

## THERMODYNAMIC AND KINETIC STABILITY OF INCLUSION COMPOUNDS UNDER HEATING

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Thermodynamic and kinetic stability of inclusion compounds (so called supermolecular compounds) is discussed. Compounds under study and discussion are clathrates (with coordination compounds matrices) and intercalates (with fluorinated graphite matrices).

**Keywords:** clathrates, compounds stability, intercalates, 'model free' kinetics, supermolecular chemistry, thermal decomposition

### Introduction

#### Supramolecular compounds

Inclusion compounds are important representatives of supramolecular systems. Their synthesis (and the existence itself) are based on their high enough kinetic (and/or thermodynamic) stability at room temperature in the processes of thermal dissociation with the breakdown to the host matrix and the guest (volatile) compound. There are no direct connections between the detailed structure of the inclusion compounds (such as strong and weak bonds, etc.) and compounds stability under heating, their steps of decomposition, stability of capable intermediate phases, and so on. However, their thermodynamic stability in thermal dissociation process is essentially connected with entropy contribution in more important way, than with energetic factor.

Clathrates and intercalates are the most studied groups of supramolecular compounds.

#### Clathrates

Regular microporous materials such as zeolites or coordination polymers (metal-organic frameworks) are well-known host matrices, which are able to encapsulate smaller guests into the interlattice voids to form host–guest inclusion compounds.

The stability of such inclusion compound can be connected with the stability of the matrix structure itself. For example, well known inclusion compounds (clathrates)  $[\text{Zn}(\text{Py})_4(\text{NO}_3)_2] \cdot 2\text{Py}$  and  $[\text{Cd}(\text{Py})_4(\text{NO}_3)_2] \cdot 2\text{Py}$  can be synthesized in the system 'Zn(NO<sub>3</sub>)<sub>2</sub>(crystal)–Py(liquid)' and 'Cd(NO<sub>3</sub>)<sub>2</sub>(crystal)–Py(liquid)', although the host compounds  $[\text{Zn}(\text{Py})_4(\text{NO}_3)_2]$  and  $[\text{Cd}(\text{Py})_4(\text{NO}_3)_2]$  itself do not exist in these systems (stable crystal phases are

$[\text{M}(\text{Py})_3(\text{NO}_3)_2]$  and  $[\text{M}(\text{Py})_2(\text{NO}_3)_2]$ ). The guest-free matrix is unstable. It is interesting that all but one studied clathrates (with Mn, Co, Ni, Zn and Cd-matrices) decompose under quasi-equilibrium condition right away to the  $[\text{M}(\text{Py})_3(\text{NO}_3)_2]$ , – because of low thermodynamic stability of Mn-, Co-, Ni-matrix  $[\text{M}(\text{Py})_4(\text{NO}_3)_2]$  at vapor pyridine pressure  $\approx 101$  kPa, without liquid pyridine support. Only  $[\text{Cu}(\text{Py})_4(\text{NO}_3)_2] \cdot 2\text{Py}$  clathrate decomposes under quasi-equilibrium conditions up to  $[\text{Cu}(\text{Py})_4(\text{NO}_3)_2]$  (at Py pressure  $\approx 101$  kPa) at 120°C. It agrees with the strength of M–Py bonds within the coordination sphere [1, 2].

#### Intercalates on the base of fluorinated graphite

The most known intercalates are intercalates with graphite matrix and with fluorinated graphite matrices. Layered compounds (intercalates) based on graphite fluoride matrices with various guest molecules are supposed to be a particular group of inclusion compounds.

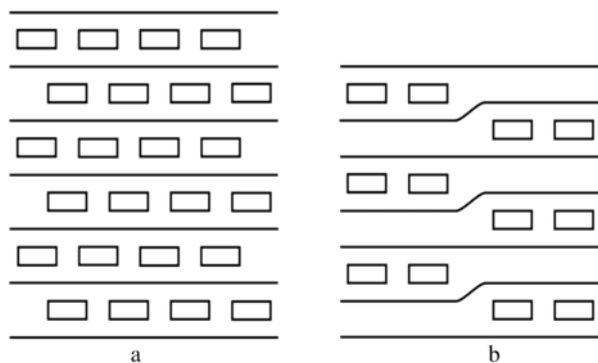
So as the phases are layered substances, there are series of different structures: the first stage of filling (alternating unit layer of the matrix and unit layer of the guest molecules, Fig. 1a), the second stage of filling (alternating double matrix layer and one guest molecule layer, Fig. 1b), the third stage of filling, etc.

Keen interest to these new materials is determined by their two applications.

They can be used as so-called 'molecular containers' both for different gases (such as CH<sub>4</sub>, NO<sub>2</sub>, HF etc.) and condensed phases (BrF<sub>3</sub>, *n*-C<sub>n</sub>H<sub>2n+2</sub>, C<sub>2</sub>H<sub>5</sub>OH, C<sub>6</sub>H<sub>6</sub>, (CH<sub>3</sub>)<sub>2</sub>CO, SOCl<sub>2</sub>, etc.) [3].

From the other hand, these intercalates with volatile guests are used for the expanded graphite pro-

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**Fig. 1** Simplified structures of the graphite fluoride inclusion compounds: a – first stage of filling and b – second stage of filling

duction (fast increase of the guest pressure under heating results in the formation of expanded graphite with low density, such as  $3\text{--}10\text{ kg m}^{-3}$ ) [4, 5].

There are only Van der Waals interaction between the fluorinated graphite and the intercalated guest molecules, while graphite inclusion compounds have mostly donor-acceptor type of interactions [6, 7]. That was shown by IR spectra, where wave numbers are considerably shifted from those in pure graphite and guest components, while wave numbers of guests, intercalated into fluorinated graphite, are nearly similar to pure guest spectra. The first stage of filling is formed usually during the synthetic process; because of low stability of this phase, the second stage of filling is the resulting phase after sample ‘drying’ in the air at room temperature.

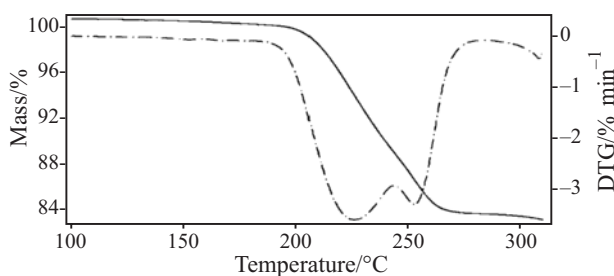
#### Stability under heating

The peculiar properties of inclusion compounds stability are discussed in literature. ‘We have found that the value of the onset temperature,  $T_{\text{on}}$ , characterizing the temperature of guest release, is a reliable measure of thermal stability. For inclusion compounds of a given host with the variety of guests, the onset temperatures are clearly a function of both the host–guest interactions and the intrinsic properties of the guest itself. The normal boiling point  $T_{\text{b}}$  of the guest is important, and a useful measure of the relative stability of an inclusion compound is the difference ( $T_{\text{on}}-T_{\text{b}}$ ). This is of interest when trying to encapsulate highly volatile guests’ [8]. Really the temperature of compound decomposition (both the onset, and maximum on DTG or DTA, DSC peaks) is a kind of valuation of ‘thermal’ stability, but from the strict physico-chemical point of view, only thermodynamic stability or kinetic stability exist. ‘Thermal’ stability depends on heating rate, the shift from the equilibrium position (evolved gas pressure, connected with sample holder shape and inert gas flow) and is susceptible to sample mass and equipment sensor sensitivity [9].

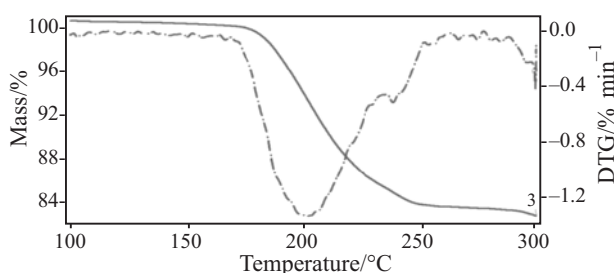
#### Kinetic stability

In physical chemistry the kinetic stability usually and traditionally discussed as kinetic lability or reactivity. The convenient presentation of such a decomposition process is any thermoanalytical curve, depending on temperature (Figs 2 and 3 [10]); the term ‘thermal stability’ originates exactly from the contemplation of such pictures. The onset temperature  $T_{\text{on}}$  (175 or  $190^{\circ}\text{C}$ ) on this picture) is found as the visible deviation of TG (DTG, DSC) curve from the baseline. It is easy to demonstrate that the onset temperature  $T_{\text{on}}$  (being determined from the DTG curves very precisely) is the temperature of the achievement of a certain rate constant, the specific constant value being depended on the used research device (both balance and monitoring) sensitivity [9]. So the onset temperature  $T_{\text{on}}$  is the kinetic parameter only; it can be used for the kinetic lability comparison indeed, but only if all compounds decomposition was studied by means of one and the same instrument (and the experiment itself is organized as the ‘kinetic’ one: small sample, the sufficient shift from the equilibrium position, selected heating rates, etc.); the dependence on heating rate is clearly evident (Figs 2 and 3).

And what is more, the above proposed measure of the relative stability of an inclusion compound: the difference between temperatures of boiling (of liquid guest) and thermal decomposition (of solid inclusion compound) ( $T_{\text{on}}-T_{\text{b}}$ ) [8] is the difference between the



**Fig. 2** TG and DTG curves for  $\text{Mn}(\text{HCOO})_2 \cdot 1/3\text{C}_4\text{H}_8\text{O}_2$  decomposition (dioxane removal),  $m=7.00\pm 0.02\text{ mg}$ , argon flow  $60\text{ cm}^3\text{ min}^{-1}$ , heating rate  $12^{\circ}\text{C min}^{-1}$



**Fig. 3** TG and DTG curves for  $\text{Mn}(\text{HCOO})_2 \cdot 1/3\text{C}_4\text{H}_8\text{O}_2$  decomposition (dioxane removal),  $m=7.00\pm 0.02\text{ mg}$ , argon flow  $60\text{ cm}^3\text{ min}^{-1}$ , heating rate  $4^{\circ}\text{C min}^{-1}$

kinetic and thermodynamic parameters and cannot be easily attributed either to kinetic stability, nor to thermodynamic one.

#### Thermodynamic stability

The formation of the inclusion compound (from the compact solid matrix and gaseous guest) can be divided into two stages: 1) the expansion of compact host matrix, and 2) the inclusion of guest molecules into the beforehand-expanded (so-called 'apohost') matrix.

The first stage is the endothermic process, and the system entropy increases ( $\Delta H_1 > 0$ ;  $\Delta S_1 > 0$ ). The second stage is the exothermic process, and the system entropy decreases ( $\Delta H_2 < 0$ ;  $\Delta S_2 < 0$ ). The disorder reduces essentially because of the guest molecules packing into the solid, guest molecules lose translational, rotational and other degrees of freedom; so the total entropy change is always negative:  $\Delta S_f = (\Delta S_1 + \Delta S_2) < 0$ . The inclusion compound is formed only if the enthalpy sum is negative:  $\Delta H_f = (\Delta H_1 + \Delta H_2) < 0$ . So then the formation reaction of the inclusion compound is controlled by *enthalpy term*. It is worth to note that the compensational enthalpy–entropy effect is observed under cyclodextrines clathrates formation [11, 12].

The decomposition of the inclusion compound under heating can be divided into two stages: 1) the guest molecules removal (without matrix change) and 2) the collapse of the empty matrix ('apohost') to the stable compact structure.

The first stage is the endothermic process, and the system entropy increases ( $\Delta H_1 > 0$ ;  $\Delta S_1 > 0$ ). The second stage is the exothermic process, and the system entropy decreases ( $\Delta H_2 < 0$ ;  $\Delta S_2 < 0$ ). The disorder increases essentially because of the guest molecules liberation from the solid, so the total entropy change is always positive:  $\Delta S_d = (\Delta S_1 + \Delta S_2) > 0$ . So as the reaction of decomposition proceeds, therefore  $\Delta G = (\Delta H_d - T\Delta S) < 0$ ; for the endothermic reaction the enthalpy sum is positive  $\{\Delta H_d = (\Delta H_1 + \Delta H_2) > 0\}$ , therefore the entropy term  $T\Delta S_d > \Delta H_d$ . So then the decomposition reaction of the inclusion compound is controlled by the entropy term [13].

It is worth to note that the scientists tried to synthesize the 'ideal inclusion compound', in which the interaction enthalpy was assumed to be negligible with respect to entropic consideration (and so  $\Delta_{\text{mix}}G$  could be considered to be ideal) [14]. This approach is valid only if the pure host matrix remains 'empty' after the thermal decomposition.

The direct way to define the thermodynamic stability of inclusion compounds is tensimetric measurements of the equilibrium guest pressure vs. temperature [1, 2] (or precise DSC measurements) for series

of compounds with one and the same matrix and different guests (or different matrices and one guest).

As to the simple comparison of stability ( $T_{\text{on}} - T_b$ ), above cited, it contains meaningful uncertainty. Really, the boiling temperature  $T_b$  is the equilibrium temperature of the achievement of 101.3 kPa pressure of the vapor under liquid guest, and the (thermoanalytical) decomposition temperature  $T_{\text{on}}$  is the temperature of decomposition beginning at casual experimental conditions (guest pressure, heating rate, sample holder shape) and it fixed the certain (usually unknown) rate constant.

The foregoing measure of inclusion compounds stability ( $T_{\text{on}} - T_b$ ) will acquire well defined physical chemical meaning if the decomposition temperature will be determined in the thermoanalytical experiment under quasi-equilibrium conditions in one and the same sample holder (the labyrinth sample holder, conical sample holder, etc). Such experiment runs at constant and small decomposition rate (say,  $0.2 \text{ mg min}^{-1}$ ), at almost constant evolved gas pressure (it is maintained at  $\approx 101 \text{ kPa}$  for labyrinth holder and  $\approx 20 \text{ kPa}$  for the standard sample holder with lid); this decomposition temperature  $T_{\text{eq}}$  remains almost constant ( $\pm 5 - 7^\circ\text{C}$ ) up to the end of decomposition step; the steps of the decomposition correspond to the thermodynamically stable intermediate phases [2, 15]. This decomposition temperature is the temperature of the achievement of the certain equilibrium constant ( $K_{\text{eq}} \approx 1$  for the reversible decomposition in the labyrinth sample holder) for so called dissociation reaction.

For the series of clathrates decomposition (with identical stoichiometry):



the row of equilibrium temperatures of decomposition ( $\text{Mn} < \text{Co} < \text{Ni} < \text{Cu}$ ) fully corresponds to row of reaction enthalpy ( $\Delta H_f$  values are equal to 53.8, 59.5, 64.6, 74.6  $\text{kJ mol}^{-1}$ ).

The decomposition of all these clathrates (because of the matrix itself instability) is connected not with the inclusion guest molecules evolving, but with the matrix  $[\text{M(Py)}_4(\text{NO}_3)_2]$  decomposition. Just therefore the row of decomposition quasiequilibrium temperatures and the row of decomposition enthalpies agrees with the strength of M–Py bonds within the coordination sphere [1, 2].

Naturally, the row of above mentioned temperature difference ( $T_{\text{eq}} - T_b$ ), with constant  $T_b$ , would be the same.

## Experimental

The thermal decomposition of clathrates  $\text{Mn}(\text{HCOO})_2 \cdot 1/3\text{C}_4\text{H}_8\text{O}_2$  and  $\text{Mn}(\text{HCOO})_2 \cdot 1/3\text{C}_4\text{H}_8\text{O}$  was studied under non-isothermal conditions [10, 16]. TG measurements were carried out on a Netzsch thermal analyzer TG 209. The experiments were performed in argon flow ( $100 \text{ cm}^3 \text{ min}^{-1}$ ), at heating rates of 4, 8 and  $12^\circ\text{C min}^{-1}$ , the sample mass was kept  $7.00 \pm 0.02 \text{ mg}$ . Thermomechanical analysis (dilatometry) was carried on a Netzsch thermal analyzer TMA 202; the powder layer thickness was 1.02–1.03 mm (with sample mass 42–45 mg).

We studied the thermal decomposition of intercalates (the 1<sup>st</sup> stage of filling) on the base of fluorinated graphite matrix (with different fluorination degree). Intercalates with acetonitrile were:  $\text{C}_2\text{F}_x\text{Br}_z \cdot y\text{CH}_3\text{CN}$  ( $x=0.92, 0.87, 0.69$  and  $0.49, z \approx 0.01, y$  varied from 0.288 to 0.174) [17, 18].

Intercalates with chloroform were  $\text{C}_2\text{F}_x\text{Br}_z \cdot y\text{CHCl}_3$  ( $x=0.92, 0.87, 0.69$  and  $0.49, z \approx 0.01, y$  varied from 0.204 to 0.139).

Intercalates with dichloroethane were  $\text{C}_2\text{F}_x\text{Br}_z \cdot y\text{CH}_2\text{ClCH}_2\text{Cl}$  ( $x=0.92, 0.87, 0.69$  and  $0.49, z \approx 0.01, y$  varied from 0.222 to 0.153).

The thermal decomposition of these intercalates was studied under isothermal conditions; the choice of the isothermal experiments (at rather low temperature) is connected with very low stability of synthesized compounds with the 1<sup>st</sup> stage of filling. Investigation of inclusion compound thermal decomposition were carried out by applying thermogravimetric method in ambient atmosphere, taking inclusion compound sample mass decrease point-by-point, using thermostatically controlled analytical balance at different temperatures from 14 to  $40^\circ\text{C}$  ( $\pm 0.2^\circ\text{C}$ ), sample mass 30–40 mg. Equilibrium shift was enough for kinetic investigations.

The decomposition of the second stage of filling of intercalates was studied under non-isothermal conditions. TG measurements were carried out on a Netzsch thermal analyzer TG 209. Thermomechanical analysis (dilatometry) was carried on a Netzsch thermal analyzer TMA 202; the powder layer thickness was 1.02–1.03 mm (with sample mass 42–45 mg).

### *Kinetic analysis under non-isothermal conditions*

The up-to-date convenient experimental path to the kinetics study is now the ‘model-free’ approach. Special computer program module ‘model-free’ allows processing several TG, DTA or DSC curves, obtained with different heating rates, without the preliminary information about the kinetic topochemical equations. Program ASTM E698 enables to calculate the

averaged values of activation energy according to temperatures of maximum decomposition rate. Programs ‘Friedman analysis’ and ‘Ozawa–Flynn–Wall analysis’ allow calculating the activation energies for the every experimental point of fractional conversion (in the interval  $0.02 < \alpha < 0.98$ ). ‘Ozawa–Flynn–Wall analysis’ is based on the dependence between the heating rate and inverted temperature; ‘Friedman analysis’ is based on the dependence between the rate of conversion degree and inverted temperature. The same set of experimental data can be used further for searching the topochemical equation (the selection from 18 equations: nucleation, chemical reaction on the interface and diffusion). The checking of the diffusion hindrance absence is very important, so as the aim of the investigation is the chemical reaction study. This calculation is made by the improved differential method of Borchardt–Daniels, with multiple linear regression method, or by nonlinear regression method (this method allows the consecutive reaction processing). This part of the calculation includes the preexponential factor determination. Special F-test is used for the search of the best kinetic description [19–25].

### *Kinetic analysis under isothermal condition*

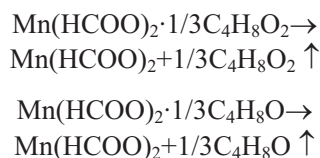
We studied the thermal decomposition of intercalates on the base of fluorinated graphite matrix (with different fluorination degree).

Experimental data of decomposition degree  $\alpha$  vs.  $\tau$  for each matrix at different temperatures were mapped by logarithmic form of Avramy–Erofeev’s equation (with Sakovich’s correlation):  $\ln[-\ln\{1-\alpha\}] = n \ln(k/n) + n \ln \tau$ , where  $n$  – nondimensional coefficient,  $k$  – generalized rate constant,  $\text{s}^{-1}$ . Equation shown above was successfully used by many authors for kinetic investigations of both thermal decomposition of different compounds (including carbamide- $n$ -alkanes clathrates) and phase transitions, solvation and absorption [26, 27]. The generalized activation energy is the sum of partial energies of nucleation, nuclei growth and diffusion. We meaningly used generalized Avramy–Erofeev’s equation for the estimation of decomposition kinetic parameters: values  $n > 1$  correspond to reaction with kinetic control,  $n < 1$  – with diffusion control [26, 27]. Such equation selection gave us the possibility to look after the imbedding from the reaction kinetics to the diffusion along the series both of different matrices (the same guest), and for different guests (the same matrix).

## Results and discussion

### Clathrates

Thermogravimetric curves of clathrates decomposition were used as kinetic ones. The mass loss corresponds to the reaction:



The data processing and is published elsewhere [10, 16], we discussed here the results:

The curves for both compounds show that the thermal decomposition occurs (rather unexpectedly) in two steps, the proportion between them being distinctly dependable on the heating rate: the second mass loss step decreases with heating rate (both temperature interval) decreasing (Figs 2 and 3) Such second step behavior can be connected with the existence of different (both porous and non-porous) structures of manganese formate  $\text{Mn(HCOO)}_2$ ; the assumption of the porous matrix framework collapse at elevated temperatures is fairly reasonable. We calculate the kinetic parameters only for the first stage of decomposition.

#### $\text{Mn(HCOO)}_2 \cdot 1/3\text{C}_4\text{H}_8\text{O}_2$

Energy of activation values are constant enough in the region for  $\alpha=0.05-0.95$  ( $E=75.0-78.2 \text{ kJ mol}^{-1}$  in Ozawa-Flynn-Wall analysis). Kinetic parameters for the better kinetic equation were calculated by Borchardt-Daniels method. The checking equations: Bna, CnB, Fn, D3, A3. It is important that here is no diffusion complication for the gas evolving during the decomposition. In accordance with F-test the best topochemical equations for the decomposition process are Bna or CnB:

$$f(\alpha)=(1-\alpha)^{1.17}\alpha^{0.49}, E_a=77.9 \text{ kJ mol}^{-1}, \log A=6.3$$

The obtained values of activation energy fully agree with the calculated ones by 'free model' approach ( $E=75.0-78.2 \text{ kJ mol}^{-1}$ ).

#### $\text{Mn(HCOO)}_2 \cdot 1/3\text{C}_4\text{H}_8\text{O}$

Energy of activation values are constant enough in the region of  $\alpha=0.35-0.80$  ( $E=69.7-70.0 \text{ kJ mol}^{-1}$  in Friedman analysis). Kinetic parameters for the better kinetic equation were calculated by Borchardt-Daniels method (the selected region of conversion is  $0.40 < \alpha < 0.95$ ). The checking equations: Fn, Bna, CnB, D3.

There is no diffusion complication for the gas evolving during the decomposition. In accordance with F-test the best topochemical equations for the decomposition process are Fn, Bna or CnB; the contribution of the second term is negligible:

$$f(\alpha)=(1-\alpha)^{0.63}, E_a=76.6 \text{ kJ mol}^{-1}, \log A=6.4$$

The obtained value of activation energy agrees with the calculated ones by 'free model' approach ( $E=69-75 \text{ kJ mol}^{-1}$ )

The removing of the 1,4-dioxane ( $\text{C}_4\text{H}_8\text{O}_2$ ) molecules from the compound is accompanied by noticeable matrix expansion (Fig. 4), which is not so remarkable for tetrahydrofuran ( $\text{C}_4\text{H}_8\text{O}$ ) moving away (Fig. 5). This can be connected with different steric impediments for the motion of these differently constructed molecules from and through micropores.

It can be expected that the simple real decomposition is more complex, which is clear from TG-DTG and DSC curves (Figs 2 and 3). We associate this with the principal existence of several different structures of the pure manganese(II) formate (including non-porous phases), therefore partial collapse of porous structure may take place along with guest molecules release from the host channels at elevated temperatures.

The obtained values of activation energy, being calculated by two different methods is reliable; these

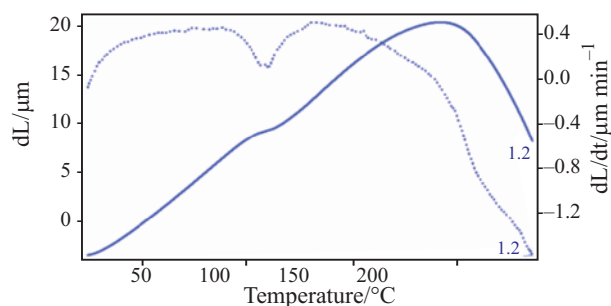


Fig. 4  $\text{Mn(HCOO)}_2 \cdot 1/3\text{C}_4\text{H}_8\text{O}_2$ . The sample volume changing under heating, measured as the powder layer increase (initial layer thickness 1 mm)

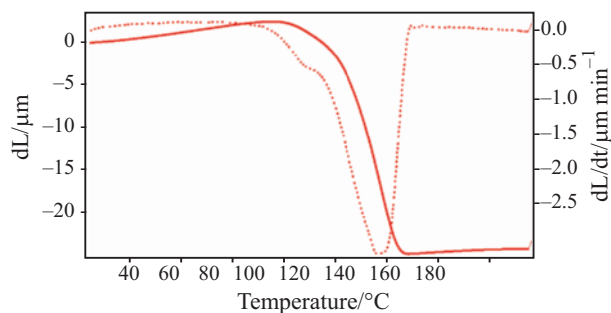


Fig. 5  $\text{Mn(HCOO)}_2 \cdot 1/3\text{C}_4\text{H}_8\text{O}$ . The sample volume changing under heating, measured as the powder layer increase (initial layer thickness 1 mm)

values (78 and 77 kJ mol<sup>-1</sup>) are identical for both compounds (identical are preexponential factors), although boiling temperatures of liquid guests are noticeably different (101.3 and 65.6°C), as the evaporation enthalpies.

We think that the equality of activation energies, but the important difference in kinetic equation (Bna and Fn), become apparent in different expansion behavior of compounds under decomposition (Figs 4 and 5).

#### Intercalates on the base of fluorinated graphite

We used generalized Avramy–Erofeev's equation for the estimation of decomposition kinetic parameters for the series of compounds, so as nondimensional coefficient  $n$  has meaningful topochemical values:  $n > 1$  corresponds to reaction with kinetic control,  $n < 1$  – with diffusion control [26, 27].

#### Intercalates with acetonitrile: C<sub>2</sub>F<sub>x</sub>Br<sub>z</sub>·yCH<sub>3</sub>CN

Coefficient  $n$  had values of 1.19, 0.98, 0.97, 0.75 for  $x=0.92, 0.87, 0.69$  and  $0.49$ , respectively. Activation energy ( $E_a$ ) values found from line slope of  $\ln k - 10000/T$  function are equal to  $51.0 \pm 4.4, 51.2, 52.6$  and  $53.3 \pm 1.8$  kJ mol<sup>-1</sup> for  $x=0.92, 0.87, 0.69$  and  $0.49$ , respectively [17].

#### Intercalates with chloroform: C<sub>2</sub>F<sub>x</sub>Br<sub>z</sub>·yCHCl<sub>3</sub>

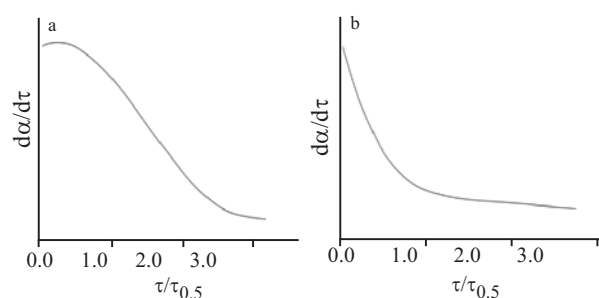
Coefficient  $n$  had values of 1.18, 0.94, 0.98, 0.86 for  $x=0.92, 0.87, 0.69$  and  $0.49$ , respectively. Activation energy ( $E_a$ ) values found from line slope of  $\ln k - 10000/T$  are 42.3, 44.3, 51.1 and 53.3 kJ mol<sup>-1</sup> for  $x=0.92, 0.87, 0.69$  and  $0.49$ , respectively.

#### Intercalates with dichlorethane:

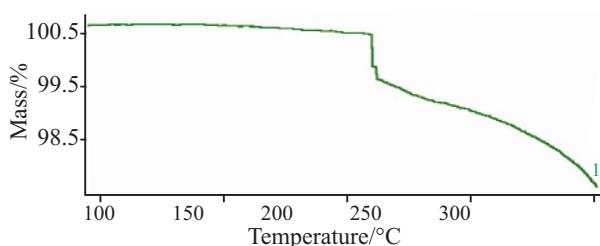


Coefficient  $n$  change values from 1.2 till 0.80 for  $x=0.92$  and  $0.49$ , respectively. Activation energy ( $E_a$ ) values found from line slope of  $\ln k - 10000/T$  are  $52.8 \pm 3.3, 62.2 \pm 0.3, 61.4 \pm 0.7$  and  $66.2$  kJ mol<sup>-1</sup> for  $x=0.92, 0.87, 0.69$  and  $0.49$ , respectively.

For control of the decomposition reaction mechanism in isothermal conditions we checked dependencies of  $d\alpha/d\tau$  vs.  $\tau/\tau_{0.5}$  (Fig. 6) ( $\tau/\tau_{0.5}$  is so called reduced time). This dependence allows telling the difference between three mechanisms: nucleation, chemical reaction on the interface and diffusion. It appears that the phase boundary reaction predominates in decomposition of intercalates C<sub>2</sub>F<sub>0.92</sub>Br<sub>0.01</sub>·0.288CH<sub>3</sub>CN, C<sub>2</sub>F<sub>0.92</sub>Br<sub>0.01</sub>·0.204CHCl<sub>3</sub> and C<sub>2</sub>F<sub>0.92</sub>Br<sub>z</sub>·0.222CH<sub>2</sub>ClCH<sub>2</sub>Cl, but the diffusion mechanism predominates for intercalates



**Fig. 6** Dependences of  $d\alpha/d\tau$  vs. reduced time  $\tau/\tau_{0.5}$  for a – C<sub>2</sub>F<sub>0.92</sub>Br<sub>0.01</sub>·0.288CH<sub>3</sub>CN at  $T=298.65$  K and for b – C<sub>2</sub>F<sub>0.49</sub>Br<sub>0.01</sub>·0.174CH<sub>3</sub>CN at  $T=293.15$  K



**Fig. 7** Thermogravimetric curve for intercalate C<sub>2</sub>F<sub>0.92</sub>Br<sub>0.010</sub>·0.136CH<sub>3</sub>CN (the second stage of filling)

C<sub>2</sub>F<sub>0.49</sub>Br<sub>0.01</sub>·0.174CH<sub>3</sub>CN, C<sub>2</sub>F<sub>0.49</sub>Br<sub>0.01</sub>·0.139CHCl<sub>3</sub> and C<sub>2</sub>F<sub>0.49</sub>Br<sub>z</sub>·0.153CH<sub>2</sub>ClCH<sub>2</sub>Cl.

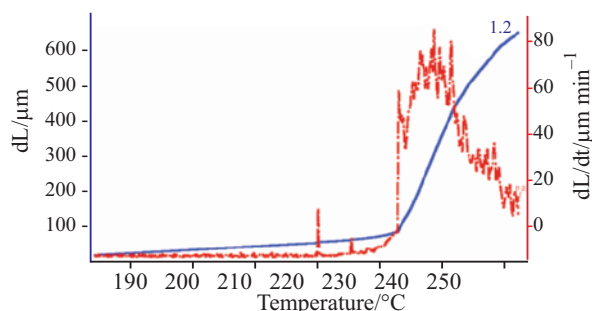
We studied the decomposition under linear heating for the more stable second stage of filling (because of more experimental simplicity). The decomposition of the second stage of filling takes place at 210°C (Fig. 7), the following irreversible decomposition (210–300°C) is both the guest removing, and the reaction of guest molecules with matrix. There is small monotonous expansion of the intercalate structure for guest molecules evolving till 230°C, but there is tenfold expansion at 230–260°C (Fig. 8). The latter volume enlargement really is the process of expanded (exfoliated) graphite formation [5].

## Conclusions

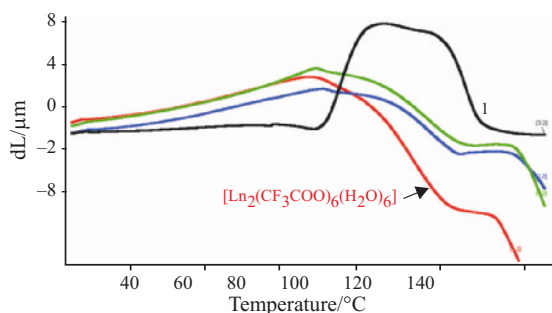
For the fluorinated graphite intercalates the monotonous change of the matrix structure is easily provided by fluorination degree.

The phase boundary reaction predominates in decomposition of intercalates C<sub>2</sub>F<sub>0.92</sub>Br<sub>0.01</sub>·0.288CH<sub>3</sub>CN, C<sub>2</sub>F<sub>0.92</sub>Br<sub>0.01</sub>·0.204CHCl<sub>3</sub> and C<sub>2</sub>F<sub>0.92</sub>Br<sub>z</sub>·0.222CH<sub>2</sub>ClCH<sub>2</sub>Cl, but the diffusion mechanism predominates for intercalates C<sub>2</sub>F<sub>0.49</sub>Br<sub>0.01</sub>·0.174CH<sub>3</sub>CN, C<sub>2</sub>F<sub>0.49</sub>Br<sub>0.01</sub>·0.139CHCl<sub>3</sub> and C<sub>2</sub>F<sub>0.49</sub>Br<sub>z</sub>·0.153CH<sub>2</sub>ClCH<sub>2</sub>Cl.

So the fluorination decrease leads to the diffusion hindrance increase. Effective thickness of the guest layer (about 4 Å for all matrices) [28] is



**Fig. 8**  $C_2F_{0.92}Br_{0.01} \cdot 0.136CH_3CN$  (the second stage of filling). The sample volume changing under heating, measured as the powder layer increase (initial layer thickness 1 mm)



**Fig. 9**  $[Ln_2(CF_3COO)_6(H_2O)_6]$  and  $\{[La(CF_3COO)_3(H_2O)_2]\}_n \cdot nH_2O$ . The sample volume changing under heating, measured as the powder layer increase (initial layer thickness 1 mm). Black thick line (1) – dehydration of  $\{[La(CF_3COO)_3(H_2O)_2]\}_n \cdot nH_2O$

considerably less than both the  $CH_3CN$  molecule size (it is shaped as symmetrical top molecule of 5.9 Å height and 4.1 Å width), and  $CHCl_3$  molecule size (in minimal projection 6.44 Å), so guest molecules are distributed in the interlayer space by the principle of ‘the closest packing’ of molecules into the cavities of relief ‘surface’ of matrix layers.

Nevertheless the decomposition reaction takes place without the structure expansion. It seems that guests removing from the lamellar matrix, such as intercalate of the first stage of filling, takes place without marked structure expansion: guest molecules are moving throughout the layer with middle hindrance. The second stage of filling decomposes incongruently without marked structure expansion to the first and the forth stages of filling [29]. The phase with the irregular arrangement of partially confounded layers (both filled, and unfilled ones) can evolve included gas molecules only with the great structure expansion (Fig. 8). Just such decomposition results in the expanded graphite formation [5].

The interesting example of the cruel necessity for such expansion is the dehydration of lanthanide trifluoroacetates  $Ln(CF_3COO)_3 \cdot 3H_2O$ . The detailed structures of these compounds are known: the Sm-, Eu-, Gd-, Tb- and Ho-complexes are binuclear:

$[Ln_2(CF_3COO)_6(H_2O)_6]$ , four  $CF_3COO^-$ -anions are bidentate bridge ligands, two are monodentate ones, all water molecules are coordinated, so the lanthanide coordination number is eight [30]. Lanthanum complex  $[La(CF_3COO)_3(H_2O)_2] \cdot H_2O$  has two-dimensional polymeric structure, all  $CF_3COO^-$ -anions are coordinated (by oxygen atoms) as a bridge ligands, only two water molecules are coordinated, the third one occupies a lattice site, so the lanthanum coordination number is eight too [31, 32]. The dehydration of all but one salts can proceed without remarkable structure expansion, but the evolving of uncoordinated water molecules, packed between stretched two-dimensional layers of lanthanum complex, demands the expansion of the compact structure. One can see this difference in the structure behaviour on Fig. 9. From the general point of view just such type of layers broadening may be observed during the decomposition of lamellar inclusion compounds with inflexible host layers.

Guest molecules in clathrates are packed (in channels and cages) in coordination compounds framework. The guest removing from this coordination compound framework needs the structure reorganization, but the realization of the expansion will be connected with the correlation between the framework flexibility and guest molecules size.

The flexibility of solid intercalate  $C_2F_xBr_z$  matrix is smallish, but the guest layer removing is fully let from the first stage of filling. So for intercalates decomposition, the expansion of the structure becomes important only for high stages of filling (the third and the forth ones) because of the impossibility for well ordering of differently filled layers.

Decomposition reaction under heating both for clathrates, and intercalates are studied rather seldom [33–36]. The thermoanalytical study of decomposition reaction for series of inclusion compounds allows obtaining quantitative straight information about their thermodynamic and kinetic stabilities. The observation of the structure expansion and compression helps in the topochemical mechanism understanding.

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DOI: 10.1007/s10973-007-8473-1