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Non-isothermal kinetics of dehydration of some selenite hexahydrates

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Abstract

The kinetics of dehydration of $Al_2(SeO_3)_3 \cdot 6H_2O$, $Ga_2(SeO_3)_3 \cdot 6H_2O$ and $In_2(SeO_3)_3 \cdot 6H_2O$ were studied under non-isothermal heating on a derivatograph. The method of Coats–Redfern was used with different kinetics models. The values of the kinetics parameters characterizing the process were calculated. The dependencies observed were interpreted according to the generalized perturbation theory of chemical reactivity. Kinetic compensation effect was found.

Keywords: Aluminum; gallium and indium selenite hexahydrates; Dehydration; Non-isothermal kinetic; Compensation effect

1. Introduction

It is well known that metal selenites are used in glass and ceramics industries as pigment for glasses, enamels and glazes, repellents in forest industry, antioxidants in pharmacy but mostly in semiconductor techniques due to their semiconductor properties [1,2]. Besides, they are precursors for preparation of their corresponding selenides, which also possess semiconductor properties.

A number of papers have been published on the preparation [3–6] and structure [6,7] of aluminum, gallium and indium selenites. The solubility isotherms of the systems Me_2O_3–SeO_2–H_2O, where Me = Al, Ga or In have been described in Refs. [8–10] and their IR spectra—in Refs. [11–13]. No data, however, were found in the available literature on the dehydration kinetics of the crystallohydrates of these selenites and the preparation of the corresponding anhydrous selenites from which their selenides can be obtained by reduction with H_2 or CO.

With regard to this, the aim of the present work is to study the dehydration kinetics of the hexahydrates of aluminum, gallium and indium selenites under non-isothermal heating and find the values of the parameters characterizing this process.

2. Experimental

2.1. Materials and measurements

The hexahydrates of aluminum, gallium and indium selenites were prepared by mixing solutions of the corresponding chlorides and Na_2SeO_3 (Aldrich) in equimolar quantities at room temperature and under continuous agitation. The solid phase was separated by filtration; the residue was washed with distilled water until absence of chloride ions in washed water. Portions of these residues were placed in glass ampoules together with SeO_2 solutions in concentrations selected to be in the crystallization field of the corresponding hexahydrate [8–10]. The ampoules were then sealed and placed in an oven at 373 K for 3 months. Thus, under conditions of hydrothermal synthesis at autogeneous pressure, well-crystallized solid phases were obtained. Further, the ampoules were opened, the solid phase was filtered, washed with distilled water and dried in air for 3 days. According to the data obtained from X-ray powder analysis, the substances could be described by the following formulae: $Al_2(SeO_3)_3 \cdot 6H_2O$, $Ga_2(SeO_3)_3 \cdot 6H_2O$ and $In_2(SeO_3)_3 \cdot 6H_2O$.

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The thermo-gravimetrical measurements were carried out in a flow of nitrogen at a rate of $20\,\mathrm{cm^3\,min^{-1}}$ under non-isothermal conditions in a derivatograph system Paulik–Paulik–Erdey (MOM, Hungary) at heating rate of $6\,\mathrm{K\,min^{-1}}$ up to 573 K. Samples of 100 mg were weighted into a 7 mm diameter 14 mm high platinum crucible, without pressing. α-Alumina calcined up to 1373 K was used as a standard reference material. The TG, DTA and DTG curves were recorded graphically with 1 mg sensitivity.

2.2. Theoretical background

Dehydration of crystal hydrates is a solid-state process of the type:

$$A(\text{solid}) \rightarrow B(\text{solid}) + C(\text{gas}).$$

The kinetics of such reactions is described by various equations taking into account the special features of their mechanisms. The reaction rate can be expressed through the degree of conversion α (the ratio between the weight loss at moment t and the total weight loss by the end of dehydration) and its temperature dependence:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha). \tag{1}$$

The temperature dependence of the rate constant k for the process is described by the Arrhenius equation:

$$k = A\exp\left(-\frac{E}{RT}\right), \tag{2}$$

where A is the pre-exponential factor, T is the absolute temperature, R is the gas constant, and E is the activation energy. Substitution of (2) in (1) gives

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)f(\alpha). \tag{3}$$

When the temperature increases at a constant rate,

$$\frac{\mathrm{d}T}{\mathrm{d}t} = q = \text{const}, \tag{4}$$

therefore:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{q}\exp\left(-\frac{E}{RT}\right)f(\alpha). \tag{5}$$

The conversion function $f(\alpha)$ for a solid-state reaction depends on the reaction mechanism and can generally be considered to be as follows:

$$f(\alpha) = \alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p, \tag{6}$$

where m, n and p are empirically obtained exponent factors, one of them always being zero [14,15].

After substitution in Eq. (5), separation of variables and integration, the following equation was obtained:

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p} = \frac{A}{q}\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T. \tag{7}$$

The solutions of the left-hand side integral depend on the explicit expression of the function $f(\alpha)$ and are denoted as $g(\alpha)$. Their algebraic expressions are presented in Table 1.

Several authors [16–18] suggested different ways to solve the right-hand side integral. For the present study, the method Coats–Redfern [19] was used. Data from TG and DTG curves in the decomposition range $\alpha = 0.1-0.9$ were used to determinate the kinetics parameters of the process and mathematical analysis was performed by the integral method of Coats–Redfern. This method has been successfully used for studies on the kinetics of dehydration and decomposition of different solid substances [16–18,20]. The kinetics parameters can be derived using a modified Coat–Redfern equation:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{qE} - \frac{E}{RT}, \tag{8}$$

where $g(\alpha)$ is a function, the expression of which depends on the kinetics model of the occurring reaction. If the correct $g(\alpha)$ is used, a plot of $\ln[g(\alpha)/T^2]$ against $1/T$ should give a straight line with the highest correlation coefficient at the linear regression analysis. The values of the activation energy E and the pre-exponential factor A in Arrhenius equation can be calculated from the slope and cut-off on the ordinate axes. The formal expressions of the functions $g(\alpha)$ depend on the conversion mechanism and its mathematical model [16–18,20]. The latter usually represents the limiting stage of the reaction—the chemical reactions; random nucleation and nuclei growth; phase boundary reaction or diffusion. Table 1 shows the most common kinetics models and their algebraic expressions [16–18,20].

The other kinetics parameters of the process can be calculated using the fundamental theory of the activated complex (transition state) and Eyring equation [21,22]

$$k = \frac{e\chi k_\mathrm{B}T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{E}{RT}\right), \tag{9}$$

where χ is the transition factor, which is unity for monomolecular reaction, k_B is the Boltzmann constant, h is the corresponding Plank constant, $e = 2.7183$ is the Neper number and $\Delta S^{\neq}$ is the change of entropy for the activated complex formation from the reagent.

Taking into account Eq. (9) and the pre-exponential factor from the Arrhenius Eq. (2), the following expression is obtained:

$$A = \frac{e\chi k_\mathrm{B}T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right) \tag{10}$$

and $\Delta S^{\neq}$ can be calculated according to the formula:

$$\Delta S^{\neq} = R\ln\frac{Ah}{e\chi k_\mathrm{B}T_\mathrm{P}}, \tag{11}$$

Table 1
Algebraic expressions of $f(\alpha)$ and $g(a)$ for the kinetics models of solid-state reactions considered in the present work

Symbol	$f(\alpha) =$ $\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p$	$.g(a) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt.$	Reaction model
1. Chemical decomposition process or mechanism non-invoking equations			
$F_{3/2}$	$(1-\alpha)^{3/2}$	$2[(1-\alpha)^{-1/2}-1]$	Three-halves order kinetics
F_2	$(1-\alpha)^2$	$\alpha/(1-\alpha)$	Second-order kinetics
F_n	$(1-\alpha)^n$	$[1-(1-\alpha)^{1-n}]/(1-n)$	n-th-order kinetics ($n \neq 1$)
2. Acceleratory rate equations			
$P_{3/2}$	$\alpha^{-1/2}$	$(2/3)\ \alpha^{3/2}$	Power law ($\alpha = kt^{2/3}$)
P_2	$\alpha^{1/2}$	$2\alpha^{1/2}$	Power law ($\alpha = kt^2$)
P_3	$\alpha^{2/3}$	$3\alpha^{1/3}$	Power law ($\alpha = kt^3$)
P_4	$\alpha^{3/4}$	$4\alpha^{1/4}$	Power law ($\alpha = kt^4$)
$Đ_5$	α	$\ln\alpha$	Exponential law ($\alpha = 1-\exp(-kt)$)
3. Sigmoid rate equations or random nucleation and subsequent growth			
A_1, F_1	$1-\alpha$	$-\ln(1-\alpha)$	Random nucleation or first-order kinetics
$A_{3/2}$	$(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$(3/2)[-\ln(1-\alpha)]^{2/3}$	Avrami–Erofe'ev Eq. ($n = 1.5$)
A_2	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$2[-\ln(1-\alpha)]^{1/2}$	Avrami–Erofe'ev Eq. ($n = 2$)
A_3	$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$3[-\ln(1-\alpha)]^{1/3}$	Avrami–Erofe'ev Eq. ($n = 3$)
A_4	$(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$4[-\ln(1-\alpha)]^{1/4}$	Avrami–Erofe'ev Eq. ($n = 4$)
A_u	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$	Prout–Tompkins Eq.
4. Deceleratory rate equations			
4.1. Phase boundary reaction			
R_1, P_1, F_0	$(1-\alpha)^0$	α	One-dimensional advance of the reaction interface, power law ($\alpha = kt$) or zero-order kinetics
R_2, $F_{1/2}$	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	Contracting area (cylindrical symmetry) or one-half order kinetics
R_3, $F_{2/3}$	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	Contracting volume (spherical symmetry) or two-thirds order kinetics
4.2. Based on the diffusion mechanism			
D_1	$1/\alpha$	$\alpha^2/2$	One-dimensional diffusion or parabolic law ($\alpha = kt^{1/2}$)
D_2	$1/-\ln(1-\alpha)$	$\alpha + (1-\alpha)\ln(1-\alpha)$	Two-dimensional diffusion (Valensi equation)
D_3	$(1-\alpha)^{2/3}/1-(1-\alpha)^{1/3}$	$(3/2)[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D_4	$(1-\alpha)^{1/3}/1-(1-\alpha)^{1/3}$	$(3/2)[1-(2/3)\alpha-(1-\alpha)^{2/3}]$	Three-dimensional diffusion (Ginstling—Brounshtein Eq.)
D_5	$(1-\alpha)^{5/3}/1-(1-\alpha)^{1/3}$	$(3/2)[(1-\alpha)^{-1/3}-1]^2$	Zuravlev–Lesokhin–Tempelman Eq.
D_6	$(1+\alpha)^{2/3}/[(1+\alpha)^{1/3}-1]$	$(3/2)[(1+\alpha)^{1/3}-1]^2$	Komatsu–Uemura or anti-Jander Eqs.

where T_p is the peak temperature from the DTG curve. Since

$$\Delta H^{\neq} = E - RT, \tag{12}$$

the change of the enthalpy $\Delta H^{\neq}$ and Gibbs free energy $\Delta G^{\neq}$ for the activated complex can be calculated using the well-known thermodynamical equation [21,23]:

$$\Delta G^{\neq} = \Delta H^{\neq} - T\,\Delta S^{\neq}, \tag{13}$$

where $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ were calculated at $T = T_p$, since this temperature characterizes the highest rate of the process and, therefore, is the important parameter.

In the kinetics study of the thermal dehydration or decomposition of solids, the determination of the appropriate mechanistic function $g(\alpha)$ is one of the most important subjects. A proper selection of the formal expression of this function should give linear dependence between $\ln A$ and E. This relation is referred to as the "compensation effect" or "isokinetic effect" or the θ rule [20, 24–29], and may be written as follows:

$$\ln A = \ln k_{\mathrm{iso}} + \frac{E}{RT_{\mathrm{iso}}}, \tag{14}$$

where k_{iso} is the isokinetic rate constant and T_{iso} is the isokinetic temperature. According to Ref. [25], the value of rate constant depends mainly on $\Delta H^{\neq}$ at temperature below T_{iso}, whereas above T_{iso}—mainly on $\Delta S^{\neq}$. Various hypotheses have been put forward to elucidate the compensation effect [20,25,29]. Two of these hypotheses may be useful for discussion on the applicability of Eq. (14) for some reactions of thermal dissociation. According to one of them, a part of the reaction is a transfer of electron or proton by means of tunnel effect. In this case, a transition factor appears in the formula describing the rate constant. The transition factor χ is described by following equation [25]:

$$\chi = \exp\left\{-\frac{8\pi r}{3h}[2m(V-W)]^{1/2}\right\}, \qquad (15)$$

where V is the height of tri-dimensional potential barrier; W is the energy of tunneling molecule; m is the molecule mass and r is the barrier width. Considering Eq. (14), it can be seen that the higher the value of $W(\approx E)$, the greater the transition probability and the higher the A value. This hypothesis seems to be valid only for some electron mechanisms and for reactions of protons at low temperatures.

The other hypothesis is based on the assumption that the compensation effect resulting from reaction acts on active centers of different activation energies according to exponential distribution.

3. Results and discussion

Fig. 1 shows the TG, DTA and DTG curves of the dehydration of $Al_2(SeO_3)_3 \cdot 6H_2O$, $Ga_2(SeO_3)_3 \cdot 6H_2O$ and $In_2(SeO_3)_3 \cdot 6H_2O$.

As can be seen from the curves in Fig. 1, the temperature at which the dehydration rate is maximal was different for the different selenites. It suggests that the crystallohydrates have different thermal stabilities. The weight losses determined by the TG curves correspond exactly to the selenite hexahydrate.

Since dehydration of the hexahydrates studied to their anhydrides proceeds in single step at relatively low temperature and within a narrow temperature interval, the method of Coats–Redfern [19] was used with all the functions $g(\alpha)$ presented in Table 1. The highest values of the coefficient of correlation R^2 of the linear regression were obtained when mechanism non-invoking equations were used with different values of n. Fig. 2 shows the plot $\ln[g(\alpha)/T^2]$ vs. $1/T$ for dehydration of $In_2(SeO_3)_3 \cdot 6H_2O$ at three values of n.

Fig. 2 clearly shows that the closest match to linear dependence was obtained at $n = 1.5$, i.e., mechanism $F_{1.5}$. This was considered enough to conclude that the dehydration occurs as chemically controlled reaction. For the other two selenites, it was found that their dehydration can be described best by $g(\alpha)$ functions of type F_n at different values of n (Table 2).

Analyzing the data in Table 2, it can be seen that the values of the kinetics parameters E and A depend strongly on the type of the selected function and, respectively, on the value of n. It means that a certain value of n must be found, at which the experimental data obey the linear dependence. The best linear correlation of the dependence $\ln[g(\alpha)/T^2]$ vs. $1/T$ for the dehydration of $Al_2(SeO_3)_3 \cdot 6H_2O$ was obtained at $n = 1.33$ and for $Ga_2(SeO_3)_3 \cdot 6H_2O$—at $n = 0.66$. With the expression of the function $g(\alpha)$ which was found to give the

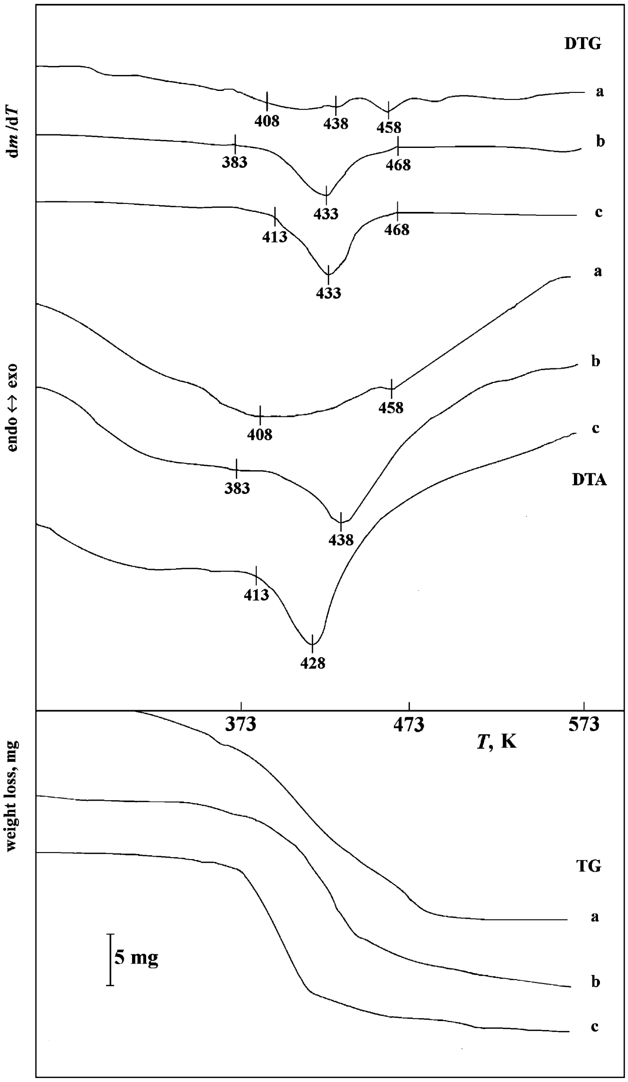


Fig. 1. TG, DTA and DTG curves at dehydration of: (a) $Al_2(SeO_3)_3 \cdot 6H_2O$, (b) $Ga_2(SeO_3)_3 \cdot 6H_2O$, and (c) $In_2(SeO_3)_3 \cdot 6H_2O$.

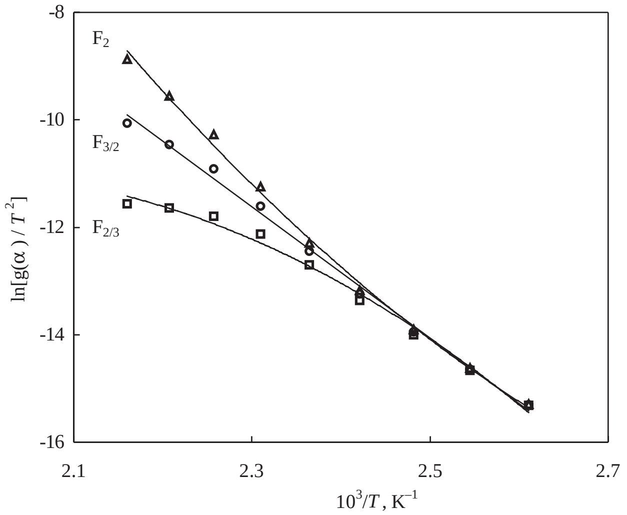


Fig. 2. Evaluation of a model reactions for the thermal dehydration of $In_2(SeO_3)_3 \cdot 6H_2O$.

Table 2
Dependence of kinetics characteristics of non-isothermal dehydration of some selenite hexahydrates from the values of *n*

Symbol	$Al_2(SeO_3)_3 \cdot 6H_2O$			$Ga_2(SeO_3)_3 \cdot 6H_2O$			$In_2(SeO_3)_3 \cdot 6H_2O$		
	R^2	E (kJ mol^{-1})	A (min^{-1})	R^2	E (kJ mol^{-1})	A (min^{-1})	R^2	E (kJ mol^{-1})	A (min^{-1})
$F_{0.66}$	0.9307	19.5	0.14×10^2	**0.9929**	**46.9**	$\mathbf{1.08 \times 10^5}$	0.9574	67.5	3.91×10^7
F_1	0.9669	23.3	0.61×10^2	0.9884	55.5	1.904×10^6	0.9858	83.6	6.17×10^9
$F_{1.25}$	0.9784	26.4	1.90×10^2	0.9809	63.1	2.26×10^7	0.9929	92.04	8.83×10^{10}
$F_{1.33}$	**0.9976**	**27.5**	$\mathbf{2.90 \times 10^2}$	0.9763	66.8	7.13×10^7	0.9742	102.9	2.52×10^{12}
$F_{1.5}$	0.9757	29.9	7.10×10^2	0.9697	72.8	4.80×10^8	**0.9956**	**101.4**	$\mathbf{1.68 \times 10^{12}}$
$F_{1.66}$	0.9681	32.3	1.70×10^3	0.9613	77.6	2.28×10^9	0.9954	107.9	1.28×10^{13}
$F_{1.75}$	0.9624	33.7	2.90×10^3	0.9563	81.07	6.84×10^9	0.9946	111.7	4.17×10^{13}
F_2	0.9436	37.9	1.30×10^4	0.9910	116.8	2.29×10^{14}	0.9905	122.8	1.30×10^{15}

Table 3
Kinetics characteristics of non-isothermal dehydration of some selenite hexahydrates

Parameter	$Al_2(SeO_3)_3 \cdot 6H_2O$	$Ga_2(SeO_3)_3 \cdot 6H_2O$	$In_2(SeO_3)_3 \cdot 6H_2O$
r_{cat} (Å)	0.50	0.62	0.92
T_p (K)	408	438	428
R^2	0.9976	0.9929	0.9956
n	1.33	0.66	1.5
E (kJ mol^{-1})	27.5	46.9	101.4
A (min^{-1})	2.90×10^2	1.08×10^5	1.68×10^{12}
$-\Delta S^{\neq}$ (J mol^{-1} K^{-1})	246.9	198.5	60.5
$\Delta H^{\neq}$ (kJ mol^{-1})	24.1	42.9	97.8
$\Delta G^{\neq}$ (kJ mol^{-1})	124.9	129.9	123.7

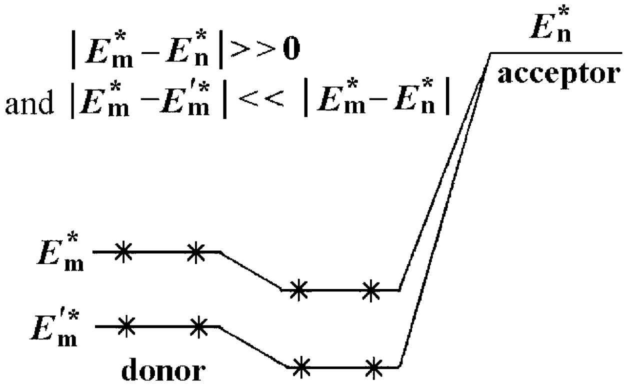
The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ were calculated at the peak temperature T_p from the DTG curves, respectively.

closest match to the linear dependence, the values of the kinetics parameters characterizing the dehydration process were calculated (Table 3).

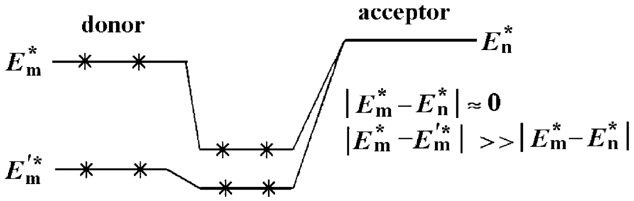
Table 3 clearly shows that the values of the activation energy *E* and pre-exponential factor *A* increased with the increase of cation radius. It means that the thermal stability of the crystallohydrates studied increased regularly with the increase of cation radius. To explain the tendency observed, the approach of Klopman and Hudson [30] was used as a consequence of the generalized perturbation theory of chemical reactivity (GP). According to this theory the following fundamental equation can be written:

$$\Delta E_{\text{total}} = \underbrace{-\frac{q_c q_a}{R_{ca}\varepsilon}}_{\text{electrostatic term}} \underbrace{+ 2\sum_{\text{occ}}(C_c^m)^2 \sum_{\text{unocc}}(C_a^n)^2 \frac{\Delta\beta_{ca}^2}{(E_m^* - E_n^*)_{\text{average}}}}_{\text{covalent term}}, \quad (16)$$

where ΔE_{total} is the total change in perturbation energy due to the partial formation of a bond between an anion and cation, respectively, q_a and q_c are the total initial charges for anion and cation, R_{ca} is the distance between two ions, ε is related to the local dielectric constant of the solvent, $(C_c^m)^2$ and $(C_a^n)^2$ are the frontier electron density, $\Delta\beta_{ca}^2$ is the change in the resonance integral between the interacting orbitals of anion and cation, $(E_m^* - E_n^*)$ is the difference in energy between the highest occupied orbital of the anion and the lowest empty orbital of the cation. When the difference between E_m^* and E_n^* for the frontier orbitals is large, $|E_m^* - E_n^*| \gg 0$, then very little charge transfer occurs (Scheme 1).



Scheme 1. Charge-controlled effect.



Scheme 2. Orbital-controlled effect.

It is apparent that in such a case the perturbation energy is primarily determined by the total charges on the two ions. Very little electron transfer occurs, and the reaction will thus be called a charge-controlled reaction. On the other hand, when the two frontier orbitals are degenerate, i.e., $|E_m^* - E_n^*| \approx 0$, then, their interaction becomes predominant (Scheme 2), and strong electron transfer occurs between them. When such a case happens, we well call the reaction a orbital-controlled reaction.

According to this approach, the interactions between cations and anions in aqueous solutions may take place as charge-controlled or orbital-controlled reactions. The charge-controlled reactions are facilitated when highly hydrated cations with small radii (Mg^{2+}, Al^{3+}) take part. Vice versa, the orbital-controlled reactions are facilitated when little hydrated cations with big radii (Ag^+, In^{3+}) take place. Since the same anion takes part in selenites formation (SeO_3^{2-}), the reaction by which the interaction with the cation would proceed to obtain the corresponding selenite should depend on its radius or, respectively, on its atomic orbital. It has been shown in the framework of the perturbation model that the most energy-efficient reactions occur between ions, which facilitate either electrostatic, interaction only, or orbital interactions. In the first case, the reacting ions are denoted as "hard" (hard donor-anions or hard acceptor-cations). These are cations with small radii, which form ionic type of bond. In orbital interactions, the reacting ions are "soft"—these are ions with big radii, which form covalent type of bond. Using the nucleophility and electrophility orders reported in Ref. [30], it can be concluded for the formation of $Al_2(SeO_3)_3 \cdot 6H_2O$ in aqueous solutions that the bond between cation and anion would be most probably ionic while for the formation of $In_2(SeO_3)_3 \cdot 6H_2O$—the bond would be covalent. Since SeO_3^{2-} anion is "soft" donor of electrons, however, mostly orbital-controlled reactions would take place with the participation of "soft" acceptors of electrons. Such interactions occur during the formation of indium selenite hexahydrate. It means that the crystallization water is more strongly bonded and, therefore, the dehydration would be more difficult and with higher activation energy. On the contrary, the bonds in $Al_2(SeO_3)_3 \cdot 6H_2O$ would be weaker, the thermal dehydration would be facilitated and with smaller activation energy. As it had been shown in our previous work [31], the thermal decomposition of the anhydride $In_2(SeO_3)_3$ occurs actually at higher temperature and at higher activation energy compared to $Ga_2(SeO_3)_3$ and especially to $Al_2(SeO_3)_3$. The experimental data obtained convincingly showed the existence of correlation between the thermal stability of the compounds and the covalent nature of the bond between their ions, as well as the water molecules in their crystallohydrates.

A confirmation of the proper choice of the $g(\alpha)$ function can be obtained with the establishment of the linear dependence between $\ln A$ and E (Fig. 3).

Fig. 3 confirmed the presence of kinetics compensation effect described by the empiric equation:

$$\ln A = -3.1521 + 0.3038 \times 10^{-3} E. \tag{17}$$

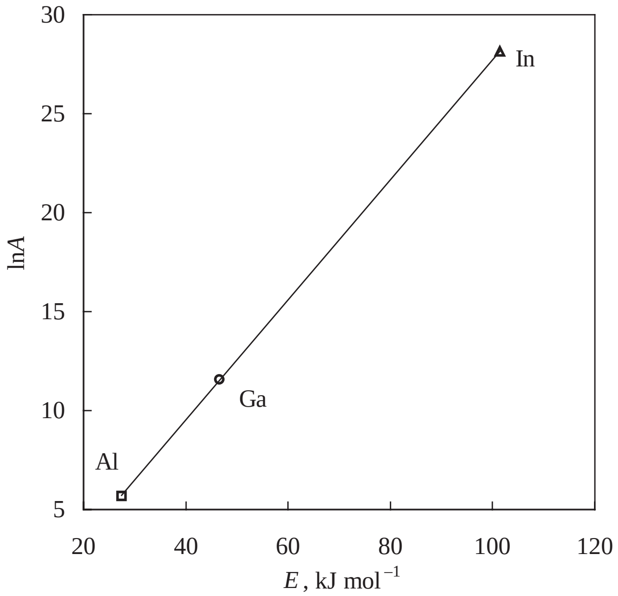


Fig. 3. Kinetics compensation effect upon dehydration of some selenite hexahydrates.

The high value of the correlation coefficient of the linear regression ($R^2 = 0.9998$) sustains the opinion stated above. Based on this dependence, the values of the isokinetic parameters ($k_{iso} = 4.28 \times 10^{-2}\,min^{-1}$ and $T_{iso} = 395.9\,K$) were calculated. At temperatures higher than T_{iso}, the reaction characterized by the highest value of E proceeds at higher rate compared to that characterized by smaller E. According to Ref. [25], the kinetic compensation effect observed can be attributed to proton transfer due to a tunneling effect. Hydrogen bonds $O \cdots HO$ existing in these compounds are asymmetrical and have a double minimum on the potential energy curve. The passage of a proton through the energy barrier ($8.4\,kJ\,mol^{-1}$) is possible due to the tunneling effect. The dehydration process is a result of many intermediate processes [29], among which one of importance is the transition of proton to the conductance band.

Using Eqs. (11)–(13), the values of the changes of entropy $\Delta S^{\neq}$, enthalpy $\Delta H^{\neq}$ and free energy of Gibbs $\Delta G^{\neq}$ were calculated for the formation of the activated complex by the reagent. As can be seen from Table 3, in all the cases studied, the change of entropy was negative which means that the formation of the activated complex is connected with decrease of entropy, i.e., the activated complex is "more organized" structure compared to the initial molecule. Besides, a tendency of increase of the absolute value $\Delta S^{\neq}$ with the decrease of cation radius was observed. This fact can be explained with the necessity of major rearrangement during the dehydration of $Al_2(SeO_3)_3 \cdot 6H_2O$ where the interaction between the reacting ions had occurred by the energetically more inefficient orbital-controlled reaction.

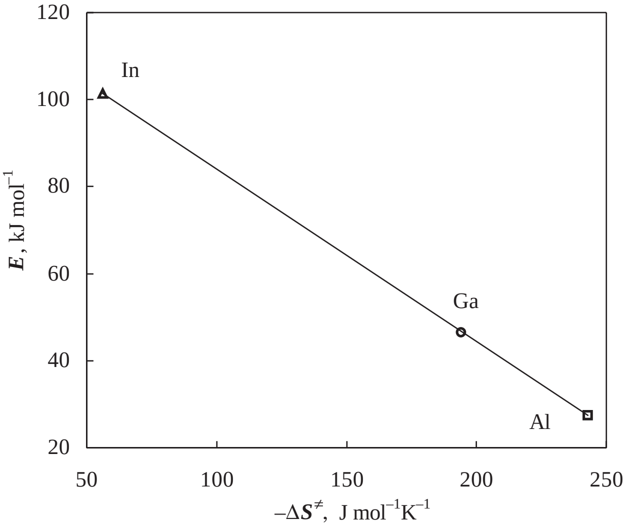


Fig. 4. Plots of E vs. $\Delta S^{\neq}$ values for the dehydration of crystal hydrates.

Besides, linear dependence between E and $\Delta S^{\neq}$ was also established (Fig. 4).

It can be seen from Fig. 4 that a system with a higher entropy change $\Delta S^{\neq}$ will require less energy of activation E for its thermal dehydration. Such dependence was observed also for the thermal decomposition of other compounds [32–34].

4. Conclusion

The results obtained provide enough grounds to conclude that there is a connection between the thermal stability and the kinetics parameters of the selenites dehydration and the radii of their cations, determined by their different polarizability and the nature of the chemical bond in the molecule.

References

[1] V.P. Verma, Thermochim. Acta 327 (1999) 63.
[2] W.C. LaKourse, Int. Rev. Glass Prod. Manuf. Technol. (London) (1995) 23.
[3] C. Rocehiccioli, C.R. 247 (1958) 1108.
[4] T.T. Mityureva, Thesis, Kiev, 1960.
[5] G.S. Savchenko, I.V. Tananaev, A.N. Volnolina, Izv. AN SSSR Ser. Neorg. Mater. 4 (1968) 369.
[6] R.E. Morris, W.T.A. Harrison, G.D. Stucky, A.K. Cheetham, J. Solid State Chem. 94 (1991) 227.
[7] G.G. Gospodinov, Int. Center Diffraction Data Set 51 (2001) 444; G.G. Gospodinov, Int. Center Diffraction Data Set 53 (2003) 144, 146.
[8] G.G. Gospodinov, Thermochim. Acta 82 (1984) 364.
[9] G.G. Gospodinov, Thermochim. Acta 82 (1984) 375.
[10] G.G. Gospodinov, Thermochim. Acta 180 (1991) 169.
[11] G.G. Gospodinov, L.M. Sukhova, K.I. Petrov, Zh. Neorg. Khim. 33 (1988) 1970.
[12] K.I. Petrov, I.V. Tananaev, A.N. Volodina, N.K. Bolchecov, Zh. Neorg. Khim. 22 (1977) 1453.
[13] R. Ratheesh, R. Morris, Spectrochim. Acta A 53 (1997) 1975.
[14] J. Šestak, G. Berggen, Thermochim. Acta 3 (1971) 1.
[15] J. Kwarciak, J. Therm. Anal. 30 (1985) 177.
[16] V. Mamleev, S. Bourbigot, M. LeBras, S. Duquesne, J. Šestak, Phys. Chem. Chem. Phys. 2 (2000) 4708.
[17] C.L. Albano, R. Sciamanna, T. Aquino, J. Martinez, European Congress on Computational Methods in Applied Sciences and Engineering, Barcelona, September 2000.
[18] J.J.M. Orfao, F.G. Martins, Thermochim. Acta 390 (2002) 195.
[19] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[20] K.R. Agrawal, J. Therm. Anal. 31 (1986) 73.
[21] Ya. Gerasimov, V. Dreving, E. Eremin, A. Kiselev, V. Lebedev, G. Panchenkov, A. Shlygin, Physical Chemistry, Vol. 2, Mir, Moscow, 1974.
[22] A.M. Urzhenko, A.V. Usherov-Marshak, Neorg. Mater. 10 (1974) 888.
[23] P.V. Khadikar, S.M. Ali, B.D. Heda, J. Therm. Anal. 30 (1985) 1967.
[24] A.V. Nikolaev, V.A. Logvinenko, V.M. Gorbatchov, L.I. Myachina, Thermal analysis, in: I. Buzas (Ed.), Proceedings of the Fourth ICTA, Budapest, Vol. 1, 1974, p. 47.
[25] T. Zmijewski, J. Pysiak, Thermal analysis, in: I. Buzas (Ed.), Proceedings of the Fourth ICTA, Budapest, Vol. 1, 1974, p. 205.
[26] N. Koga, H. Tanaka, J. Therm. Anal. 34 (1988) 177.
[27] S.V. Vyazovkin, A.J. Lesnikovich, I.S. Romanovsky, J. Therm. Anal. 34 (1988) 609.
[28] H. Tanaka, N. Koga, J. Therm. Anal. 34 (1988) 685.
[29] N.M. Dombrowsky, Kinetika i Kataliz 9 (1968) 251.
[30] G. Klopman, Chemical Reactivity and Reaction Paths, Wiley, New York, 1974.
[31] L.T. Vlaev, G.G. Gospodinov, Thermochim. Acta 370 (2001) 15.
[32] R. Roy, M. Chaudhury, S. Mandal, K. Nag, J. Chem. Soc., Dalton Trans. (1984) 1681.
[33] L.K. Singh, S. Mitra, Thermochim. Acta 138 (1989) 285.
[34] A. Sharma, T.R. Rao, Biores. Technol. 67 (1999) 53.