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CALCULATION OF ACTIVATION ENERGIES USING THE SINUSOIDALLY MODULATED TEMPERATURE

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Abstract

Activation energy is calculated from a single curve of a derivative of mass loss perturbed by a sinusoidal modulation of a temperature-time relationship. The method is based on a prediction of a hypothetical derivative of mass loss that corresponds to the absence of this modulation (perturbation). Simple considerations show that the unperturbed derivative coincides with the modulated derivative at inflection points of the modulated temperature–time relationship. The ratio of the perturbed and unperturbed derivatives at the points of time corresponding to maxima and minima of the sinusoidal component of the modulated temperature immediately leads to activation energy. Accuracy of the method grows with decreasing in the amplitude of the modulation.

All illustrations are prepared numerically. It makes possible to objectively test the method and to investigate its errors. Two-stage decomposition kinetics with two independent (parallel) reactions is considered as an example. The kinetic parameters are chosen so that the derivative of mass loss would represent two overlapping peaks. The errors are introduced into the modulated derivative by the random-number generator with the normal distribution. Standard deviation for the random allocation of errors is selected with respect to maximum of the derivative. If the maximum of the derivative is observed within the region from 200 to 600°C and the amplitude of the temperature modulation is equal to 5°C, the error in the derivative 0.5% leads to the error in activation energy being equal to 2–6 kJ mol^{-1}. As the derivative vanishes, the error grows and tends to infinity in the regions of the start and end of decomposition. With the absolute error 0.5% evaluations of activation energy are impossible beyond the region from 5 to 95% of mass loss.

Keywords: activation energy, chemical kinetics, programmed temperature, thermogravimetry

Introduction

Determination of kinetic constants from data of thermogravimetry is usually associated with a selection of a model of decomposition [1–4]. Unfortunately, without cor-

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roboration by other independent methods, kinetic curves are not sufficiently informative to make unambiguous conclusions about a mechanism of decomposition, although correct activation energies in case of one-stage processes can be obtained for different models of decomposition, in other words, without exact knowledge of the mechanism. With increasing accuracy of the formal approximation, a calculated activation energy converges to a correct value [4–6].

The situation becomes much more complicated for multistage decomposition. In this case, in addition to the selection of models, the calculation of activation energies for different stages is problematic. If the number of stages and a manner of their conjugation are assumed incorrectly, realistic values of activation energies are unobtainable. The best indication for the number of stages, which should be assigned in a conjectural model of decomposition, is the number of peaks in derivatives of curves of mass loss. However, one can foresee the most difficult situation, when decomposition progresses as a multistage process, but the derivative curve presents only one peak. If different stages are not separated, a proof that the decomposition under study is really a multistage process, and not a one-stage process, becomes an independent serious problem. To solve this problem it is necessary to use the model-free methods that make possible to calculate activation energy in the absence of a kinetic model of the process at all.

The well known model-free method is based on calculation of the integral of Arrhenius exponential over time (the reduced time) for a set of isoconversional levels on normalized kinetic curves. The isoconversional method was developed in different modifications that differ in a procedure of calculation of this integral [7–13]. One can avoid the calculation of the integral, if using derivatives of a mass change at the isoconversional levels. The slope of the straight line expressing dependence of logarithm of the derivatives *vs.* inverse temperature is proportional to activation energy [14].

The variant of isoconversional method developed by Ozawa [8], Flynn and Wall [9] underlies the standard ASTM E1641 for determination of Arrhenius constants [15]. According to the standard, for implementation of the isoconversional procedure an experimenter has to measure a series of kinetic curves at different heating rates.

Under linear heating an activation energy E is calculated by the isoconversional method approximately as a slope of the straight line plotted in the coordinates $\ln(T_i^2/a_i)$ *vs.* $1/RT_i$, where R is the gas constant, T_i is a temperature of reaching certain isoconversional level a_i is the i^{th} heating rate. In principle, two experiments with two heating rates are sufficient for these calculations; however, an acceptable estimation of E is possible only in the case if these heating rates considerably differ. We note that, in practice, for an accurate statistical manipulation, the experiment should include many measurements at four or more different heating rates [16].

The isoconversional method is only justified for one-stage processes. However, applications of the improved isoconversional method [17, 18] were described for systems with multistage kinetics [19]. Such approach implies a formal dependence of activation energy E upon the degree of conversion α, i.e., $E=E(\alpha)$. This approach contradicts the physical sense of Arrhenius equation. As regards accuracy of such an empiric approximation, it obviously should depend upon the extent of overlap of different stages of decomposition or upon the region of passing of different reactions. If the stages do not overlap each other, $E(\alpha)$ is a stepwise function and the prediction of thermal behavior of a studied material can be done with the same success as in case of one-stage decomposition. Unfortunately, as a general rule, different stages (reactions) of decomposition substantially overlap each other. It is the main source of difficulties in the thermal analysis.

Recently developed high-precision thermobalance (Model 2950, TA Instruments, Inc.) allows experimenters to set the modulated temperature mode [16, 20]. Temperature in the pan of this thermobalance rises by linear law by analogy with the classical technique. However, the linear temperature-time relationship is perturbed by a sinusoid with a controlled amplitude and frequency. The high precision makes possible not only analysis of the integral (smoothed) dependencies but also the deviations caused by the small sinusoidal perturbations. This technique allows a calculation of activation energy by using an only one curve of decomposition and not a series of curves as in the classical method. Moreover, this procedure is model-free, just like the isoconversional method.

Besides the economy of experimental time and the enhancement of accuracy the modulated thermogravimetric analysis (MTGA) has one more important advantage in comparison to the classical isoconversional method. In case of multistage kinetics an overall mass change in a complicated manner reflects mass changes of components participating in different processes. If the processes are not conjugated, the mass loss corresponding to individual processes does not depend on heating rate, and so different ranges of an overall α can really correspond to individual stages. However, for conjugated processes a calculation of isoconversional levels *via* the overall α contradicts physical sense, even if different stages are manifested as separate peaks in the derivatives of mass loss. For example, in case of competing reactions, at different heating rates specimens with equal initial masses can have different final masses, and so temperature dependencies of α at different heating rates can not be confronted at all. For the calculation of activation energy by using MTGA, the degree of conversion is unnecessary. Thus, if the stages of decomposition are well resolved, MTGA gives activation energies for these stages independently of a manner of their conjugation.

Despite the absence of a physical sense of the dependence $E(\alpha)$ in case of multistage kinetics, it can be used for a formal approximation of thermogravimetric data and for finding of rough evaluations of activation energies for different stages. Probably a form of this dependence can provide information concerning a manner of conjugation of stages of decomposition, although, until now, this question was not investigated properly. Efficiency of the calculation of activation energies by using MTGA was demonstrated for the experiments with specimens undergoing both one-stage and multistage decomposition [20]. However, to investigate details of the method it is desirable to repeat similar calculations with kinetic data simulated numerically.

The present paper is devoted to numerical illustration of MTGA. The purpose of the work is to verify the procedure of calculation of activation energies and to elucidate corresponding errors.

Calculation of activation energy

In principle, modulations (perturbations) can be carried out experimentally in different ways [21]. However, controlled sinusoidal modulations have some advantages [16, 20]. According to the technique of TA Instruments, Inc. realized in Model 2950, the modulated temperature is specified in the form

$$T_m(t)=T_o+at+A\sin(2\pi\omega t) \tag{1}$$

where T_o is the initial temperature (as a rule, T_o is approximately equal to the room temperature), a is a heating rate, ω is a frequency (the number of oscillations per one second), A is the amplitude of the modulation.

In our calculations A=5°C, 1/ω=200 s. It is the standard mode of operation for Model 2950.

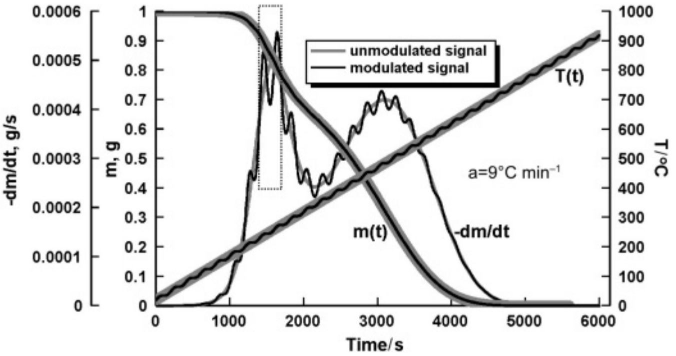

Fig. 1 The kinetic data simulated for artificial system with two independent reactions. The fragment shown in the box is enlarged in Fig. 2

The numerical example shown in Fig. 1 corresponds to decomposition passing through two stages. These obey the differential equations describing second order decomposition kinetics at the first stage and first order decomposition kinetics at the second stage, namely

$$d\alpha_1/dt=k_1(1-\alpha_1)^2\exp[-E_1/RT(t)] \tag{2}$$

$$d\alpha_2/dt=k_2(1-\alpha_2)\exp[-E_2/RT(t)] \tag{3}$$

where α_1, α_2, k_1, k_2 and E_1, E_2 are the degrees of conversion (fractional mass losses), rate constants and activation energies for the first and second stage, respectively, $T(t)$ is a temperature–time relationship that hereinafter will be denoted as $T_m(t)$ and $T_u(t)$ for the modes of operation with the modulation and without the modulation, respectively.

We consider the case where the reactions are not conjugated (independent); therefore the mass change is explicitly expressed *via* α_1 and α_2 as follows:

$$m(t)=w_1(1-\alpha_1)+w_2(1-\alpha_2)$$

$$m_0=w_1+w_2,\ t=0$$

where w_1 and w_2 are the limits of mass losses for the first and second reaction, respectively, m_0 is an initial mass. Note that in the modern thermobalances an actual initial mass of a sample can be equal to 1–20 milligrams. By convention, the normalized initial mass, for convenience, can be expressed as 1 g. This will be implied below in the figures.

The constants used in the calculations are listed in Table 1. Differential Eqs (2) and (3) were solved numerically by using Runge–Kutta method of fifth order providing six correct decimal digits [22].

Table 1 The constants for simulated two-stage decomposition

Stage	E/kJ mol^{-1}	k/s^{-1}	w_1/g	w_2/g	Model
First	83.736	$1\cdot10^6$	0.3	0.7	second order kinetics
Second	41.868	1			first order kinetics

Maxima and minima of $T_m(t)$ are found from the condition

$$dT_m(t)/dt=a+2\pi\omega A\cos(2\pi\omega t)=0 \tag{4}$$

If $a\geq2\pi\omega A$, the function $T_m(t)$ becomes monotonous. In our example the monotony is reached at $a\geq9.425$°C min^{-1}. Data shown in Fig. 1 were simulated with $a=9$°C min^{-1}. This heating rate is very close to the critical value (Figs 1, 2d and 2e); however even with a monotonous function $T_m(t)$ the modulated derivative presents the oscillating function (Fig. 1).

The period 200 s does not restrict MTGA to investigation of only slow processes, inasmuch as one can arbitrarily decelerate decomposition by decreasing heating rate. The amplitude 5°C seems to be small; however, it excites considerable oscillations in the derivative of mass loss. Typical noise in the derivatives of mass loss in measurements with older thermobalances probably most often arose because of unmonitored changes of temperature. Usually this noise should be eliminated by methods of smoothing of derivatives. However, in contrast to the standard TG, in MTGA the oscillations of the derivatives are the main source of kinetic information.

For the sake of simplicity let us consider MTGA by addressing the modulation to a one-stage decomposition.

The difference between derivatives corresponding to the modulated (A>0) and unmodulated (A=0) temperature is expressed as follows:

$$F(t)=-[(dm/dt)_m-(dm/dt)_u]=kf(\alpha_m)\exp[-E/RT_m(t)]-kf(\alpha_u)\exp[-E/RT_u(t)] \tag{5}$$

where α is the degree of conversion, $f(\alpha)$ is a function corresponding to certain mechanism of decomposition; the indices 'm' and 'u' relate to the cases of the modulated and unmodulated temperature-time relationship, respectively.

If the frequency of the modulation ω is sufficiently high and the amplitude of modulations A is sufficiently small, the modulated and unmodulated mass changes

(Fig. 1) differ insignificantly: $m_m(t)\approx m_u(t)$, $\alpha_m(t)\approx\alpha_u(t)$. Hence, the main contribution to the difference between two terms in Eq. (5) is caused on account of the difference in the exponentials. Therefore, one can represent Eq. (5) in the following approximate form:

$$F(t)\approx kf(\alpha_u)\{\exp[-E/RT_m(t)]-\exp[-E/RT_u(t)]\} \qquad (6)$$

One can see that, according to the approximation in Eq. (6), perturbed (modulated) and unperturbed (unmodulated) derivatives coincide in points of intersection of modulated and unmodulated temperatures $T_m(t)=T_u(t)$ or at the points of time corresponding to the equality $t_j=j(2\omega)^{-1}$, where j=0, 1, 2… Unfortunately, because of inaccuracy of Eq. (6) the zeros of the function $F(t)$ are somewhat shifted. However, their displacements with respect to zeros of the sinusoid are sufficiently small (Fig. 2b). Thus, having form the experiment two functions $(dm/dt)_m$ and $T_m(t)$ one can predict the function $(dm/dt)_u$ that with good accuracy is equal to $(dm/dt)_m$ at the inflection points of $T_m(t)$.

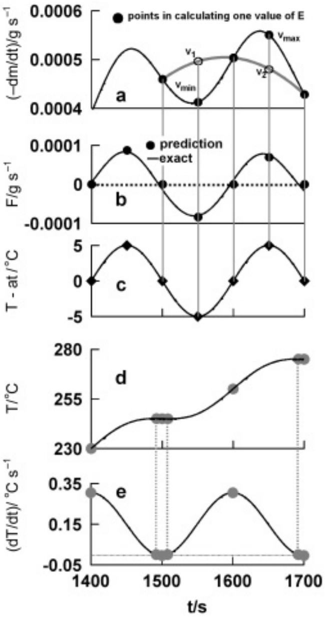

Fig. 2 The connection of the perturbation of the derivative of mass loss with features of the temperature-time relationship: a – the derivative of mass loss, b – the difference between the modulated and unmodulated derivative, c – the modulation of temperature $A\sin(2\pi\omega t)$, d – the function $T(t)$ under measure, e – the derivative of the temperature modulation added to heating rate. The shown fragment corresponds to the box in Fig. 1

In a real experiment the temperature-time relationship $T_m(t)$ is measured as some tabulated function. It should be numerically approximated and then differentiated. At the stage of differentiation one should envisage smoothing to exclude random noise. The differentiation leads to the function expressed by Eq. (4) (Fig. 2e). Then the inflection points of $T_m(t)$ are calculated numerically by finding the maxima and minima of $T_m(t)/dt$. Approximation of $T_m(t)$ in the form of Eq. (1) allows an extraction of the sinusoidal component (Fig. 2c). Interpolation of the points on the curve $(dm/dt)_m$ corresponding to the inflection points of $T_m(t)$ allows to plot the function $(dm/dt)_u$. In particular, the example of quadratic interpolation is shown in Fig. 2a. Thus, it is possible to determine $F(t)$ (points in Fig. 2b) by using only simple numerical procedures. Thereupon, the function $F(t)$ can be considered as some new experimental information for determination of the kinetic constants.

Note that all calculations for finding of $F(t)$ can be carried out both for one-stage and for multistage kinetics. In a future work we shall consider the method of determination of constants w_1, k_1, E_1 and w_2, k_2, E_2 for two-stage kinetics by using $F(t)$ as original information. Here we consider only formulae for activation energy that, unfortunately, are accurate only for a one-stage process.

According to the assumption $\alpha_m(t)\approx\alpha_u(t)$, the ratio of derivatives of mass change for modulated and unmodulated temperature is expressed in the form

$$(dm/dt)_m/(dm/dt)_u=\exp[-E/RT_m(t)]/\exp[-E/RT_u(t)] \tag{7}$$

Having determined the values of the derivatives at the points corresponding to minima and maxima for the periodic component of temperature (Fig. 2a), from Eq. (7) we obtain two values of activation energy for each period, namely

$$v_{\min}/v_1=\exp\{-(\breve{E}/R)[1/(T_1-A)-1/T_1]\} \tag{8}$$

$$\breve{E}=[RT_1(T_1-A)/A]\ln(v_1/v_{\min}) \tag{9}$$

$$v_{\max}/v_2=\exp\{-(\hat{E}/R)[1/(T_2+A)-1/T_2]\} \tag{10}$$

$$\hat{E}=[RT_2(T_2+A)/A]\ln(v_{\max}/v_2) \tag{11}$$

where $v_{\min}$, v_1 and $v_{\max}$, v_2 are the values of the modulated and unmodulated derivative at the points of the minima and maxima of the periodic component of $T_m(t)$; T_1 and T_2 are the values of unmodulated temperature at these points. To enhance accuracy it is reasonable to use averaging

$$E=(1/2)(\breve{E}+\hat{E}) \tag{12}$$

Let us assume that $A<<T_1$ and $A<<T_2$. Having divided Eq. (10) by Eq. (8) we obtain

$$v_{\max}/v_{\min}=(v_2/v_1)\exp\{(E/R)[A(1/T_2^2+1/T_1^2)]\}$$

Assuming that within a period the decomposition rate changes mainly due to the modulation, whereas $v_2/v_1\approx 1$, and by using the approximation $1/T_2^2+1/T_1^2\approx 2/[(T_1+T_2)/2]^2$, we come to the following formula:

$$E=(R\overline{T}^{\,2}/2A)\ln(v_{\max}/v_{\min}) \tag{13}$$

where $\overline{T}=(T_1+T_2)/2$ is the temperature at the point of the intersection of $T_m(t)$ and $T_u(t)$.

Formula (13) was used earlier for the calculation of activation energies by means of MTGA [16, 20]. However, this formula is less accurate than Eqs (9), (11) and (12). Moreover, the only assumption that predetermines correctness of Eqs (9), (11) and (12) is the smallness of an amplitude of the modulation. In addition to this assumption, Eq. (13) implies the smallness of a period of the modulation.

Evaluation of errors

In the thermogravimetric experiments the source of main errors is usually hidden in the measurements of mass. Errors in a derivative of mass loss are the consequence of errors in the function $m(t)$.

Direct differentiation of the random function $m(t)$ is impossible, and so the numerical differentiation of $m(t)$ should be regularized, namely, the obtained derivative $\mathrm{d}m(t)/\mathrm{d}t$ is always artificially smoothed. The regularization (smoothing) is equivalent to a cut-off of the random high-frequency noise in a derivative. Such smoothing can be implemented by various numerical methods. However, a filtration of random noise in the modulated derivative $(\mathrm{d}m/\mathrm{d}t)_m$ entails serious difficulties, since a digital filter should eliminate noise with frequencies higher than ω, but it should not influence the modulation with carrier frequency ω. Perhaps, to calculate both the perturbed derivative $(\mathrm{d}m/\mathrm{d}t)_m$ and the perturbation $F(t)$ with good accuracy, the signal should be passed through two filters. The first one should delete noise with frequency higher ω; the result will be the function $(\mathrm{d}m/\mathrm{d}t)_m$. The second filter should delete both the oscillations caused by the temperature modulation and random noise with frequencies being commensurable and higher to ω. The result will be the function $(\mathrm{d}m/\mathrm{d}t)_u$. Than one can calculate the difference $F(t)=-[(\mathrm{d}m/\mathrm{d}t)_m-(\mathrm{d}m/\mathrm{d}t)_u]$.

In the standard software of Model 2950 a signal is handled by using the technique of the discrete Fourier transformation. Unfortunately, details of this procedure were not described in the articles [16, 20]. From general considerations, the methods of a digital filtration can hardly allow a reliable elimination of random noise with frequency $\cong\omega$ to extract the perturbation $F(t)$ with good accuracy. Perhaps, a properly selected method for approximation of the function $(\mathrm{d}m/\mathrm{d}t)_m$ could give better results. However, a solution of this serious problem remains outside the present article. We should keep in mind only that the derivative $(\mathrm{d}m/\mathrm{d}t)_m$ always contains noise, and so the calculations of activation energy by Eqs (8)–(12) give an appreciable error.

Let us assume that the functions $(\mathrm{d}m/\mathrm{d}t)_m$ and $(\mathrm{d}m/\mathrm{d}t)_u$ were measured in different experiments in which the derivative $(\mathrm{d}m/\mathrm{d}t)_u$ was measured exactly, whereas the derivative $(\mathrm{d}m/\mathrm{d}t)_m$ contains noise, namely

$$(\mathrm{d}m/\mathrm{d}t)_m=(\mathrm{d}m/\mathrm{d}t)_m^{(i)}+\xi(t) \tag{14}$$

where $(\mathrm{d}m/\mathrm{d}t)_m^{(i)}$ is a derivative that could be measured in an imaginary ideal experiment without errors, $\xi(t)$ is noise included in the real derivative.

If the amplitude A is small, we can rewrite Eq. (6) in the form

$$F(t)\approx -E(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}\{[T_{\mathrm{m}}(t)-T_{\mathrm{u}}(t)]/RT_{\mathrm{u}}^{2}(t)\} \tag{15}$$

One can see that the perturbation $F(t)$ and the unperturbed derivative of mass loss $(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}$ are connected by the scale transformation in which activation energy is the scale multiplier. This fact, in particular, can be useful for designing a technique of smoothing of the modulations and suppression of random noise.

Extraction of activation energy from Eq. (15) leads to the following equation:

$$E\approx -RT_{\mathrm{u}}^{2}(t)F(t)/\{[T_{\mathrm{m}}(t)-T_{\mathrm{u}}(t)](\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}\} \tag{16}$$

All functions in the right-hand part of Eq. (16) are calculated from experimental information.

The absolute error ΔE in activation energy due to noise in the signal is equal to

$$\Delta E\approx -(-1)^{j}RT_{\mathrm{u}}^{2}(t_{\mathrm{j}})\xi(t_{\mathrm{j}})/[A(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}] \tag{17}$$

The relative error is defined by the equation

$$\Delta E/E\approx \xi(t)/F(t) \tag{18}$$

If $(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}\rightarrow 0$ and, consequently, $F(t)\rightarrow 0$, the denominators of the expressions in the right-hand parts of Eqs (17) and (18) tend to zero, hence, both absolute and relative error tends to infinity. Therefore, a calculation of activation energy is impossible in the flat parts of the curve $m(t)$.

At the points of time, where $T_{\mathrm{m}}(t)=T_{\mathrm{u}}(t)$, the denominators also equal zero. Therefore, it is rational to carry out the calculations at the points of extrema in the modulated derivative in order to provide the maximal swings of the decomposition rate and, hence, to increase a ratio of a useful signal with respect to random noise. At these points Eq. (17) has the form

$$\Delta E\approx -RT_{\mathrm{u}}^{2}(t_{\mathrm{j}})\xi(t_{\mathrm{j}})/[A(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}]$$

where $t_{\mathrm{j}}=(1/2+j)/2\omega$; $j=0, 1, 2\dots$. Closely disposed points in the random function $\xi(t)$ are correlated because this function corresponds to a smoothed derivative and is smoothed as well; however, the points situated at the distances $1/(2\omega)$ are weakly correlated. We can assume that the values $\xi_{\mathrm{j}}=\xi(t_{\mathrm{j}})$ are random numbers with the normal (Gaussian) distribution. This implies an even absolute error within entire range of measurement of mass loss. Such an assumption seems to be most acceptable for fast a priori estimations, according to which the error in activation energy can be expressed as

$$\Delta E\approx -(-1)^{j}RT_{\mathrm{u}}^{2}(t_{\mathrm{j}})\overline{\sigma}\,\Xi_{\mathrm{j}}/[A(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}]$$

where $\overline{\sigma}$ is a standard deviation, Ξ_{j} are random numbers with the normal distribution and the unit variance. The numbers Ξ_{j} can be set in a computer by the random-number generator [22].

It is convenient to evaluate the absolute error with respect to the maximum of the derivative, namely, $\bar{\sigma}=\sigma\ \max[-(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}]\approx\sigma\ \max[-(\mathrm{d}m/\mathrm{d}t)_{\mathrm{m}}]$ where $\sigma\times100\%$ is percent tage of error in the derivative at its maximum. Then an average scattering of activation energy at the maximum of the derivative is

$$\Delta E\cong\pm RT_{\mathrm{u}}^{2}(t_{\mathrm{j}})\sigma/A$$

If the maximum of the derivative is observed inside the region from 200 to 600°C, with A=5°C and σ=0.005, we have $\Delta E\cong\pm2$–6 kJ mol^{-1}. As the derivative vanishes, this error grows proportionally to the ratio $\max[-(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}]/-(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}$.

We considered the situation where the derivative $(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}$ is known exactly. In our calculations this derivative is searched from the derivative $(\mathrm{d}m/\mathrm{d}t)_{\mathrm{m}}$ and, consequently, contains random noise $\xi_1(t)$. However, for significant fragments of the derivative, when we can assume $-(\mathrm{d}m/\mathrm{d}t)_{\mathrm{u}}>>|\xi_1(t)|$, Eq. (17) remains valid, we should only replace $\xi(t)$ by $\xi(t)-\xi_1(t)$.

By using Eqs (9) and (11) one can make the following simplest estimation of the confidence interval for activation energy:

$$\begin{aligned}E\pm\Delta E\cong\{&[RT_1(T_1-A)/A]\ln[(v_1\pm\bar{\sigma})/(v_{\min}-(\pm)\bar{\sigma})]+\\&+[RT_2(T_2+A)/A]\ln(v_{\max}\pm\bar{\sigma})/(v_2-(\pm)\bar{\sigma})\}/2\end{aligned}\tag{19}$$

Results and discussion

In Fig. 3 the difference between the modulated and unmodulated derivatives is plotted at different heating rates. One can see that the prediction resulting from the interpolation shown in Fig. 2a becomes worse with increasing in heating rate. The real experiment contains restrictions both on amplitude and on period of the modulation. If these restrictions are exhausted, the remaining experimental parameter, which can govern accuracy, is the heating rate. To reach good accuracy one should select a heating rate so as to provide at least 10–15 periods of modulation for each stage of decomposition.

Numerical mathematics can give an additional reserve of accuracy. Probably the quadratic interpolation is not the best variant for the prediction of unperturbed derivatives. The known digital filters [23] can probably provide a better resolution of modulated derivatives into the periodic and systematic component. Variants of a theoretical approximation of $F(t)$ could be yet better.

In Fig. 4 the calculated activation energies are shown depending on mass loss under decomposition at three heating rates. Each curve in Fig. 4 was plotted point by point by using the procedure described in the previous section. High accuracy of evaluation of correct activation energy for the second stage (Fig. 4b) proves legitimacy of the method for one-stage processes. Indeed, over wide range of mass loss the second stage is controlled by the rate of the second reaction with smaller activation energy. That is why within the interval $0.6<m_0-m<1$ the calculated activation energy (Fig. 4b) is constant. At the smallest heating rate 3°C min^{-1} it corresponds to the correct value E_2=41.868 kJ mol^{-1} with accuracy ≅99%.

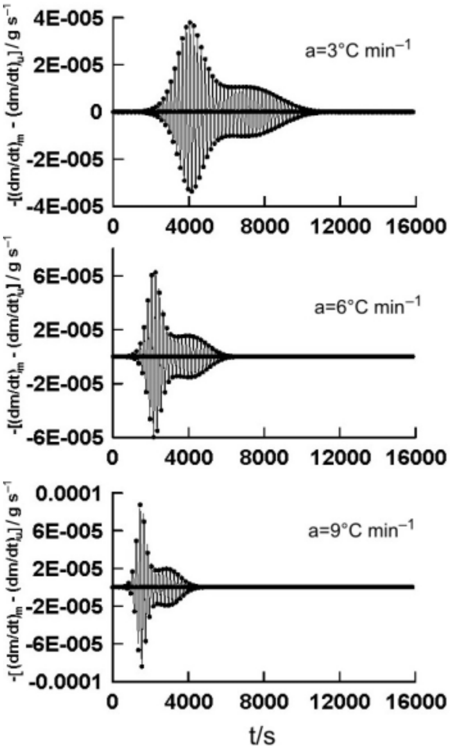

Fig. 3 The perturbations of the derivatives of mass loss calculated as the difference between the modulated and unmodulated derivatives. The points result from the procedure shown in Fig. 2a

The assumption concerning constancy in a rate of decomposition within each period of modulation, which was assumed for the derivation of Eq. (13), leads to the appreciable errors (compare Fig. 4a and Fig. 4b). In other words, when using the interpolation shown in Fig. 2a, accuracy is improved. However, in the case of multistage decomposition this technique is imperfect, since an interpretation of $E(m)$ for multistage kinetics encounters serious difficulties.

Note that despite the apparent domination of the first reaction (Fig. 1) at the first stage of decomposition, the calculated activation energy does not reach the magnitude of E_1=83.736 kJ mol^{-1}, and at the limit $m_0-m\to 0$ the calculated activation energy tends to the value corresponding to the second reaction E_2=41.868 kJ mol^{-1}. This observation can be readily explained.

At a small degree of decomposition we have

$$-\mathrm{d}m/\mathrm{d}t=w_1k_1\exp(-E_1/RT)+w_2k_2\exp(-E_2/RT)$$

Two terms become equal at the temperature expressed by the following formula:

$$T_a=(E_1-E_2)/[R\ln(w_1k_1/w_2k_2)]$$

In our example T_a=115°C. If $T<T_a$ the second reaction prevails. This situation takes place within the region of very small mass loss (Fig. 4). Nevertheless, accurate computations allow its detection.

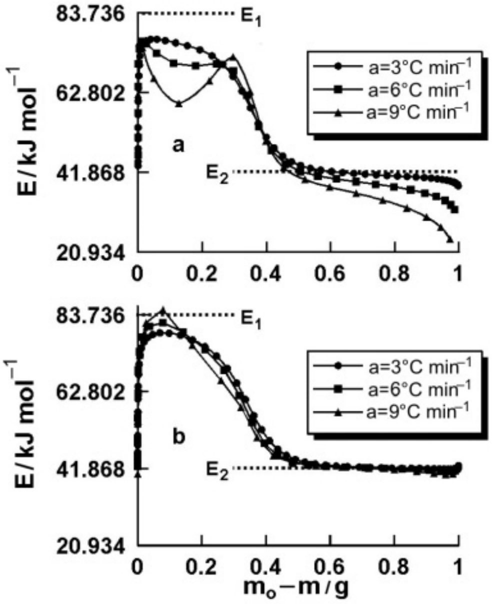

Fig. 4 Activation energy calculated as a formal function of mass loss a – by using the technique of TA Instruments, Inc. [16, 20] and b – by using the procedure shown in Fig. 2a

According to Fig. 4b, the dependence $E(m)$ has a reproducible form at different heating rates. This fact to some extent justifies its use for empirical predictions. However, it is possible only for systems with independent reactions like the system under consideration. A competition of reactions undoubtedly will hinder such predictions. Hence, the next step of the theory of MTGA should be directed to approximation of the kinetic data by using models of multistage kinetics.

Data shown in Fig. 4 were generated with the accurate derivative $(\mathrm{d}m/\mathrm{d}t)_m$, as if we had a ‘fantastical’ device allowing its measurement with accuracy 99.999%. The results shown in Fig. 5 are related to the case where the modulated derivative is perturbed at the reference points by the random number generator Ξ_j with the normal distribution. The standard deviation $\overline{\sigma}$ was calculated with respect to the maximum of the modulated derivative. One can see that the change of the chance error in E occurs in full accordance with the predictions made in the previous section.

The confidence interval (see the gray bands in Fig. 5) was calculated by Eq. (19). It is seen that the latter equation gives sufficiently reliable estimations. With the standard deviation ≅0.5% a significant calculation of activation energy is possible only within the interval of mass loss from 5 to 95%. At the beginning and at the end of decomposition the calculations become uncertain due to errors.

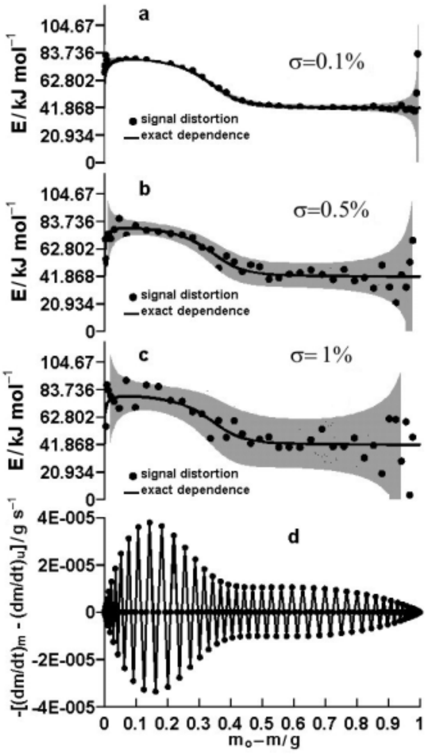

Fig. 5 The influence of chance errors a–c on the results of calculation of activation energy and the corresponding curve d of the perturbation of the derivative of mass loss calculated at heating rate 3°C min^{-1}

The deviation ≅0.5–1% probably is most close to the real resources of Model 2950. Additional reserve of accuracy could give a smoothing of $E(m)$. However, a maximally accurate experimental determination of the difference $F(T)$ between perturbed and unperturbed derivatives should forego manipulations with $E(m)$. Naturally, all possible methods of the signal processing should be examined and substantiated by using a numerical simulation.

Conclusions

The implemented calculations show that MTGA is more informative in comparison with the traditional technique. In particular, the calculation of activation energy, which requires a series of kinetic curves in the isoconversional method, can be carried out by using an only one curve. Moreover, the activation energies for different stages of decomposition can be evaluated in MTGA, even if these stages are conjugated.

Illustrations in this paper are made relative to the numerical example. This allows a maximally strict and objective substantiation of principles of MTGA. Nevertheless, practical realization of the method necessitates an additional detailed analysis of experimental errors and their influence on accuracy of final results.

The main idea consists in a recalculation of the modulated (perturbed) derivatives of mass loss into unmodulated (unperturbed) derivatives. Perhaps, the discrete Fourier transformation envisaged at present for this purpose in standard software is not the best technique for such recalculations. In any case, experimental derivatives should be preliminarily smoothed. The best result could be obtained, if smoothing would include a priori information about the kinetic effects caused by the temperature modulation.

Activation energies for multistage kinetics cannot be determined sufficiently accurately by means of the model-free procedure. However, their evaluation values could be useful for subsequent MTGA of decomposition by using complicated models of multistage kinetics.

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References

1 J. Šesták, Thermophysical Properties of Solids, Elsevier, Amsterdam 1984.
2 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 27 (1983) 89.
3 A. V. Nikolaev, V. A. Logvimenko and V. M. Gorbachev J. Thermal Anal., 6 (1974) 473.
4 V. Mamleev, S. Bourbigot, M. Le Bras, S. Duquesne and J. Šesták, Phys. Chem. Chem. Phys., 2 (2000) 4708.
5 V. Mamleev, S. Bourbigot, M. Le Bras, S. Duquesne and J. Šesták, Phys. Chem. Chem. Phys., 2 (2000) 4796.
6 V. Mamleev, S. Bourbigot, M. Le Bras, S. Duquesne and J. Šesták, Euroasian Chemico Technological Journal, 2 (2000) 201.
7 H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
8 T. Ozawa, Bull. Chem. Soc. Japan, 38 (1965) 1881.
9 J. H. Flynn and L. A. Wall, Polym. Lett., 4 (1966) 323.
10 D. Price, D. Dollimore, N. S. Fatemi and R. Whitehead, Thermochim. Acta, 42 (1980) 323.
11 C. H. Li, AIChE J., 31 (1985) 1036.
12 R. K. Agrawal, J. Therm. Anal., 32 (1987) 149.
13 A. A. Zuru, R. Whitehead and D. L. Griffiths, Thermochim. Acta, 164 (1990) 285.
14 J. Opfermann, F. Giblin, J. Mayer and E. Kaisersberger, American Laboratory, Febr., 1995, p. 34.
15 'Standard Test Method for Decomposition Kinetics by Thermogravimetry' ASTM Test method E1641. ASTM Book of Standards 14.02, 1042–1046, American Society for Testing and Materials, 1994.
16 R. Blaine, American Laboratory, Jan., 1998, p. 21.
17 S. Vyazovkin, J. Thermal Anal., 49 (1997) 1493.
18 S. Vyazovkin, J. Comput. Chem., 18 (1997) 393.

19 S. Vyazovkin, Thermochim. Acta, 355 (2000) 155.
20 R. L. Blaine and B. K. Hahn, J. Thermal Anal., 54 (1998) 695.
21 J. H. Flynn, Thermal Analysis, Vol. 2, R. F. Schwenker and P. D. Garn, Eds, Plenum Press, New York, 1969, p. 1111.
22 G. F. Forsite, M. A. Malcolm and C. B. Moler, Computer Methods for Mathematical Computations, New Jersey: Englewood Cliffs, Prentice-Hall 1977.
23 R. K. Otnes and L. Enochson, Applied time series analysis, New York, Wiley-Interscience Publication, Wiley&Sons, 1978