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THREE MODEL-FREE METHODS FOR CALCULATION OF ACTIVATION ENERGY IN TG

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Abstract

Two well-known isoconversion methods, the first one developed by Ozawa–Flynn–Wall and the second one developed by Friedman, are confronted with calculations made using modulated thermogravimetry (MTG). The latter variant is free from a number of assumptions and restrictions made in the isoconversion computations. In particular, it allows the use of a single decomposition curve and it remains in force even in the case of multistage decomposition with conjugated processes.

To obtain the model-fitting methods from the model-free methods one should replace some functions averaged over isoconversion levels by the functions calculated on the basis of kinetic models. In the Ozawa–Flynn–Wall method it is the averaged reduced time (integral of Arrhenius exponential over time). In the method of Friedman it is the averaged differential conversion function.

In MTG, the perturbations caused by the sinusoidal temperature modulation are connected with derivatives of mass loss by simple scaling, where activation energy plays a role of a scaling parameter. The ratio of the experimentally measured perturbations to the experimental derivative is used for the model-free computation of activation energy. If a theoretical derivative replaces the experimental one, this procedure leads to the model-fitting method. Even a rough approximation of the experimental derivative should not lead to an excessive error in activation energy. If in a vicinity of peaks' maxima in derivatives of mass loss the decomposition is controlled by single rate-limiting processes, modulated thermogravimetry should give realistic activation energies for these processes. Inasmuch as the results of MTG are weakly sensitive to selection of kinetic models, this method should have a high predictive force.

Keywords: activation energy, kinetics, temperature modulation, TG, thermal analysis

Introduction

The development of mathematical models for decomposition is always connected with a number of assumptions, and the physical sense of the modeling can be par-

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tially lost. Therefore, one can put the question as to whether the formal approximation implemented with unrealistic (or rough) models for kinetic data measured within certain temperature–time range can be used for a prediction of thermokinetic properties of a studied system beyond this range. We undoubtedly can give the affirmative answer to this question, if we have a proof that the decomposition in nature occurs as a one-stage (one-step) process. To find such a proof one should resort to the so-called model-free methods that allow calculation of activation energy by using minimal a priori information about a system under study.

In the literature devoted to thermal analysis two methods are most popular and famous. The first one is based on the isoconversion procedure of Ozawa, Flynn and Wall (OFW) [1, 2] and can be called the 'integral isoconversion method'. The second method developed by Friedman [3] for derivatives of mass loss can be called the 'differential isoconversion method'. Friedman developed his approach [3] for the *n*-order reaction. Ozawa [4] has generalized his approach as really model-free method. The generalization was rather trivial, and so we do not see any reason to call this procedure as the Ozawa–Friedman method. In the modern literature [5–7] the historical nuances are omitted and the method is called only by the name of Friedman.

Many variants of the model-free methods tested in the article of Vyazovkin [5], in fact, are minor modifications of the above mentioned procedures. For example, the Kissinger–Akahira–Sunose (KAS) procedure [8, 9] is not a methodologically independent approach. It is based on the general concept of the reduced time proposed by Ozawa [1]. In our opinion, the approximate evaluation of the temperature integral (the reduced time) cannot be a reason to regard this method as an independent one. Just like the modification of Coats and Redfern [10] with the approximate evaluation of the temperature integral cannot be called as an independent method. Indeed, mathematical approximations leading to a loss of accuracy can only mislead researchers. Having computers, one should tend to avoid the computational artifacts and inaccuracies at all.

Similar remarks can be made in relation to the Li–Tang (LT) procedure [11]. It follows from the Friedman method.

Thus, in classical thermogravimetry we can rigorously specify only two methods. These are the OFW method and the Friedman method. Below we describe these methods in the form of a short synopsis.

The third methodologically independent technique results from possibilities of modulated thermogravimetry (MTG) [12–14]. It is really a fundamentally new approach in comparison with two methods above mentioned. The main advantage of MTG [14] is that it allows one to avoid the isoconversion computations and to use for kinetic analysis only one kinetic curve instead of a set of curves [12–14]. Taking into account the rapid development [15–17] of MTG, the method seems to need an additional clarification.

The purpose of the present article is to discuss the differences between the classical approaches and a new approach that is being disclosed in modulated analysis. We compare results of three model-free methods and state an idea as to how one may create a model-fitting procedure based on MTG.

The Ozawa–Flynn–Wall method

The thermogravimetric experiment implements a measurement of an overall mass change $\widetilde{m}_{\mathrm{v}}(t)$ of M samples at M temperature programs $T(t)$ $(1\leq v\leq M)$. If in the system under study only one process takes place, we can normalize $\widetilde{m}_{\mathrm{v}}(t)$ so that to describe the change of the normalized mass from 1 to 0, that is

$$m_{\mathrm{v}}(t)=\frac{\widetilde{m}_{\mathrm{v}}(t)-m_{\infty}}{m_0-m_{\infty}}\ (1\leq v\leq M) \tag{1}$$

where $m_0=\widetilde{m}_{\mathrm{v}}|_{\mathrm{t=0}}$ and $m_{\infty}=\widetilde{m}_{\mathrm{v}}|_{\mathrm{t}\to\infty}$ are the initial and final masses of the sample at the v^{th} test. By convention, such normalization can be attributed to the change of mass from 1 to 0 g. In the case of a one-stage process, the use of the degree of mass conversion $\alpha^{(\mathrm{v})}(t)$ (normalized mass loss) practically is equivalent to the normalized mass $m_{\mathrm{v}}(t)$. They are connected by the simple relationship

$$\alpha^{(\mathrm{v})}(t)=1-m_{\mathrm{v}}(t)\ (1\leq v\leq M)$$

If only one activation process controls the change of mass and the Arrhenius equation is valid for the system, we can write

$$\frac{\mathrm{d}\alpha^{(\mathrm{v})}}{\mathrm{d}t}=Af(\alpha^{(\mathrm{v})})\exp\left(-\frac{E_{\mathrm{j}}}{RT_{\mathrm{v}}(t)}\right)(1\leq v\leq M) \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant, f is the differential conversion function (reaction model). The initial condition for differential Eq. (2) is $\alpha^{(\mathrm{v})}(0)=0$.

For a one-stage process with one activation energy, Eq. (2) is very accurate. Moreover, if we know that the process under study is really such one, for a prediction of the function $\alpha(t)$ with arbitrary temperature–time relationship $T(t)$ we can use any empiric function f that leads to an accurate approximation of the measured kinetic curves. This fact can explain, in particular, why the conversion function for reaction kinetics with the fractional order $f=(1-\alpha)^{\mathrm{n}}$ and other multiparametric models are being used up to now as a suitable approximation formulae.

The exact approximation of the curves $\alpha^{(\mathrm{v})}(t)$ yields correct values of E and A. Thus, if we accept Eq. (2) as an initial postulate and the decomposition in nature strictly conforms to it, the difficulties in evaluating two unknown constants and one unknown function (E, A and f – so called 'triplet' [18]) are connected exceptionally with experimental errors and with the weak sensitivity of approximation error to a selection of a model.

To find the searched triplet by using experimental kinetic curves, it is convenient to integrate Eq. (2), that is

$$g(\alpha^{(v)}) = \int_0^{\alpha^{(v)}} \frac{1}{f(\alpha)} \mathrm{d}\alpha = A\tau^{(v)}$$
$$\tau^{(v)}[T_v(x)]_{|x=t} = \int_0^t \exp\left(-\frac{E}{RT_v(x)}\right)\mathrm{d}x \tag{3}$$

where x is the parameter of integration. The value of $\tau^{(v)}$ can be called the reduced time [1]. For all dependencies $T_v(t)$ the functions $\alpha^{(v)}$ plotted *vs.* $\tau^{(v)}$ coincide with each other.

In the systems with multistage kinetics, the notion of reduced time loses generally its physical sense. If only one rate-limiting process determines the decomposition rate in a vicinity of maxima of some peaks in derivatives of mass loss, from the simplest considerations, for evaluating activation energy, at least roughly and only about points of the peaks' maxima, one can assume

$$\frac{\mathrm{d}\alpha^{(v)}}{\mathrm{d}t} \cong w_r A_r f_r(\{c_i^{(v)}\})\exp\left(-\frac{E_r}{RT_v(t)}\right)(1 \le v \le M) \tag{4}$$

where 'r' is the subscript corresponding to the rate-limiting stage, w_r is the normalized mass of gaseous products released at this stage, c_i ($1\le i\le I$) are the concentrations of I components in the system. In general, the function $f_r = f_r(\{c_i^{(v)}\})$ depends on the manifold $\{c_i^{(v)}\}$ of concentrations of all components. For multistage kinetics with independent reactions, Eq. (4) can be written as

$$\frac{\mathrm{d}\alpha^{(v)}}{\mathrm{d}t} \cong w_r \frac{\mathrm{d}\alpha_r^{(v)}}{\mathrm{d}t} = w_r A_r f_r(\alpha_r^{(v)})\exp\left(-\frac{E_r}{RT_v(t)}\right)(1 \le v \le M)$$

In this particular case, the reduced time for the rate-limiting stage can be evaluated just like in the case of one-stage kinetics, and the hypothesis of the rate-limitation can be used to find correct activation energy E_r.

Let us assume that in the system under study only one chemical reaction takes place and a measured property X of the system (such as viscosity, or density, or electroconductivity etc.) depends unambiguously on the degree of conversion of a substance in this reaction. Suppose the value of $X(\alpha^{(v)}(t))$ has been measured at the v^{th} temperature program. Even if the model connecting X and $\alpha^{(v)}$ is absent, one can approximate any dependence $X(\alpha^{(v)})$ on the basis of Eq. (2) for all used temperature programs $1\le v\le M$.

Each constant value of $X=X_j$ in different temperature programs corresponds to the equal values of $\alpha_j^{(v)}$, that is $\alpha_j^{(v)}=X^*(X_j)=\mathrm{const}=\alpha_j$, where X^* is the inverse function relative to $X(\alpha_j)$. Consequently, at the isoconversion value of $X=X_j$, the integrals of Arrhenius exponential over time are also equal to each other for all the programs, namely

$$\tau_{X=X_j}^{(1)} \approx \tau_{X=X_j}^{(2)} \approx \tau_{X=X_j}^{(M)} \approx \tau_j \tag{5}$$

where τ_j is a hypothetical reduced time corresponding to the real process. We used approximate equalities keeping in mind that for a real process the assumptions accepted in Eq. (5) are some idealization. Let the temperature–time relationships be measured at J isoconversion levels of X, namely: $T_{jv}=T_v(t_{jv})$ ($1\le j\le J$, $1\le v\le M$). If the corresponding grid of time $\{t_{jv}\}$ is dense enough one can calculate the integral in Eq. (3) numerically for each time t_{jv}, that is

$$\tau_{jv}(E_j)=\int_0^{t_{jv}}\exp\left(-\frac{E_j}{RT_v(x)}\right)dx$$

We used the index '*j*' for activation energy to show that this energy can be calculated at each isoconversion level. The objective function follows from the requirement of the best fulfillment of the equalities in Eq. (5), that is

$$\Gamma(\{\tau_j\},\{E_j\})=\frac{1}{MJ}\sum_{j=1}^{J}\sum_{v=1}^{M}[\tau_{jv}(E_j)-\tau_j]^2$$

Inasmuch as the derivative of Γ with respect to τ_j at the minimum of Γ should equal zero, we have

$$\tau_j=\frac{1}{M}\sum_{v=1}^{M}\tau_{jv}(E_j) \qquad (6)$$

Thus, activation energy at each isoconversion level can be determined by minimization of the sum of squares having the form

$$\Gamma_1(E_j)=\frac{1}{M}\sum_{v=1}^{M}\left[\tau_{jv}(E_j)-\frac{1}{M}\sum_{m=1}^{M}\tau_{jm}(E_j)\right]^2 \quad (1\le j\le J) \qquad (7)$$

Such minimization implicitly presupposes that activation energy can change depending on the degree of conversion. At the same time, according to the initial postulate, it should be a constant. Thus, we see some contradiction that hampers interpretation of results of such calculations.

Note that many variants are possible to assign an objective function. For example, one can use the logarithms of the reduced times [19–22], then instead of Eq. (7) we have

$$\Gamma_2(E_j)=\frac{1}{M}\sum_{v=1}^{M}\left[\ln\tau_{jv}(E_j)-\frac{1}{M}\sum_{m=1}^{M}\ln\tau_{jm}(E_j)\right]^2 \quad (1\le j\le J) \qquad (8)$$

The approximation of Kissinger–Akahira–Sunose [8, 9] allows one to calculate E_j on the basis of Eq. (8) explicitly. However, this approximation can be used only for the linear temperature–time relationship

$$T_v(t)=T_0+a_vt$$

where a_v is the heating rate at the v^{th} temperature program, T_0 is the initial temperature. The approximate expression for the reduced time [8, 9] has the form

$$\tau_{jv}(E_j)=\frac{RT_{jv}^2}{a_vE_j}\exp\left(-\frac{E_j}{RT_{jv}}\right)$$

By minimizing the sum of the squares in Eq. (8) with respect to E_j, one can find

$$E_\mathrm{j}=R\frac{M\sum_{\mathrm{v}=1}^{\mathrm{M}}\frac{\ln(T_\mathrm{jv}^2/a_\mathrm{v})}{T_\mathrm{jv}}-\sum_{\mathrm{v}=1}^{\mathrm{M}}\ln\frac{T_\mathrm{jv}^2}{a_\mathrm{v}}\sum_{\mathrm{v}=1}^{\mathrm{M}}\frac{1}{T_\mathrm{jv}}}{M\sum_{\mathrm{v}=1}^{\mathrm{M}}\frac{1}{T_\mathrm{jv}^2}-\left(\sum_{\mathrm{v}=1}^{\mathrm{M}}\frac{1}{T_\mathrm{jv}}\right)^2}$$

This formula does not lead to a considerable accuracy loss [5] and, hence, can be recommended for simple calculations by calculators.

One more variant of the method [23, 24] results from the requirement that equalities in Eq. (5) should be fulfilled with the best accuracy. It leads to numerical minimization of the quantity

$$\Gamma_3(E_\mathrm{j})=\sum_{\mathrm{v}=1}^{\mathrm{M}}\sum_{\mathrm{m}=1,\mathrm{m}\neq\mathrm{v}}^{\mathrm{M}}\frac{\tau_\mathrm{jv}(E_\mathrm{j})}{\tau_\mathrm{jm}(E_\mathrm{j})}\,(1\leq j\leq J) \tag{9}$$

The derivation of Eq. (9) is based on the theorem about the greater value of the arithmetic average in comparison to the geometric mean.

We have numbered the objective functions with several subscripts to emphasize that results of their minimization are somewhat different. However, if kinetics really obey Eq. (2), all variants of minimization will lead to one and the same activation energy. The small differences will be observed only on account of experimental errors and physical inaccuracy of Eq. (5). If Eq. (5) is accurate, all the variants of the method give the same manifold $\{E_\mathrm{j}\}$.

The function Γ_2 seems easier in a descriptive sense in comparison to Γ_3. For example, Eq. (8) allows one to trace how from the model-free method one can turn to a model-fitting method. Indeed, for the average reduced time in Eq. (6) one can use an estimation resulting from a model, that is

$$\tau_\mathrm{j}=\frac{1}{M}\sum_{\mathrm{v}=1}^{\mathrm{M}}\tau_\mathrm{jv}(E_\mathrm{j})\approx\frac{g(\alpha_{\mathrm{j,exper}})}{A} \tag{10}$$

Then Eqs (8) and (10) lead to a method of evaluation of triplets [19, 21] that are searched by minimization of the function

$$\Gamma_4(A,E)=\frac{1}{MJ}\sum_{\mathrm{j}=1}^{\mathrm{J}}\sum_{\mathrm{v}=1}^{\mathrm{M}}[\ln(\tau_\mathrm{jv}(E))+\ln A-\ln(g(\alpha_{\mathrm{j,exper}}))]^2$$

Now it is unnecessary to use the isoconversion levels, since the summands for each temperature program can be calculated in arbitrary points.

The strongest advantage of the OFW method, in contrast to other methods, is that it can be used for many properties $X(\alpha^{(\mathrm{v})})$ and not only for the kinetic curves $\alpha^{(\mathrm{v})}$. This idea from Ozawa [1] was extremely useful for applied chemistry. An explicit functional form of $X(\alpha^{(\mathrm{v})})$ can be very complex and even inaccessible at all for existing theories; nevertheless, OFW method allows the prediction of the change of $X(\alpha^{(v)})$ with temperature.

Unfortunately, the OFW method has serious limitations [6]. In particular, it cannot be used for systems with conjugated reactions. In this case the integral in Eq. (3) can not correspond to reduced times for individual processes.

Formally, one may assume the dependence of activation energy on overall conversion [5]. The fact that E changes should testify the presence of several stages, but it would be desirable not only to detect a multistage process but also to estimate activation energies at different stages. However, the considered equations by no means allow a derivation of the dependence $E(\alpha)$; they merely do not contain it. Nevertheless, in the case of independent reactions the reduced times are calculated independently, hence, within regions where kinetics is defined by one rate-limiting process, the OFW method can give acceptable evaluations of activation energy for this process. This case will be considered below in the discussion.

The method of Friedman

The method of Friedman is partly rid of some defects of the OFW method. It is based on the expression of the derivative of mass loss. If all values entering in the derivative, excepting activation energy, are known, one can calculate activation energy strictly. Calculation of a set of activation energies for conjugated processes by using derivatives, in contrast to the OFW method, can be substantiated. In real practice, however, because of the absence of information about actual isoconversion levels for individual processes, the Friedman method does not have real advantages in comparison to the OFW method.

The method requires precise equipment that allows a measurement of decomposition curves with high accuracy sufficient for their numerical differentiation.

Let us take the logarithms of the left-hand and right-hand part of Eq. (2), we obtain

$$\ln\frac{\mathrm{d}\alpha^{(v)}}{\mathrm{d}t}=\ln f(\alpha^{(v)})+\ln(A)-\frac{E}{RT_v(t)}\quad(1\le v\le M)\tag{11}$$

For each isoconversion level the first two summands in the right-hand part of Eq. (11) are constants

$$\ln\left(\frac{\mathrm{d}\alpha^{(v)}}{\mathrm{d}t}\right)\Bigg|_{\alpha^{(v)}=\alpha_j}=\ln f(\alpha_j)+\ln A-\frac{E}{RT_{jv}}\quad(1\le j\le J,\ 1\le v\le M)\tag{12}$$

Thus, one can determine activation energy E_j at each isoconversion level by plotting the straight line in the coordinates: the logarithm of the derivative *vs.* $1/T_{jv}$. The method obviously permits the averaging of calculated activation energies over all isoconversion levels and the finding of a triplet by minimization of the value of

$$\Omega(A,E)=\frac{1}{MJ}\sum_{\mathrm{j}=1}^{\mathrm{J}}\sum_{\mathrm{v}=1}^{\mathrm{M}}\left\{\ln\left(\frac{\mathrm{d}\alpha^{(\mathrm{v})}}{\mathrm{d}t}\right)_{\Big|\alpha^{(\mathrm{v})}=\alpha_{\mathrm{j}}}-\ln f(\alpha_{\mathrm{j}})-\ln A+\frac{E}{RT_{\mathrm{jv}}}\right\}^{2}$$

The relative error in calculation of the derivatives grows with decreasing in their absolute values and becomes unacceptably large at the beginning and at the end of decomposition. Thus, the range of α_j in such calculations should be restricted, say, $0.05<\alpha_j<0.95$.

Li and Tang [11] have offered integration of Eq. (11) over isoconversion levels, namely

$$\int_0^{\alpha_{\mathrm{j}}}\ln\frac{\mathrm{d}\alpha^{(\mathrm{v})}}{\mathrm{d}t}\mathrm{d}\alpha^{(\mathrm{v})}=\int_0^{\alpha_{\mathrm{j}}}\ln(Af(\alpha^{(\mathrm{v})}))\mathrm{d}\alpha^{(\mathrm{v})}-\int_0^{\alpha_{\mathrm{j}}}\frac{E}{RT_{\mathrm{v}}}\mathrm{d}\alpha^{(\mathrm{v})}$$

Such a trick does not lead to a difference with the original Friedman method [3]. However, the authors [11] extracted E from under the integral

$$\int_0^{\alpha_{\mathrm{j}}}\frac{E}{RT_{\mathrm{v}}}\mathrm{d}\alpha^{(\mathrm{v})}=E_{\mathrm{j}}\int_0^{\alpha_{\mathrm{j}}}\frac{1}{RT_{\mathrm{v}}}\mathrm{d}\alpha^{(\mathrm{v})}$$

It is the source of the distinction with the original method [5]. In calculations for one-stage kinetics both the methods should give the same results. At the same time, the Friedman method is formally used for computations in the case of multistage kinetics [5]. In such computations the value of E formally is considered as a function of α and should stay under the integral. Although in all methods the formalism of the use of the function $E(\alpha)$ cannot be rigorously justified, we do not see any reasons to extend a collection of the formal methods giving different results, for example, like the Friedman method and the Li–Tang method.

The method of Friedman does not require an integration of differential equations, therefore for one-stage kinetics an optimal triplet is searched for by means of comparison of minima of $\Omega(A, E)$ inside a list of the functions f under test [7]. Each trial is implemented by the method of linear regression.

The model-free method based on modulated thermogravimetry

Modulated thermogravimetry measures perturbations caused by the sinusoidal modulation of a temperature–time relationship [12–14]. The temperature varies by the law

$$T_{\mathrm{m}}(t)=T_0+at+L\sin(2\pi\omega t)$$

where ω and L are the frequency and amplitude of the modulation. If ω is sufficiently large and L is sufficiently small, the temperature modulation very weakly influences the mass change; however, it considerably affects the derivative of mass loss [12–14]. The measurement of perturbations requires the high precision of equipment; such measurements have become possible only during the latest decade.

In the TG experiment we have only one kinetic curve (M=1) and, correspondingly, one derivative of mass loss. Therefore, we omit the index 'v' from subsequent equations.

Let us write the Eq. (2) separately for the modulated temperature (L≠0) and for the classical temperature program (L=0). We have

$$\frac{\mathrm{d}\alpha_{\mathrm{m}}}{\mathrm{d}t}=Af(\alpha_{\mathrm{m}})\exp\left(-\frac{E}{RT_{\mathrm{m}}(t)}\right) \tag{13}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=Af(\alpha)\exp\left(-\frac{E}{RT(t)}\right) \tag{14}$$

where the subscript 'm' relates to the modulations. The approximate equality $\alpha_{\mathrm{m}}\approx\alpha$ leads to the consequence $f(\alpha_{\mathrm{m}})\approx f(\alpha)$. Thus, subtracting Eq. (14) from (13) one can get

$$\begin{aligned}F(t)=\frac{\mathrm{d}\alpha_{\mathrm{m}}}{\mathrm{d}t}-\frac{\mathrm{d}\alpha}{\mathrm{d}t}=Af(\alpha_{\mathrm{m}})\exp\left(-\frac{E}{RT_{\mathrm{m}}(t)}\right)-Af(\alpha)\exp\left(-\frac{E}{RT(t)}\right)\approx\\ \approx\frac{\mathrm{d}\alpha}{\mathrm{d}t}\left[\exp\left(-\frac{E}{RT_{\mathrm{m}}(t)}+\frac{E}{RT(t)}\right)-1\right]\end{aligned} \tag{15}$$

where $F(t)$ is the perturbation in the derivative caused by the temperature modulation. If the amplitude of the modulation L is sufficiently small, linearization of the exponential in Eq. (15) gives the additional approximation

$$F(t)\approx E\frac{\mathrm{d}\alpha}{\mathrm{d}t}\left\{\frac{T_{\mathrm{m}}(t)-T(t)}{RT^{2}(t)}\right\} \tag{16}$$

From Eq. (15) or from (16) one can see that the perturbation equals zero in the points of time where the modulated temperature intersects the linear temperature–time relationship, namely, $\sin(2\pi\omega t)=0$, $T_{\mathrm{m}}(t)=T(t)$. These equalities correspond to the points $t_{\mathrm{k}}=\mathrm{k}(2\omega)^{-1}$, $k=0,1,2\ldots$

Maximal amplitudes of the perturbation (maximal absolute values) are reached in the points where $\sin(2\pi\omega t)=1$ or $\sin(2\pi\omega t)=-1$. The latter equalities give $t_{\mathrm{k}}=(k+1/2)(2\omega)^{-1}$, $k=0,1,2\ldots$ By regrouping the coefficients in Eq. (16) one can introduce the discrete function

$$F^{*}(t_{\mathrm{k}})=\frac{RT^{2}(t_{\mathrm{k}})\left|F(t_{\mathrm{k}})\right|}{L}\approx\frac{E\mathrm{d}\alpha}{\mathrm{d}t}\quad\text{where } t_{\mathrm{k}}=(1/2+k)/2\omega;\ \ k=0,1,2... \tag{17}$$

From here we obtain the simple formula for calculation of activation energy

$$E=\frac{F^{*}(t_{\mathrm{k}})}{(\mathrm{d}\alpha/\mathrm{d}t)_{|\mathrm{t}=\mathrm{t}_{\mathrm{k}}}}\quad \textit{where}\ t_{\mathrm{k}}=(1/2+k)/2\varpi; k=0,1,2... \tag{18}$$

In Fig. 1 one can see the derivatives of the degree of decomposition simulated at three heating rates with the modulated and unmodulated temperature for the system with two parallel reactions. The overall derivative is expressed as

$$\frac{d\alpha}{dt}=w_1\frac{d\alpha_1}{dt}+w_2\frac{d\alpha_2}{dt}$$

where α_1, α_2 are the partial degrees of decomposition; w_1, w_2 are the weighting contributions of each of two stages to overall kinetics. The parameters of the modulation were set as $1/\omega=200$ s, $L=5$°C. The kinetic coefficients were assigned as in the previous publication [14]. The same example will be presented below in the discussion.

One can see to what extent the temperature amplitude only in 5°C affects the derivative. Subtracting unmodulated derivatives from modulated ones we obtain the corresponding perturbations (Fig. 2). The real experiment allows one to get $\alpha_m(t)$,

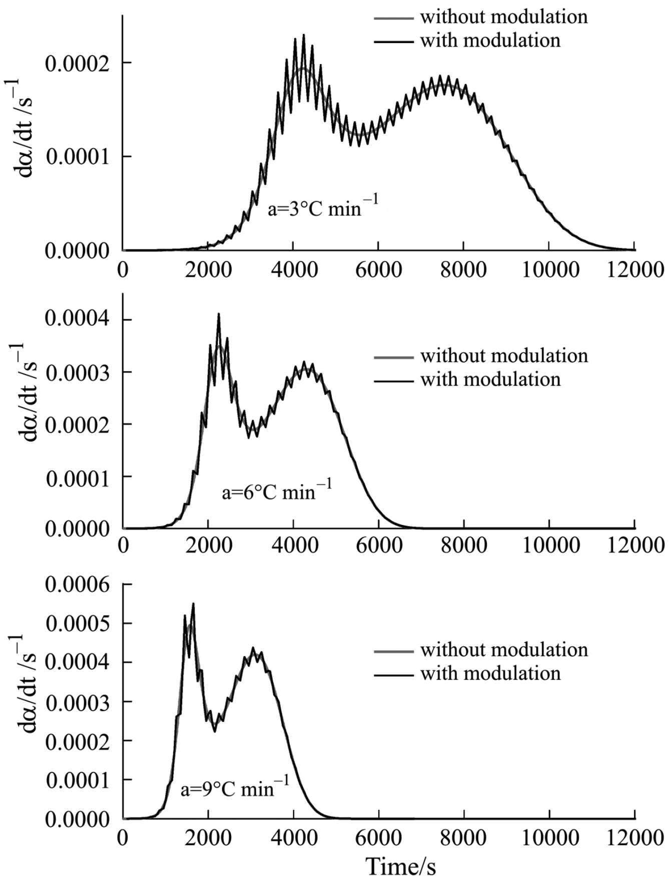

Fig. 1 The derivatives of α simulated numerically at different heating rates for the modulated temperature and for the classical temperature program

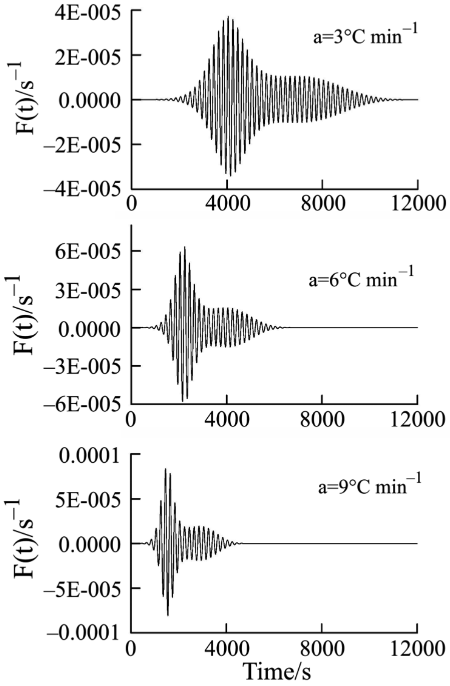

Fig. 2 The perturbations calculated as the difference between the perturbed and unperturbed derivatives

$T_m(t)$ and $d\alpha_m/dt$. The smoothed (classical) dependencies $T(t)$ and $d\alpha/dt$ can be predicted [14] from this information with good accuracy. In other words, the function $F(t)$ can be constructed by using only a perturbed kinetic curve.

After finding the perturbation $F(t)$, the function $F^*(t)$ can be calculated elementarily (Fig. 3). Since Eq. (17) can be used for each step of overall kinetics, for the superposition of two steps under consideration we have

$$F^*(t_k)=w_1E_1\frac{d\alpha_1}{dt}+w_2E_2\frac{d\alpha_2}{dt}\sqrt{t_k=\frac{1/2+k}{2\omega};\ k=0,1,2...} \qquad (19)$$

By comparing Eqs (17) and (19) one can find the expression for the effective (apparent) activation energy

$$E=\frac{\left[w_1E_1\frac{d\alpha_1}{dt}+w_2E_2\frac{d\alpha_2}{dt}\right]}{\left[w_1\frac{d\alpha_1}{dt}+w_2\frac{d\alpha_2}{dt}\right]} \qquad (20)$$

None of the methods described in the previous two sections can lead to a similar explicit expression for apparent activation energy. Calculations on the basis of

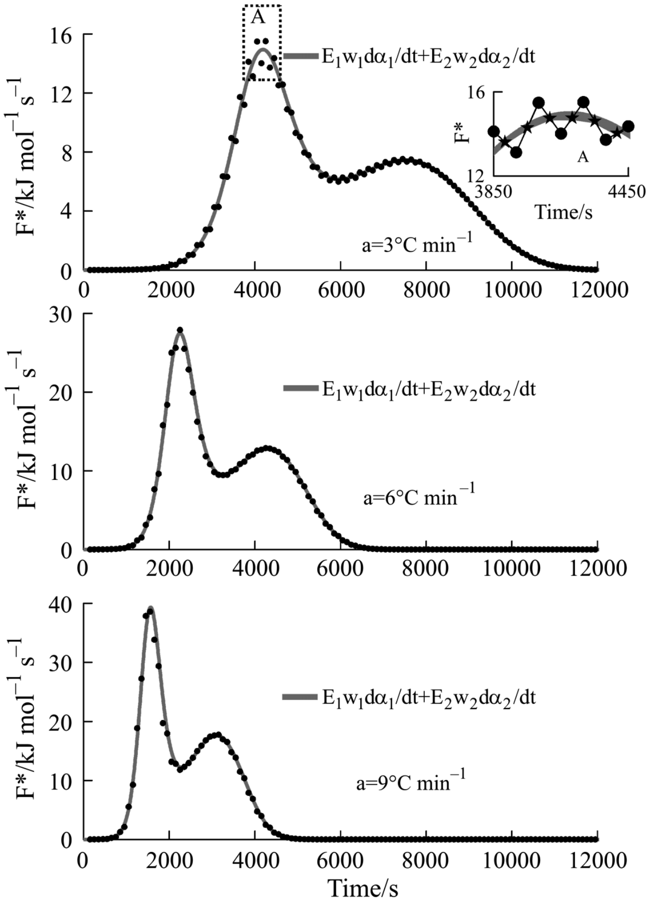

Fig. 3 The envelope of the absolute value of the perturbations multiplied by RT^2/L and the superposition of the local derivatives multiplied by activation energies. The enlarged fragment '*A*' shows the averaging when calculating activation energy

Eq. (18) show that it gives very good accuracy (Fig. 4). Data shown in Figs 1–4 prove corrections of all above presented equations. One can readily use them to obtain the model-fitting method of handling information related to MTG.

The model-fitting method based on modulated thermogravimetry

If we insert the theoretical derivative dα/dt instead of the experimental one in Eq. (16), we can find the kinetic constants by minimizing the two-parameter functional expressing the average square of the approximation error, namely

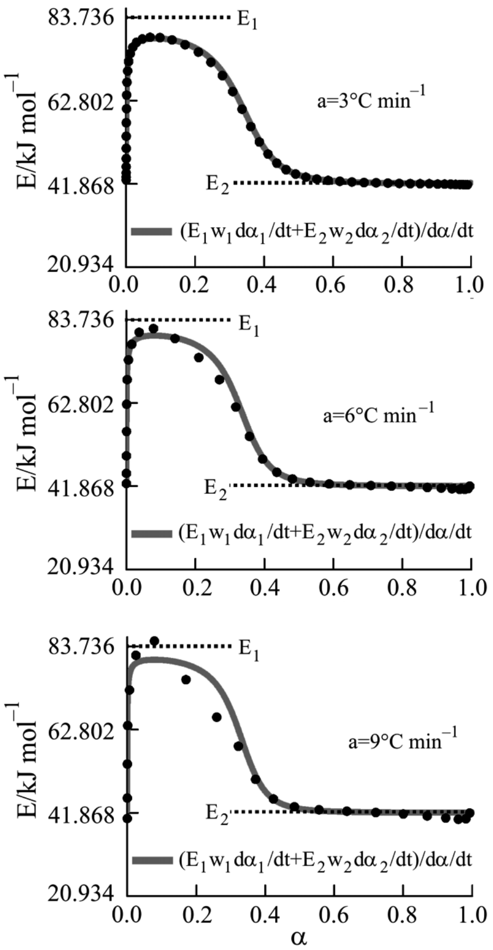

Fig. 4 Activation energies calculated at three heating rates by Eq. (18) and the theoretical prediction by Eq. (20) calculated on the basis of the solution of the kinetic equations

$$\Delta(A,E)=\frac{1}{t^*}\int_0^{t^*}\left[F^{(\mathrm{exper})}(t)-E^{(\mathrm{theor})}\gamma(t)\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)^{(\mathrm{theor})}\right]^2\mathrm{d}t \tag{21}$$

where t^* is the time of the experiment, $\gamma(t)=[T_\mathrm{m}(t)-T(t)]/RT^2(t)$. One can represent Eq. (21) in the form

$$\Delta(A,E)=\frac{1}{t^*}\int_0^{t^*}[\gamma(t)E^{(\mathrm{actual})}]^2\left[\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)^{(\mathrm{exper})}-\frac{E^{(\mathrm{theor})}}{E^{(\mathrm{actual})}}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)^{(\mathrm{theor})}\right]^2\mathrm{d}t \tag{22}$$

If we find $E^{(\mathrm{theor})}\approx E^{(\mathrm{actual})}$, the fit of the perturbations by minimizing the value of Δ automatically leads to the fit of the derivative dα/dt and, correspondingly, to the fit of

$\alpha(t)$. Although the perturbations involve information about kinetic curves in the hidden form, the approximation of the perturbations allows one to find $\mathrm{d}\alpha(t)/\mathrm{d}t$ and $\alpha(t)$.

According to Eq. (22), the derivative is being fitted so that to provide, in the best way, its match with the perturbations by means of scaling [14]. Activation energy $E^{(\mathrm{theor})}$, being the scale multiplier, can be determined with high accuracy.

One can see that any model with correct activation energy will accurately approximate the relative perturbations, namely

$$\frac{F^{(\mathrm{exper})}}{\mathrm{d}\alpha^{(\mathrm{exper})}/\mathrm{d}t}=\frac{F^{(\mathrm{theor})}}{\mathrm{d}\alpha^{(\mathrm{theor})}/\mathrm{d}t}=E^{(\mathrm{actual})}\frac{T_\mathrm{m}(t)-T(t)}{RT^2(t)}$$

One can represent Eq. (21) in the third form

$$\Delta(A,E)=\frac{1}{t^*}\int_0^{t^*}\left[\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)^{(\mathrm{theor})}\right]^2\left[\frac{F^{(\mathrm{exper})}}{(\mathrm{d}\alpha/\mathrm{d}t)^{(\mathrm{theor})}}-\frac{F^{(\mathrm{theor})}}{(\mathrm{d}\alpha/\mathrm{d}t)^{(\mathrm{theor})}}\right]^2\mathrm{d}t=$$

$$=\frac{1}{t^*}\int_0^{t^*}\left[\gamma(t)\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)^{(\mathrm{theor})}\right]^2\left[E^{(\mathrm{actual})}\frac{(\mathrm{d}\alpha/\mathrm{d}t)^{(\mathrm{exper})}}{(\mathrm{d}\alpha/\mathrm{d}t)^{(\mathrm{theor})}}-E^{(\mathrm{theor})}\right]^2\mathrm{d}t$$

Thus, one can see once again that the absolute minimum $\Delta=0$ is reached only in the case when $E^{(\mathrm{theor})}=E^{(\mathrm{actual})}$ and $(\mathrm{d}\alpha/\mathrm{d}t)^{(\mathrm{theor})}=(\mathrm{d}\alpha/\mathrm{d}t)^{(\mathrm{exper})}$.

For obtaining correct activation energy by Eq. (21) the approximation of the perturbations within a short time interval can be implemented by arbitrary model. Indeed, since we could calculate activation energy within each period of the modulation without a model at all (Fig. 4), in the model-fitting method we can find actual activation energy with arbitrary model.

Even if decomposition kinetics is a multistage process but a one-stage model is used for the approximation, the result will be correct as well. Independently of correctness or incorrectness of a model for approximation of $f_\mathrm{r}(\{c_\mathrm{i}\})$ in Eq. (4), the fit of the perturbations will give actual activation energy.

Inversely, the approximation of perturbations by arbitrary model within a short interval of time $[t_1, t_2]$, when the kinetic function $f_\mathrm{r}(\{c_\mathrm{i}\})$ is approximately a constant, should lead both to the correct activation energy and to the correct derivative of mass loss. Let us consider the functional in Eq. (21) explicitly in the case when Eq. (4) is fulfilled exactly. We have

$$\Delta(A,E)=\frac{1}{t_2-t_1}\int_{t_1}^{t_2}\gamma^2\left[w_\mathrm{r}f_\mathrm{r}(\{c_\mathrm{i}\})A_\mathrm{r}E_\mathrm{r}\exp\left(-\frac{E_\mathrm{r}}{RT}\right)-EAf^*(\alpha)\exp\left(-\frac{E}{RT}\right)\right]^2\mathrm{d}t$$

where $f^*(\alpha)$ is some empiric conversion function.

The minimum of $\Delta(A, E)$ is reached only in the case if $E=E_\mathrm{r}$ and $Af^*=w_\mathrm{r}A_\mathrm{r}f_\mathrm{r}(\{c_\mathrm{i}\})$. The results of minimization of $\Delta(A,E)$ inside the entire interval $[0, t^*]$ depend on a model for the kinetic function; however, the main contribution to the approximation error arises from deviations near the maxima of peaks on derivatives of mass loss (maximal amplitudes of perturbations [14]). On the other hand, a satisfactory approximation of the perturbations near the region of their maximal amplitudes leads to good evaluation of activation energy. Since the modulated analysis is weakly sensitive to a selection of kinetic models, it should have a very high predictive force.

Discussion

The isoconversion OFW method is illustrated in Fig. 5a. Within some regions of the kinetic curves, where both processes give comparable contributions to the mass change, the isoconversion levels for the overall mass do not correspond to the levels for the par-

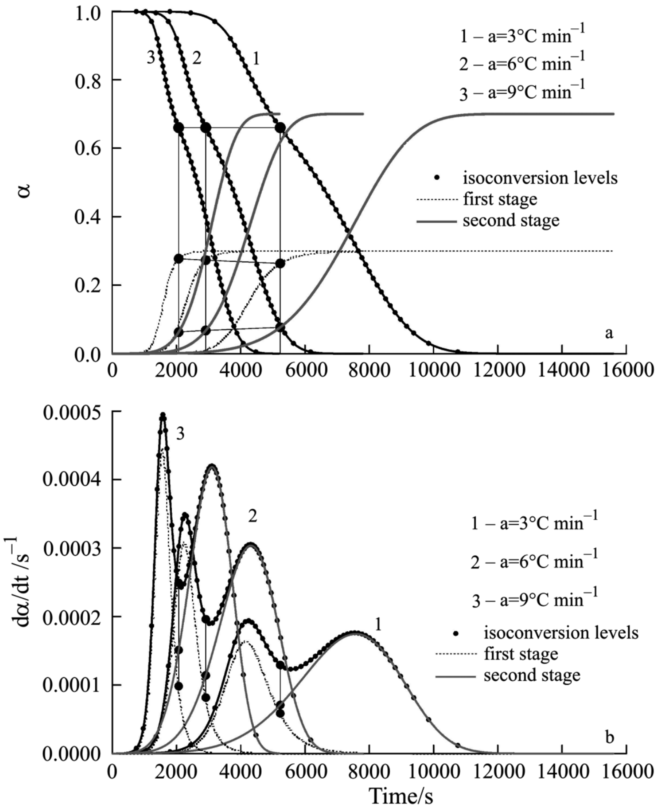

Fig. 5 Selection of isoconversion levels for calculation of activation energy a – by the Ozawa–Flynn–Wall method and b – by the Friedman method. Inasmuch as the isoconversion levels for the overall mass changes do not correspond to isoconversion levels for the partial processes, the effective activation energy should differ from activation energies for the individual processes. In the case of derivatives, a nonzero contribution of one of the derivatives to the overall derivative hinders a calculation of activation energy for another process. In the method of Friedman it is one more obstacle for calculation of activation energies, in addition to finding of partial isoconversion levels

tial processes. It is the main reason of inconstancy of calculated activation energy within the regions where different processes are reciprocally superposed. If the processes were ideally resolved, the calculated activation energy would be a stepwise function. However, theoretically, for parallel reactions with different activation energies the ideal resolution cannot be reached [14]. Despite the apparent domination of the first stage in overall kinetics (Fig. 1) calculated activation energy tends to E_2 at $\alpha \to 0$. In fact, at low conversion the second process dominates $(d\alpha_1/dt)/(d\alpha_2/dt) \to 0$ and, according to Eq. (20), we have $E \to E_2$.

The data represented in Fig. 6a have been obtained by using the different modifications of the OFW method [Eqs (7)–(9)]. It is impossible to give a preference to one of three functions Γ_1, Γ_2 or Γ_3, inasmuch as their minimization gives practically the same results. The difference in calculated activation energy lies in the third decimal digit.

The classical variant of the OFW method, namely Eq. (8) for logarithms of reduced times, provides the less number of iterations in comparison to the computations with Eq. (9). However, both equations are practically equivalent ones.

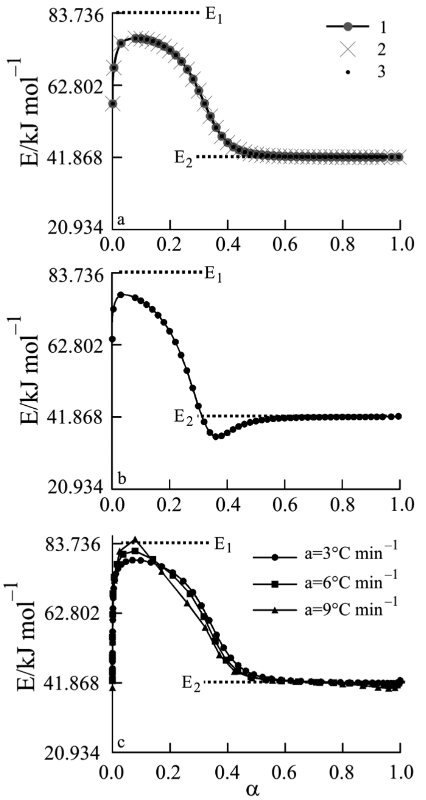

Fig. 6 Activation energies calculated by using a – the modifications of Ozawa–Flynn–Wall method [1 – Eq. (7), 2 – Eq. (8), 3 – Eq. (9)], b – the method of Friedman and c – modulated thermogravimetry

The Friedman method (Figs 5b, 6b) gives somewhat different results. To obtain activation energy for an individual process by this method, two requirements should be satisfied. Isoconversion levels of the overall mass loss and a partial mass loss should coincide, and the overall derivative should be equal to a derivative for a partial process. In the regions of overlapping of different processes both the requirements are violated simultaneously.

The dependence of activation energy on degree of conversion, which is calculated by using Eq. (18) for MTG, resembles the dependence calculated by the OFW method (compare Figs 6a and 6c). However, this resemblance is only formal. The totally different approaches underlie the computations by these methods (the model-free method section). In particular, modulated thermogravimetry makes possible to calculate activation energy for a single temperature program, while the isoconversion methods need information obtained using a few temperature programs (three heating rates in our computations). As mentioned, in the case of competitive reactions the isoconversion methods are unacceptable. In contrast to these methods, MTG can give useful estimations even in this case.

In Fig. 7a the results obtained by all three methods are combined. In the same figure the derivatives of mass loss for three heating rates are displayed *vs.* the degree

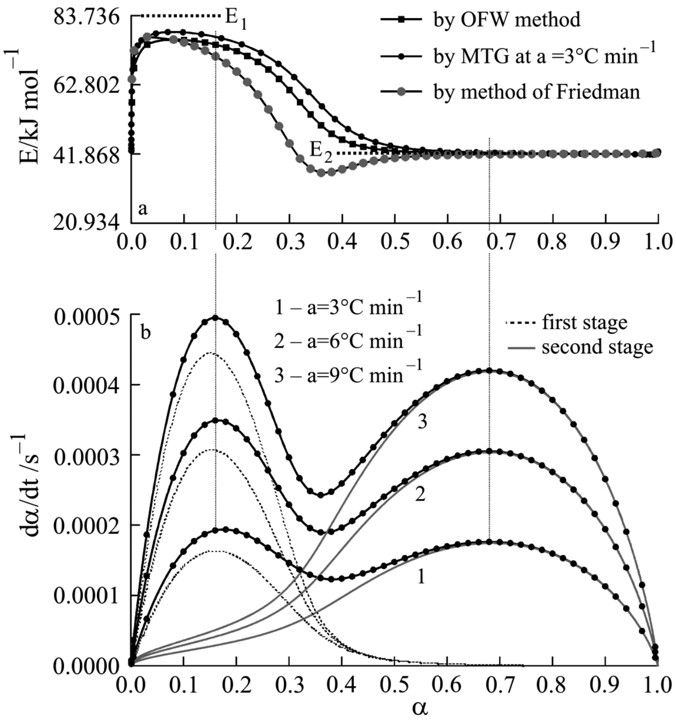

Fig. 7 Confrontation of the formal dependence *E*(α) with the derivatives dα/d*t*. The hypothesis concerning the existence of rate-limiting stages can really be useful for rough evaluation of activation energies for these stages

of conversion (Fig. 7b). Such representation seems valuable, inasmuch as maxima for all derivatives in such coordinates nearly coincide. In confirmation to the intuitive expectations, in a vicinity of peaks' maxima the calculated activation energies approximately have the values corresponding to individual processes. It allows one to use the model-free methods for preliminary evaluations.

Conclusions

Different modifications of the Ozawa–Flynn–Wall method give practically identical results. It is naturally, since all of them result from the common hypothesis about the constancy of the integral of Arrhenius exponential over time at isoconversion levels. This integral, hence, can be called effective travel-time or reduced time of a reaction. The classical approach based on calculation of logarithms of the reduced times seems most convenient. Without additional assumptions it allows one to proceed to the finding of optimal triplets (A, E, f) for one-stage kinetics or for multistage kinetics with independent (parallel) processes. The use of the dependence of activation energy on degree of conversion cannot be corroborated mathematically; nevertheless, such dependence can be formally applied to evaluate the activation energies in systems with parallel processes.

The isoconversion method of Friedman has the stricter mathematical basis; although, for correct evaluation of activation energy for an individual process in a system with multistage kinetics, it requires not only knowledge of partial isoconversion levels but also knowledge of contribution of this process to the overall derivative of mass loss. The method does not require an integration of differential equations; therefore for one-stage kinetics it allows finding an optimal triplet by the simplest method of linear regression.

For systems with conjugated reactions the isoconversion methods become unacceptable, while modulated thermogravimetry allows evaluating activation energies for rate-limiting stages even in this case.

Approximation of perturbations caused by the temperature modulation is almost equivalent to approximation of derivatives of mass loss. However, to fit the perturbations, the derivatives should be multiplied by a scaling parameter being equal to activation energy. Thus, deviations, which are observed between an experimental derivative and theoretical ones due to the difference in shapes of theoretical curves, do not affect significantly the activation energy calculated by different models. The weak sensitivity of calculated activation energies to the form of models used leads to the high predictive force of modulated thermogravimetry.

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