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KINETIC PARAMETERS OF DECOMPOSITION OF SOME SELENITES
Generalized perturbation theory of chemical reactivity

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Studying the kinetics of isothermal decomposition of thirteen selenites at isothermal heating, the values of activation energy *E* of the process, pre-exponential factor *A* in Arrhenius equation and changes of entropy $\Delta S^{\neq}$ for the formation of the activated complex of the reagent were calculated. Direct dependence between the thermal stability of the selenites and their cation radii on their 'hardness' or 'softness' was found. The dependence was interpreted in the terms of the generalized perturbation theory of chemical reactivity. Kinetic compensation effect was observed only for the selenites, which thermally decompose by the same mechanism.

Keywords: *chemical reactivity, compensation effect, generalized perturbation theory, kinetics of isothermal decomposition, selenites*

Introduction

Selenites were first synthesized in XIX century [1–4]. Later, due to their very low solubility, some of them were used in analytical chemistry for quantitative determination of some metals by the mass method [5] or by conductivity-metric titration [6, 7]. Other selenites were used as pigments in glass and ceramics industries [8, 9]. Many of them can be found in nature in the form of minerals as part of polymetallic ores [10, 11] and are used as raw material for production of selenium. As can be seen from the extensive review of Verma [12] and the references cited there, selenites have been an object of investigation for quite a long time. There are publications on the preparation and crystalline structure of different selenites, solubility and solubility product, IR and Raman spectra, thermal stability and transformations under heating, etc., but data on their kinetics of thermal decomposition was not found.

The development of microelectronics and high-end technology is connected with the synthesis and characterization of new compounds with practically valuable properties. In this respect, special attention is paid to selenites of the different elements, because many of them have interesting optical, magnetic, and photoelectric or semi-conductor properties [13, 14]. Under heating of selenites in reduction media (H_2, CO), the corresponding selenides can be obtained [15, 16]. They also possess some interesting semi-conductor properties. These considerations lead to the conclusion that studies of selenites thermal stability and particularly their kinetics of decomposition under isothermal or non-isothermal heating is interesting from both theoretical and practical point of view.

In recent years we carried out a series of studies on the decomposition kinetics of a number of selenites under isothermal and non-isothermal heating [17–25]. The results obtained and dependencies observed in the behaviour of the values of the basic kinetic parameters characterizing this process can be explained using generalized perturbation theory of chemical reactivity [26–29].

Based on our studies, the present work is an attempt to summarize the results obtained from experiments, find some more general dependencies and interpret them using the generalized perturbation theory of chemical reactivity.

Experimental

Thermal measurements

The thermogravimetric measurements were performed on a derivatograph system Paulik–Paulik–Erdey (MOM, Hungary) in nitrogen flow (25 $\text{cm}^3\ \text{min}^{-1}$) under isothermal heating in the temperature interval 723–1123 K. Depending on selenites' thermal stability, the measurements were taken at certain temperature intervals. For selenites with lower thermal stability (selenites of aluminium, gallium, germanium, antimony and bismuth), the measurements were made in the temperature interval 723–923 K while for the others – in the interval 923–1123 K. In all the cases studied, the rate constants of thermal decomposition were calculated using 4 or 5 kinetic curves in the corresponding temperature interval at 50 K step. For this purpose, 100 mg finely ground sample was placed in open platinum crucible (7 mm diameter and 14 mm

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height). α-Alumina, calcined at 1273 K was used as a standard reference material. The sample mass was measured continuously for 15–120 min with accuracy of ±1 mg. The temperature was kept constant within the interval ±2 K and the reaction progress (α) was from 0.05 to 0.95 [21, 25].

Mathematical background of kinetic calculations

The basic kinetic equation was used:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{1}$$

where k is the rate constant and the function $f(\alpha)$ involves the decomposition progress α at moment t calculated by the formula:

$$\alpha = \frac{W_0 - W}{W_0 - W_\mathrm{f}} \tag{2}$$

where W_0, W and W_f are the initial, actual and final sample mass. According to Šesták [30], the function $f(\alpha)$ can be written in a general form:

$$f(\alpha) = \alpha^\mathrm{m}(1-\alpha)^\mathrm{n}[-\ln(1-\alpha)]^\mathrm{p} \tag{3}$$

with respect to its correspondence to the models derived for homogeneous reactions, nucleation-growth process, surface process, diffusion or random nucleation, where n, m and p are empirically obtained exponent factors, one of them always being zero. Depending on the specific kinetic model of the process, the form of the function $f(\alpha)$ would be different [23, 25, 31].

The integral form of the function $g(\alpha)$

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = kt \tag{4}$$

at T=const. represents a linear dependence, the slope of which is used to calculate the rate constant k at certain temperature. The dependence of the rate constant k on the temperature is usually described by the Arrhenius equation:

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{5}$$

where A – pre-exponential factor, E – activation energy, R – gas constant and T – temperature.

Taking the logarithm of Eq. (5) gives:

$$\ln k = \ln A - \frac{E}{RT} \tag{6}$$

The value of E – calculated from the slope of the straight line and A – from the cut-off from the ordinate. Using the equation of Eyring [23, 25] from the theory of the activated complex (transition state):

$$k = \frac{\mathrm{e}\chi k_\mathrm{B}T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{E}{RT}\right) \tag{7}$$

where e=2.7183 is the Neper number, χ is a transmission coefficient, which is unity for monomolecular reactions, k_B is the Boltzmann constant, h is the Plank constant and $\Delta S^{\neq}$ is the change of entropy for the activated complex formation from the reagent. The comparison the equations of Arrhenius Eq. (5) and Eyring Eq. (7) gives:

$$A = \frac{\mathrm{e}\chi k_\mathrm{B}T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right) \tag{8}$$

The change of entropy $\Delta S^{\neq}$ for the activated complex formation from the reagent can be calculated by the formula:

$$\Delta S^{\neq} = R\ln\frac{Ah}{\mathrm{e}\chi k_\mathrm{B}T} \tag{9}$$

The existence of a linear dependence between ln$A$ and E in reactions of the same type described by the equation:

$$\ln A = \ln k_\mathrm{iso} + \frac{E}{RT_\mathrm{iso}} \tag{10}$$

is often discussed in the literature [32–37]. This dependence is known as kinetic compensation effect, isokinetic effect or θ rule. T_iso is the temperature at which the decomposition of substances proceeding along the same mechanism is characterized by the same rate constant k_iso. At temperatures higher than T_iso, the decomposition of the substance with higher activation energy continues at a rate higher than that of the substance with lower value of E.

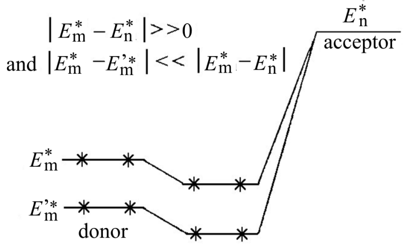
Background of generalized perturbation theory of chemical reactivity

Since the preparation of all selenites takes place in aqueous solutions by interaction of $\mathrm{SeO_3^{2-}}$ anion with the corresponding cation, the generalized perturbation theory of chemical reactivity of Klopman and Hudson [26–29] can be successfully used for estimation of the strength of the bond between them. So far as the activation energy of thermal decomposition of selenites depends on the strength of the bonds in the molecule, we used the basic principles of this theory for the interpretation of the changes observed in the kinetic parameters of the process. It is based on the supposition that the formation of transitional state is stipulated by both the mutual perturbation of the molecular orbitals of the two reagents and the electrostatic interaction between the ions. The relative reactivity of the ions in the solution is assessed by the decrease of energy of the system

ΔE_{total}. The highest reactivity and, respectively, the highest bond strength showed the ions the interaction of which leads to the highest values of ΔE_{total}. The basic equation used to determine ΔE_{total} for the interaction between the ions is as follows [28, 29]:

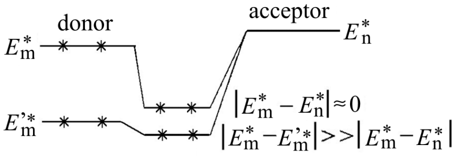
$$\Delta E_{\text{total}} = \underbrace{\frac{q_{\text{c}} q_{\text{a}}}{R_{\text{ca}}\varepsilon}}_{\text{electrostatic term}} + \underbrace{2\sum_{\text{occ}}(C_{\text{c}}^{\text{m}})^2\sum_{\text{unocc}}(C_{\text{a}}^{\text{n}})^2\frac{\Delta\beta_{\text{ca}}^2}{(E_{\text{m}}^* - E_{\text{n}}^*)_{\text{average}}}}_{\text{covalent term}} \qquad (11)$$

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, $(C_{\text{c}}^{\text{m}})^2$ and $(C_{\text{a}}^{\text{n}})^2$ are the frontier electron density, $\Delta\beta_{\text{ca}}^2$ is the change in the resonance integral between the interacting orbitals of anion and cation, $(E_{\text{m}}^* - E_{\text{n}}^*)$ 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, $|E_{\text{m}}^* - E_{\text{n}}^*| >> 0$, then very little charge transfer occurs (Scheme 1).



Scheme 1 Charge-controlled effect

In such a case, obviously, the perturbation energy is determined mainly by the total charge of the two ions. Since the electron transfer is quite small, the reaction will be called a charge-controlled reaction. On the other hand, when the two frontier orbitals are degenerate, i.e. $|E_{\text{m}}^* - E_{\text{n}}^*| \approx 0$, then, there interaction becomes predominant (Scheme 2),



Scheme 2 Orbital-controlled effect

In this case the electron transfer between them is extensive. Therefore, such reactions will be called orbital-controlled reactions. In this connection, we have established two possible pathways and energetic controls for any couple of ions.

According to this approach, the interactions between cations and anions in aqueous solutions may take place as charge controlled reactions or orbital controlled reactions. The charge-controlled reactions are facilitated when highly hydrated cations with small radii (Be^{2+}, Mg^{2+}, Al^{3+}, etc.) take part. Vice versa, the orbital controlled reactions are facilitated when little hydrated cations with big radii (Ag^+, In^{3+}, Au^+, etc.) take part [29]. 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 or orbital interaction only. 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. The differences in the thermal stabilities of the selenites studied and the dependencies observed in the change of the kinetic parameters characterizing their thermal decomposition can be explained using generalized perturbation theory of chemical reactivity [26–29] and empirical classification of ions as 'hard' or 'soft' donors/acceptors of electrons reported in [29, 38].

Results and discussion

On Fig. 1 are shown the curves of thermal decomposition of $Ge(SeO_3)_2$, $Sn(SeO_3)_2$, $PbSeO_3$, $Sb_2(SeO_3)_3$ and $Bi_2(SeO_3)_3$ at several temperatures. It can be seen that selenites with higher cation radii have higher thermal stability at T=const, i.e. their degree of decomposition (α) decreases from top to bottom of the group in the Periodic table.

The study of the kinetic of isothermal decomposition of 13 selenites [17–25] showed that the best linear dependence between $g(\alpha)$ and t (Eq. (4)) was obtained when the $f(\alpha)$-function (Eq. (3)) was used where m and p are zero, while $0.50<n<1.0$. Then, after separation of variables and integration of Eq. (4) gives:

$$\frac{1-(1-\alpha)^{1-\text{n}}}{1-n} = kt \qquad (12)$$

This linear equation is known as mechanism non-invoking equation and, according to a number of authors [31, 39, 40], describes quite well the kinetics of thermal decomposition of various compounds if proper values of the parameter *n* are selected. On this basis, the rate constants of thermal decomposition of the selenites studied were calculated at certain temperatures. Then, using Eqs (6) and (9), the values of the activation energy of decomposition *E*, pre-exponential factor in Arrhenius equation *A* and the change of entropy $\Delta S^{\neq}$ for the activated complex formation from the reagent were calculated. We found a relationship between the values of these parameters, cation radius of selenites and their thermal stability (Table 1).

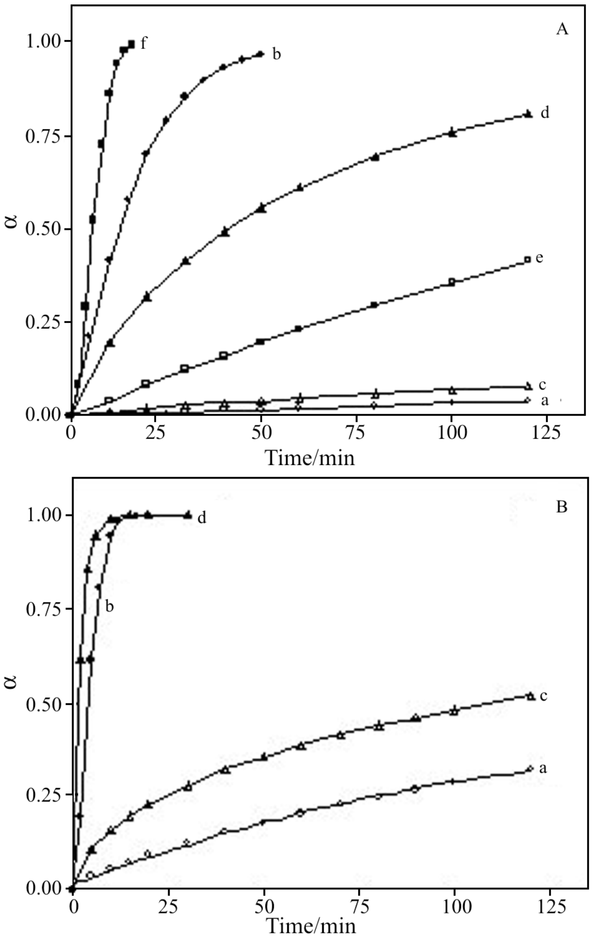


Fig. 1 Kinetics curves of isothermal decomposition of: A – $Ge(SeO_3)_2$: a – 723; b – 873; $Sn(SeO_3)_2$: c – 773; d – 873; $PbSeO_3$: e – 1023; f – 1173 and B – $Sb_2(SeO_3)_3$: a – 623; b – 773; $Bi_2(SeO_3)_3$: c – 773; d – 923 K

As can be seen from Table 1, the values of the activation energy of thermal decomposition increase with the radius of selenite cation from top to bottom of the groups. The thermal stability increased by the same order. It has been reported [40] that the stronger the bond or bonds which are to be broken, the higher is the value of the activation energy.

It is well-known that the pre-exponential factors for solid-phase reaction are expected to have a wide range of values (six or seven orders of magnitude). Empirical first order pre-experimental factors may vary from 10^5 to 10^{16} min^{-1} [40–43]. The low factors will often indicate a surface reaction, but if the reactions are not dependent on surface area, the low factor may indicate a 'tight' complex. The high factors will usually indicate a 'loose' complex. In case of bulk decomposition, any molecule is as likely to react as any other, irrespective of its location – corners, edges, surface, defects or sites of previous decomposition. There are four special cases, which will indicate the range in values for the pre-exponential factors for the rate constants. In case I ($A\approx10^{14}$ min^{-1}) there is no change in degree of the rotational excitation between the reactions and the complex. There are two subcases – completely free rotation and completely restricted rotation. The first one probably can only refer to unimolecular reactions. In case II ($A\approx10^{15}$ min^{-1}) the complex has a 'freer' condition than the reagents [42]. This may be most likely to occur on a surface where the complex might extend itself from the surface and perhaps rotate parallel to the surface. The reactant is assumed to be completely restricted. In case III ($A\approx10^{11}$ min^{-1}) the

Table 1 Cation radii and kinetic characteristics of isothermal decomposition of some selenites

r_{ion}/Å E/kJ mol^{-1} $Me_m(SeO_3)_n$ A/min^{-1} $\Delta S^{\neq}$/J mol^{-1} K^{-1}		0.50 164 $Al_2(SeO_3)_3$ $1.23\cdot10^9$ –121		
0.72 232 $CuSeO_3$ $8.31\cdot10^{11}$ –68	0.83 241 $ZnSeO_3$ $1.74\cdot10^{13}$ –62	0.62 209 $Ga_2(SeO_3)_3$ $1.58\cdot10^{11}$ –80	0.53 189 $Ge(SeO_3)_2$ $1.47\cdot10^{10}$ –101	
1.13 314 Ag_2SeO_3 $6.91\cdot10^{12}$ –51	1.03 257 $CdSeO_3$ $6.11\cdot10^{12}$ –51	0.92 238 $In_2(SeO_3)_3$ $1.48\cdot10^{12}$ –63	0.71 212 $Sn(SeO_3)_2$ $5.66\cdot10^{10}$ –90	0.90 137 $Sb_2(SeO_3)_3$ $5.72\cdot10^8$ –126
		1.05 136 $Tl_4(SeO_3)_4$ $1.82\cdot10^8$ –137	1.21 272 $PbSeO_3$ $2.18\cdot10^{13}$ –42	1.16 203 $Bi_2(SeO_3)_3$ $1.41\cdot10^{11}$ –82

complex is highly restricted in rotation. For the unimolecular reaction the complex would be expanded in size and hence interact more strongly with its neighbors. In case IV ($A \approx 10^5$ min^{-1}) the reagents are in equilibrium with a surface adsorbed layer. The adsorbed species on the surface then react via the activated complex to give products. In conclusion of the activated complex has freer rotation than the reactant; the first order pre-exponential factor is high [42].

As can be seen from Table 1, the values of the pre-exponential factor A varied from 10^8 to 10^{12} cm^{-1}, increasing from top to bottom of each group of the Periodic table.

This dependence was interpreted using Klopman's generalized perturbation theory of chemical reactivity and Pearson's empirical classification of ions as a 'hard' or 'soft' donors/acceptor of electrons. Table 2 shows some orbital electronic characteristics according to the empirical classification of Pearson [29, 38].

Table 2 clearly shows that the differences in orbital energy ΔE ($\Delta E = E_1 - E_2$) of cations depend on their radii and degree of oxidation. Highly hydrated ions (small radii, Be^{2+}, Al^{3+}, etc.) behave as 'hard' while lowly hydrated ones (big radii, Ag^+, Au^+, etc.) – as 'soft' [29, 38]. Since SeO_3^{2-} anion behaves, as 'soft' electron donor, then its bond with the cation would be as stronger as the 'softer' is the corresponding cation and the thermal stability of the selenite would be higher. Therefore, the selenites of heavy metals would be characterized by higher thermal stability and, respectively, higher values of the thermal decomposition activation energy. Vice versa, the selenites of light metals would be characterized with low thermal stability and lower values of E_A. This tendency is quite clear within a single group of the Periodic table. Taking into account the values of ΔE shown in Table 2, it could be predicted that the thermal stabilities of $BeSeO_3$ and $MgSeO_3$ would be close to that of $Al_2(SeO_3)_3$. Similarly, the thermal stabilities of Au_2SeO_3 and $HgSeO_3$ would be close to that of Ag_2SeO_3 since their cations behave as 'soft' ions and all the three selenites decompose along the same scheme with formation of the corresponding metal.

According to Klopman's generalized perturbation theory of chemical reactivity and Pearson's empirical classification of ions, a strong ionic bond is formed by the interaction of 'hard' cations and anions while the interaction between 'soft' cations and anions results in a strong covalent bond. Therefore, the more similar are the interacting ions, the stronger is the bond between them. Since the SeO_3^{2-} behaves as 'soft', it would form stronger bonds with 'soft' cations. As cation 'softness' increases from top to bottom of the groups in the Periodic table and from left to right, the bond strength in selenites should increase by the same directions as well as their thermal stability. The hypothesis suggested was confirmed by the tendency of increase of activation energy E values observed by the thermal decomposition of the selenites studied. Similar relationships for the thermal stability of some sulfates and carbonates depending on their cation radius have been reported in [40, 44]. The explanation of the effect, however, was based on the different polarization ability of the cations. Studying the kinetics of decomposition of hydroxides from the IIA and IIB groups of the Periodic table, L'vov and Ugolkov [45] also found that the thermal stability, activation energy and the change of enthalpies of the processes increased from $Be(OH)_2$ to $Ba(OH)_2$ and from $Zn(OH)_2$ to $Cd(OH)_2$. Besides, these values are higher for the hydroxides of IIA group compared to these of IIB group of the Periodic table which conforms absolutely with Pearson's empiric orders of electrophility and nucleophility and Klopman's generalized perturbation theory of chemical reactivity. This was considered enough to conclude that the hypothesis suggested has other experimental confirmations, too.

Table 2 Hydrated radii and calculated orbital electro negativity of ions in water [29]

Ion	Ionization potential/eV	Electron affinity/eV	Orbital energy, E_1/eV	r_{ion}+0.82/Å	Desolvation energy, E_2/eV	Differences of energy, ΔE/eV	Characteristic of ions
Al^{3+}	28.44	18.82	26.04	1.33	32.05	6.01	
Be^{2+}	18.21	9.32	15.98	1.17	19.73	3.75	
Mg^{2+}	15.03	7.64	13.18	1.48	15.60	2.42	↑
Ga^{3+}	30.70	20.51	28.15	1.44	29.60	1.45	hardness
Cu^{2+}	17.57	9.05	15.44	1.54	14.99	–0.55	softness
Zn^{2+}	17.96	9.39	15.82	1.56	14.80	–1.02	↓
Cd^{2+}	16.90	8.99	14.93	1.79	12.89	–2.04	
Ag^{+}	7.57	2.20	6.23	2.08	3.41	–2.82	
Tl^{3+}	29.30	20.42	27.45	1.77	24.08	–3.37	
Au^{+}	9.22	2.70	7.59	2.19	3.24	–4.35	
Hg^{2+}	18.75	10.43	16.67	1.92	12.03	–4.64	

These considerations, as well as the correctness of the values E calculated, are confirmed by the existence of kinetic compensation effect revealed by the linear dependence between ln$A$ and E [35–38]. According to [32–37] at temperatures higher than T_{iso}, the compounds characterized by higher activation energy begin to decompose with a rate higher than that of compounds having low values of E. Arrhenius plots for thermal decomposition of studying selenites are presented in Fig. 2.

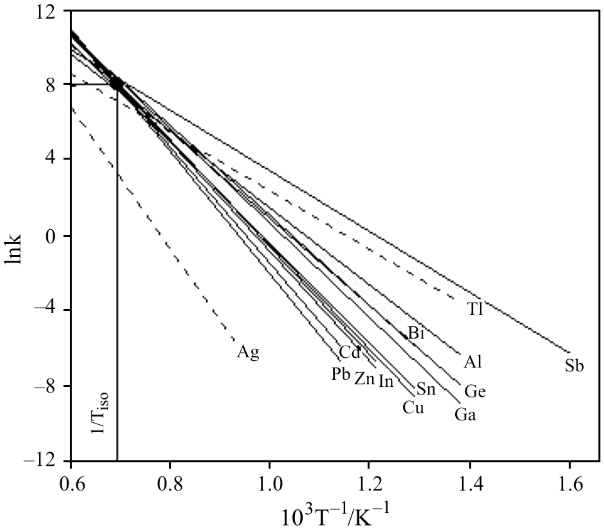


Fig. 2 Arrhenius plots for thermal decomposition of some selenites

As can be seen from Fig. 2, the Arrhenius plot displays a single point of concurrence. Such a plot generally indicates the occurrence of true compensation effect. The straight lines representing the kinetics of thermal decomposition of selenites in Arrhenius co-ordinates cross at the so-called isokinetic point. At this point the rate constants of the decomposition of the different selenites are equal and the temperature at which this can be observed is about 1455 K. Above this temperature, the selenites characterized by higher values of E begin to decompose at a rate higher than that of selenites with lower values of E. The only exceptions are Ag_2SeO_3 and $Tl_4Se_3O_{12}$ due to their different scheme of decomposition. The decomposition of all the other selenites can be schematically summarized by:

$$M_m(SeO_3)_n \rightarrow M_mO_n + nSeO_2$$

while silver selenite decomposes to metal silver, selenium dioxide and oxygen by the scheme [46]:

$$Ag_2SeO_3 \rightarrow 2Ag + SeO_2 + 0.5O_2$$

and the decomposition of $Tl_4Se_3O_{12}$ involves intramolecular reduction of Tl^{3+} to Tl^{+} and oxidation of Se^{4+} to Se^{6+} according to [47]:

$$Tl_4Se_3O_{12} \rightarrow 2Tl_2SeO_4 + SeO_2 + O_2$$

Using the values of the activation energy presented in Table 1 and the pre-exponential factor in Arrhenius equation, the dependence of ln$A$ on E was plotted (Fig. 3).

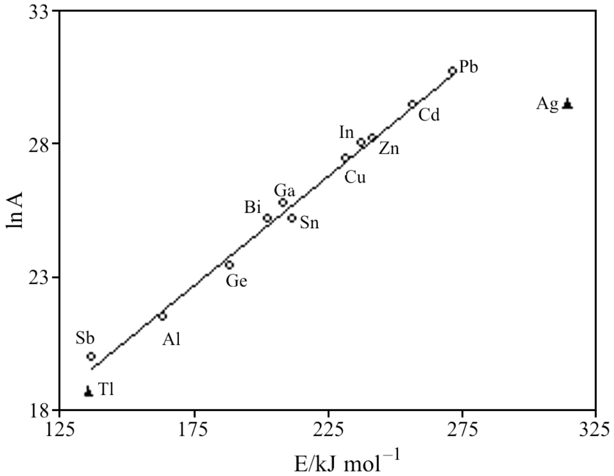


Fig. 3 Kinetics compensation effect of thermal decomposition of some selenites

The linear dependence found between ln$A$ and E confirms the existence of kinetic compensation effect by the thermal decomposition of the selenites studied. The exceptions are silver and thallium selenites due to their specific schemes of decomposition.

It can be seen also from the data presented in Table 1 that the values of the change of entropy for the formation of the activated complex from the reagent $\Delta S^{\neq}$ was negative in all the cases studied. It means that the activated complex has more ordered structure than the reactant, and that the reaction is slower than normal [48]. Besides, the more complex is the configuration of the activated complex and the more limited are its degrees of freedom, the more negative would be the value of $\Delta S^{\neq}$. Furthermore, it can be seen that the values of $\Delta S^{\neq}$ become less negative with the increase of cation radius within each group of the Periodic table. In addition, a correlation between the values of the activation energy and the change of entropy for the formation of the activated complex from the reagent was found. The linear dependences found between ln$A$ and E, as well as between E and $\Delta S^{\neq}$, are directly connected with selenite cation radius and its ‘softness’ or ‘hardness’ as an acceptor of electrons. Obviously, harder is the cation, the higher is the thermal stability of the selenite and the higher are the values of E, A and $\Delta S^{\neq}$ by its thermal decomposition. The suggested hypothesis can be sustained by redundant data reported by other authors [40, 44, 45, 49–51] who also observed similar tendencies in their studies on the kinetics of decomposition of various types of compounds. These authors, however, did not use the generalized perturbation theory of chemical reactivity to interpret the relationships they observed.

Conclusions

In conclusion, we believe that the generalized perturbation theory of chemical reactivity can be very useful not only to understand the tendencies in the change of kinetic parameters of the reactions of chemical decomposition but also for the interpretation of the regularities in the change of solubility and solubility product of slightly soluble compounds and the shift of characteristic absorption bands in IR spectra of compounds of similar type.

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