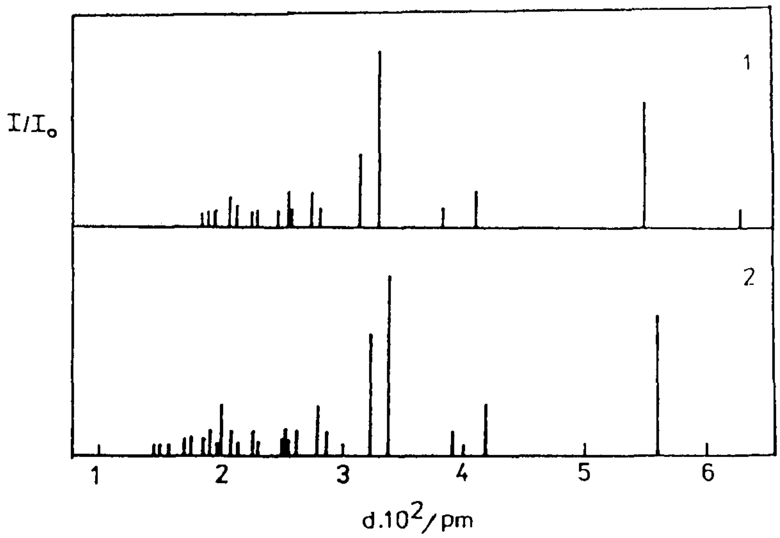

Fig. 1. X-ray powder data of: 1 – $K_2Mg(IO_3)_4{\cdot}4H_2O$ [3]; 2 – $K_2Mg(IO_3)_4{\cdot}2H_2O$.

sponds to the decomposition of $K_2Mg(IO_3)_4{\cdot}2H_2O$ to KIO_3, $Mg(IO_3)_2$ and H_2O and the evaporation of the water of crystallization. The change in mass (Δm) determined from the TG curve exactly corresponds to the water of crystallization in the initial salt. The value T_{max}=330°C, found from the DTA curve, is higher than the dehydration temperature of $Mg(IO_3)_2{\cdot}4H_2O$ (T_{deh}=165°C [10]), which indicates the higher thermal stability of the double salt. An analogous pattern of behavior for $K_2Me(IO_3)_4{\cdot}2H_2O$ where Me=Zn, Co, Ni [1], is observed. Corresponding to the examined endothermic effect in the DTA curve at T_{max}=330°C, is an analogous endothermic effect in the DSC curve (Fig. 4). The following endothermic effect is characterized by two closely separated maxima (T_1=291.20°C and T_2=295.1°C), with a considerable width of the peak base. The value of ΔH^0=181.5 kJ mol^{-1} includes the change in enthalpy during the decomposition of the double salt to KIO_3, $Mg(IO_3)_2$ and H_2O and the evaporation of the water of crystallization.

The following two endothermic effects along the DTA curve (Fig. 3) describe the decomposition of KIO_3 or of $Mg(IO_3)_2$, respectively. According to the published data [10,11] $Mg(IO_3)_2$ is converted first into orthoperiodate, followed by the decomposition of $Mg_5(IO_6)_2$ to MgO.

$$Mg(IO_3)_2 \rightarrow 1/5Mg_5(IO_6)_2 + 4/5I_2 + 9/5O_2 \quad T_{max} = 610°C$$
$$Mg_5(IO_6)_2 \rightarrow 5MgO + I_2 + 7/2O_2 \quad T_{max} = 670°C$$

According to [12,13], KIO_3 is decomposed in the 590–640°C temperature interval by two paths, namely:

$$KIO_3 \rightarrow KI + 3/2O_2 \text{ and}$$
$$KIO_3 \rightarrow K_2O + I_2 + 5/2O_2$$

The two reactions take place in parallel.

The last peak appearing in the derivatogram at T_{max}=770°C (Fig. 3) can be attributed to the melting of KI [1,14].

The kinetic analysis has been made using the TG curve (Δm=$f(T)$) obtained for the purpose with heating up to 500°C at a rate of 5°C min^{-1}. Thus, the kinetic parameters obtained concern the evaporation of the water of crystallization alone, which depends on the specific behavior of the system. A differential method for kinetic analysis of non-isothermal data has been used in calculating the formal kinetic parameters (E^* and Z) and for determining the type of the kinetic equation characterizing the process of dehydration and decomposition of the double salt to simple iodates [15]. The following results were obtained by means of a computer program based on the data from the TG curves and on the 25 known kinetic equations

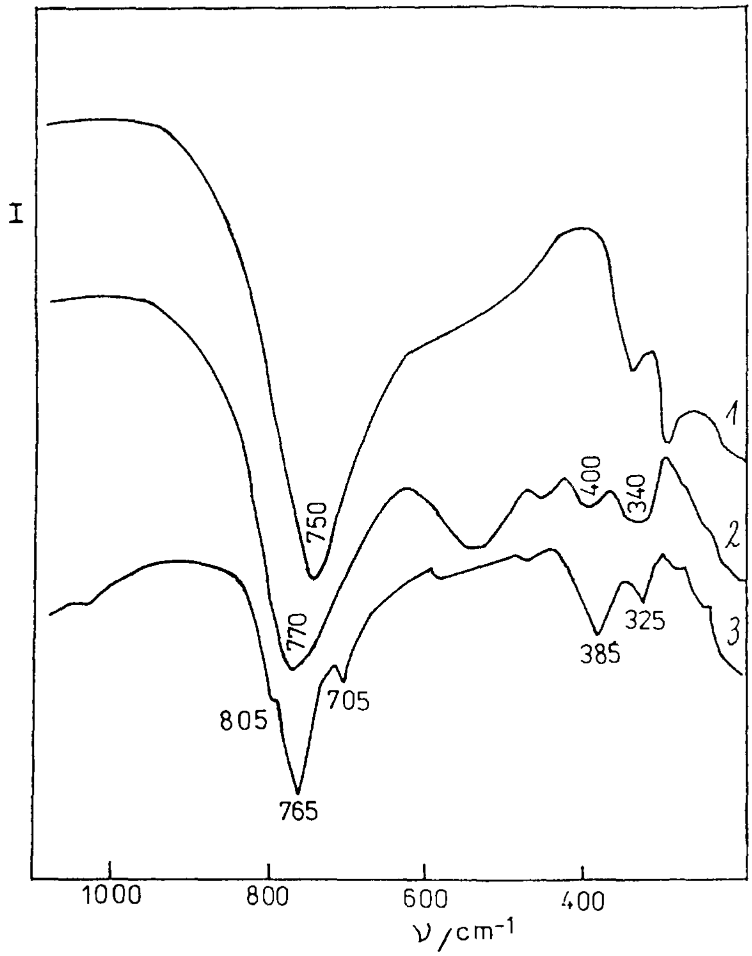

Fig. 2. IR spectra of: 1 – KIO_3; 2 – $Mg(IO_3)_2{\cdot}4H_2O$; 3 – $K_2Mg(IO_3)_4{\cdot}2H_2O$.

[15,16]:

$$E^* = 152.81\ \mathrm{kJ\,mol^{-1}}$$
$$Z = 1.418.10^{12}\ \mathrm{s^{-1}}$$

where E^* is the activation energy, and Z the pre-exponential factor.

The correlation coefficient for the quantities determined is 0.9946, while the standard deviation is 0.1214.

The kinetic equation corresponding to the process is of the following type:

$$F(\alpha) = \frac{(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}}$$

where α is the degree of change of the mass as calculated from the TG curve.

The kinetic equation obtained is of the diffusion type.

In order to expand the existing information on the newly obtained $K_2Mg(IO_3)_4{\cdot}2H_2O$, we carried out research to determine its solubility in the 20–50°C interval. The experimental data obtained are presented in Table 2. The same table also shows the measured densities of the saturated solutions at different

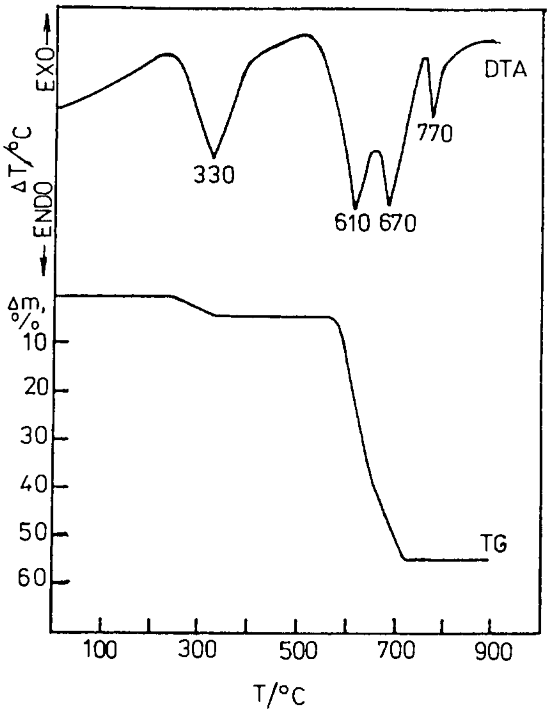

Fig. 3. DTA and TG curves of $K_2Mg(IO_3)_4{\cdot}2H_2O$.

temperatures. Fig. 5 presents the solubility curve. The solid phase composition is the same over the entire temperature range investigated. On the basis of the results obtained, it is possible to calculate the $\Delta_{dissol}H^0_{298}$ of the double salt using a method described in [17].

The thermodynamic equilibrium constant characterizing the equation

$$\text{solid phase} \rightleftharpoons \text{saturated solution}$$

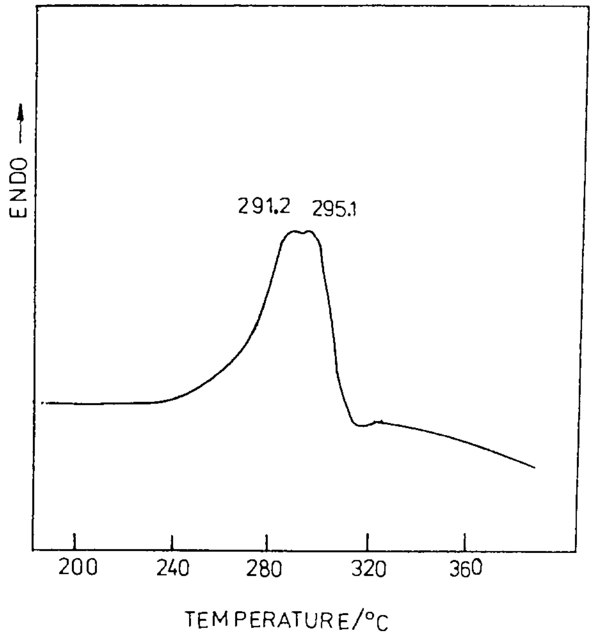

Fig. 4. DSC curve of $K_2Mg(IO_3)_4{\cdot}2H_2O$.

for the salt $K_2M_g(IO_3)_4{\cdot}2H_2O$ can be expressed in the following manner:

$$K = \frac{a^2_{K^+} a_{Mg^{2+}} a^4_{IO_3^-}}{a_{K_2Mg(IO_3)_4\cdot 2H_2O}} \quad \text{but}\, a_{K_2Mg(IO_3)_4\cdot 2H_2O} = 1,$$

$$\text{consequently}, K = a^2_{K^+} a_{Mg^{2+}} a^4_{IO_3^-}$$

$$= \left(c^2_{K^+} c_{Mg^{2+}} c^4_{IO_3^-}\right)\left(\gamma^2_{K^+}\gamma_{Mg^{2+}}\gamma^4_{IO_3^-}\right)$$

$$= (2S)^2 S (4S)^4 \left(\gamma^2_{K^+}\gamma_{Mg^{2+}}\gamma^4_{IO_3^-}\right) = 1024 S^7 \gamma^7_{\pm}$$

where $\gamma_{\pm}$ is the mean ionic activity coefficient and S the solubility of $K_2Mg(IO_3)_4{\cdot}2H_2O$ in mol/dm^3.

Table 2
Solubility data of $K_2Mg(IO_3)_4{\cdot}2H_2O$

T (°C)	Concentration of the saturated solution (mol/dm^3)	Density of the saturated solution (kg/dm^3)	Composition of the solid phase
20	0.0411	1.0253	$K_2Mg(IO_3)_4{\cdot}2H_2O$
25	0.0424	1.0256	$K_2Mg(IO_3)_4{\cdot}2H_2O$
30	0.0461	1.0257	$K_2Mg(IO_3)_4{\cdot}2H_2O$
35	0.0535	1.0338	$K_2Mg(IO_3)_4{\cdot}2H_2O$
40	0.0596	1.0384	$K_2M_g(IO_3)_4{\cdot}2H_2O$
45	0.0617	1.0397	$K_2Mg(IO_3)_4{\cdot}2H_2O$
50	0.0699	1.0423	$K_2Mg(IO_3)_4{\cdot}2H_2O$

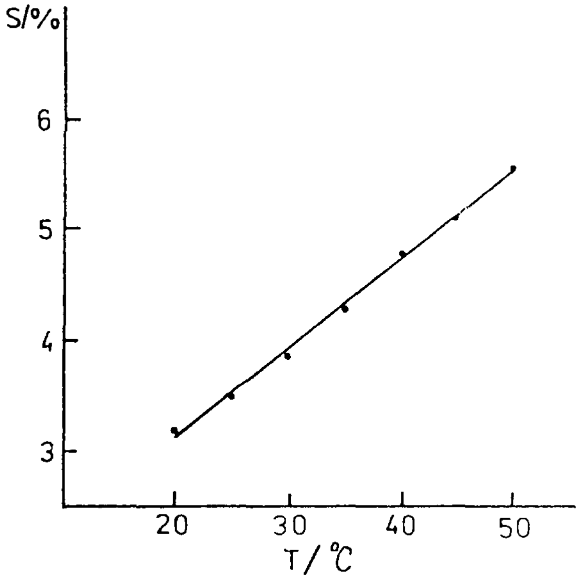

Fig. 5. Solubility curve of $K_2Mg(IO_3)_4{\cdot}2H_2O$ (*S*, concentration of the saturated solution in mass %).

The $\gamma_\pm$ values can be calculated from the Davies equation [18] in which the ionization energy (*I*) and the constant *A*, which depends only on the temperature [19], participate.

The values calculated for *I*, *A*, $\gamma_\pm$ and *K* for each one of the working temperatures are shown in Table 3.

Under the condition of equilibrium, $\Delta G^0 \equiv \Delta H^0 - T\Delta S^0 = -RT\ln K$ and the plot of $\ln K$ vs. $f(1/T)$ is a straight line with gradient $\tan\alpha = (\Delta_{\mathrm{dissol}}H^0_{298})/R$ as shown in Fig. 6. The most probable straight line between the experimental points was calculated by means of a computer program.

$$\Delta_{\mathrm{dissol}}H^0_{298} = 69\,\mathrm{kJ\,mol^{-1}}$$

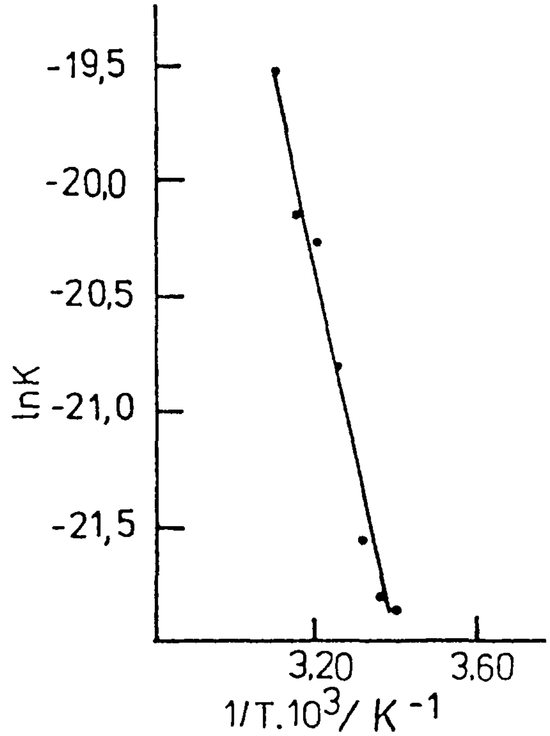

Fig. 6. Dependence $\ln K = f(1/T)$.

For the equilibrium

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

we can write the equilibrium

$$\Delta_f H^0_{298_{K_2Mg(IO_3)_4\cdot 2H_2O}} = 2\Delta_f H^0_{298_{K^+}} + \Delta_f H^0_{298_{Mg^{2+}}} + 4\Delta_f H^0_{298_{IO_3^-}} + 2\Delta_f H^0_{298_{H_2O(l)}} - \Delta_{\mathrm{dissol}}H^0_{298l}$$

Table 3
Data on the calculated values of *I*, *A*, $\gamma_\pm$ and the equilibrium constant (*K*)

T (°C)	*I* (mol/dm³)	*A* (kg/mol)$^{1/2}$	$\gamma_\pm$	$K\times 10^{10}$	ln *K*
20	0.1874	0.5086	0.3947	3.17	−21.87
25	0.1965	0.5126	0.3874	3.30	−21.83
30	0.2305	0.5184	0.3692	4.24	−21.58
35	0.2675	0.5218	0.3549	9.11	−20.82
40	0.2973	0.5265	0.3440	16.60	−20.28
45	0.3087	0.5314	0.3381	17.60	−20.16
50	0.3541	0.5365	0.3262	32.80	−19.54

The values of $\Delta_f H^0_{298}$ for the corresponding ions in water solution are taken from available sources [20] and for $\Delta_f H^0_{298_{H_2O}}$ – from [14].

$$\Delta_f H^0_{298_{K_2Mg(IO_3)_4\cdot 2H_2O}} = -2549\,\mathrm{kJ\,mol^{-1}} \qquad (1)$$

$\Delta_f H^0_{298_{K_2Mg(IO_3)_4\cdot 2H_2O}}$ can also be calculated on the basis of ΔH^0 from the DSC curve by taking into account the equation

$$K_2Mg(IO_3)_4 \cdot 2H_2O \rightleftharpoons KIO_3 + Mg(IO_3)_2 + 2H_2O(g) - \Delta H^0$$

$$\Delta_f H^0_{298_{K_2Mg(IO_3)_4\cdot 2H_2O}} = 2\Delta_f H^0_{298_{KIO_3}} + \Delta_f H^0_{298_{Mg(IO_3)_2}} + 2\Delta_f H^0_{298_{H_2O(g)}} - \Delta H^0$$

The ΔH^0_f for the corresponding salts have been taken from existing sources [13,21].

$$\Delta_f H^0_{298_{K_2Mg(IO_3)_4\cdot 2H_2O}} = -2573\,\mathrm{kJ\,mol^{-1}} \qquad (2)$$

The accuracy of the determination of ΔH^0 according to the DSC method depends on the error of the apparatus, i.e. ±0.5% kJ, as well as the error of measurement. The accuracy of determination of $\Delta_{dissol} H^0_{298}$ depends on the errors of the different analytical methods applied to the determination of the composition of the liquid and solid phases. Since the error of calculation of the separate thermodynamic quantities is 8–10%, the presentation of the $\Delta_f H^0_{298_{K_2Mg(IO_3)_4\cdot 2H_2O}}$ values by whole numbers answers the requirements.

The data on the solubility, on the basis of which the $\Delta_f H^0_{298_{K_2Mg(IO_3)_4\cdot 2H_2O}}$ (Eq. (1)) value has been calculated, have been determined under the conditions of thermodynamic equilibrium. This allows using the foregoing value in a comparison with the $\Delta_f H^0_{298_{K_2Mg(IO_3)_4\cdot 2H_2O}}$ (Eq. (2)) value, calculated from data obtained by DSC method. The good agreement between the two values, in this case, shows that the enthalpy changes during phase transitions in the DSC curve may be used for calculating $\Delta_f H^0_{298}$ for the compounds under consideration with a sufficient accuracy.

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