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# THE EFFECTS OF IMPERFECT TEMPERATURE PROGRAMMING ON THE KINETIC EVALUATION OF THERMOANALYTICAL CURVES. PART 2. CONCAVE AND CONVEX CURVATURES ON THE ACTUAL TEMPERATURE–TIME FUNCTIONS

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## ABSTRACT

Estimation of the kinetic parameters is examined when a linear temperature program is assumed in the calculations while, due to experimental shortcomings, the actual temperature inside the sample is a slightly curved function of the time. The factors responsible for the change of the kinetic parameters are pointed out and the signs of the errors are discussed.

## NOTATION

| | |
|---|---|
| $a$ | heating rate |
| $A$ | pre-exponential factor |
| $c$, $c'$ | constants |
| $E$ | activation energy (molar) |
| $n$ | formal reaction order |
| $R$ | gas constant |
| $t$ | time |
| $T$ | temperature |
| $x$ | reacted (or converted) mole fraction |
| $\langle\ \rangle$ | indicates average |

### *Subscripted symbols*

| | |
|---|---|
| $T_{act}$, $T_{meas}$, $T_{prog}$ | the actual, measured and prescribed temperature of the sample |
| $x_p$, $t_p$, $T_p$ | data belonging to the maximum of $dx/dt$ |

### *Functions*

| | |
|---|---|
| $f(x)$ | describes the dependence of $dx/dt$ on $x$ |
| $g(x)$ | the integral of $1/f(x)$ |

$q(E/RT)$ a function approximately equal to $(E/RT+1)/(E/RT+3)$

## INTRODUCTION

In thermal analysis, at least three different quantities should be distinguished in connection with the temperature of the sample: the actual temperature inside the sample $T_{act}$, which may vary from point to point; the measured temperature, $T_{meas}$; and the prescribed temperature, $T_{prog}$. Unfortunately, these temperatures are not always equivalent. A typical example: in the case of inappropriate experimental conditions (sample size, heating rate, etc.), the thermal effects of the studied reactions may cause a deviation between the measured and the actual temperature. The magnitude of this deviation is roughly proportional, among others, to the reaction rate. In this way, slightly curved actual temperature–time functions can develop. Since the reaction rate–time function is convex in the central part of the thermoanalytical curves (where the reaction rate has higher values), it can be supposed that the really significant part of the $T_{act}-T_{meas}$ difference is a convex function of the time at exothermal reactions and a concave one at endothermal reactions. Thus it may be interesting to study how convex and concave curvatures influence the kinetic evaluation. In this paper, the direction of the changes of the kinetic parameters will be discussed and the factors responsible for the errors will be pointed out. Though special emphasis will be given to the concave and convex $T_{act}(t)$ functions, the outlined considerations may also be useful in other cases. The magnitude of the errors of the kinetic parameters will be discussed in a subsequent paper [1], where upper limits will be deduced for the errors caused by the alteration of the actual temperature from the linear.

## ESTIMATION OF THE ACTIVATION ENERGY

Let $x$ be the reacted (or converted) mole fraction and let us suppose that the kinetics of the examined process can be described by

$$dx/dt = Ae^{-E/RT}f(x) \tag{1}$$

where $f(x)$ is a continuous positive function in the domain $0<x<1$. In this section, the estimation of $E$ will be discussed when the function $f(x)$ is known and does not contain unknown parameters. As pointed out earlier [2], two types of errors may arise here in connection with the imperfect temperature programming:

(i) the temperature data introduced into the equations are not equal to the actual temperature inside the sample;

(ii) the equations themselves contain some systematic errors if their deduction involves the integration of eqn. (1) at linear temperature–time functions. Errors of type (i) have already been discussed [2,3], thus only the second type of errors will be treated here.

At increasing $T(t)$ functions, rearrangement and integration of eqn. (2) give

$$g(x) = A\int e^{-E/RT} dt = A\int e^{-E/RT} (dT/dt)^{-1} dT \tag{2}$$

Thus the equations used in the kinetic evaluations, e.g. the theoretical $x(T)$ or $(dx/dt)(T)$ functions, should be derived from eqn. (2). In practice, however, equations deduced for linear heating programs are usually applied, which means that eqn. (2) is formally replaced by

$$g(x) = A_{\text{appar}} a^{-1} \int e^{-E_{\text{appar}}/RT} dT \tag{3}$$

where $A_{\text{appar}}$ and $E_{\text{appar}}$ are apparent values of $A$ and $E$ respectively, and $a$ is the nominal heating rate. Equation (3) is obviously exact at linear $T(t)$ functions when $dT/dt = a$. It is interesting to note that eqn. (3) gives an exact description of the examined processes in every case when

$$dT/dt = c e^{c'/T} \tag{4}$$

where $c$ and $c'$ are constants describing the dependence of the heating rate on temperature. If eqn. (4) is valid or approximates formally the change of the heating rate during the reaction, then a comparison of eqns. (2) and (3) gives

$$E_{\text{appar}} = E + c'/R \tag{5}$$

and

$$A_{\text{appar}} = Aa/c \tag{6}$$

Note that the linear temperature program is a special case of eqn. (4) (then $c' = 0$ and $c = a$). Since eqn. (3) is valid if, and only if, eqn. (4) is valid, the application of eqn. (3) at a non-linear $T(t)$ is equivalent to the formal approximation of the actual heating rate by eqn. (4). If eqn. (4) cannot give a good approximation for the actual heating rate, then probably eqn. (3) will give only a poor description of the experimental data.

Now let us examine briefly the meaning of the coefficient $c'$ when the actual heating rate is formally approximated by eqn. (4). Developing $e^{c'/T}$ into a Taylor series, it can immediately be seen that $c'$ is correlated with the slope of the $dT/dt$ vs. $1/T$ plot. If $1/T$ is also expanded into a Taylor series, it can be seen that $c'$ is roughly proportional to the negative of the slope of function $dT(t)/dt$. [Note that only increasing $T(t)$ functions are treated here.] At concave $T(t)$ functions, when $d^2T/dt^2 > 0$, $dT/dt$ is an increasing function of $t$ and $c'$ is negative. In a similar way, $c'$ is positive at convex $T(t)$

functions. Thus a concave curvature of $T(t)$ decreases the apparent value of $E$ while a convex curvature increases it.

## THE ASYMMETRY OF CURVES $x(t)$ AND $\mathrm{d}x(t)/\mathrm{d}t$

As is well known [4–9], the asymmetry of curves $x(t)$ or $\mathrm{d}x(t)/\mathrm{d}t$ is strongly correlated with the formal reaction order, $n$. If $\mathrm{f}(x)$ has a form other than $(1-x)^n$, the asymmetry can obviously be correlated with other adjustable parameters of $\mathrm{f}(x)$ [3]. In this section we shall examine how the curvature of the actual $T(t)$ function changes the asymmetry of curves $x(t)$ or $\mathrm{d}x(t)/\mathrm{d}t$. In other words, we shall compare the asymmetry at linear and non-linear temperature programs. At linear temperature programs, the asymmetry slightly depends on the value of $E/RT_\mathrm{p}$, where $T_\mathrm{p}$ is the temperature of the peak maximum. For this reason, we have to suppose that the values of $T_\mathrm{p}$ are approximately equal at the compared curves. (Note that a difference of $\pm 10\%$ in $T_\mathrm{p}$ does not change the degree of asymmetry significantly [3], thus the term "approximately equal" here may also include differences of 50–100 K.)

The characterization of the asymmetry will be based on the value of the reacted mole fraction at the peak maximum, $x_\mathrm{p}$ (at symmetrical curves, $x_\mathrm{p}=0.5$). Of course, there is an endless number of ways to characterize the degree of asymmetry. The only reason for choosing $x_\mathrm{p}$ is the relative simplicity of the corresponding mathematical deductions [3,5–10].

Let us start the deductions by writing the condition of the maximum of $\mathrm{d}x/\mathrm{d}t$. Differentiatng eqn. (1) and rendering it equal to zero gives

$$\mathrm{f}(x_\mathrm{p})\frac{\mathrm{d}T}{\mathrm{d}t}(t_\mathrm{p})E/RT_\mathrm{p}^2+\frac{\mathrm{d}f}{\mathrm{d}x}(x_\mathrm{p})\frac{\mathrm{d}x}{\mathrm{d}t}(t_\mathrm{p})=0 \tag{7}$$

where subscript p refers to the maximum of $\mathrm{d}x/\mathrm{d}t$. The equation has been divided by $A\mathrm{e}^{-E/RT_\mathrm{p}}$ which appeared in both terms.

As in the previous section, the integral of eqn. (1) will be written in the form

$$\mathrm{g}(x_\mathrm{p})=A\int_0^{t_\mathrm{p}}\mathrm{e}^{-E/RT}\mathrm{d}t=A\int_{T_0}^{T_\mathrm{p}}\mathrm{e}^{-E/RT}(\mathrm{d}t/\mathrm{d}T)\mathrm{d}T \tag{8}$$

where $T_0$ is the starting point of the given temperature program. To obtain a formal relationship between the right-hand side and the integrals arising at linear heating programs,let us define a weighted average of $\mathrm{d}t/\mathrm{d}T$ by

$$\langle\mathrm{d}t/\mathrm{d}T\rangle=\int_{T_0}^{T_\mathrm{p}}\mathrm{e}^{-E/RT}(\mathrm{d}t/\mathrm{d}T)\mathrm{d}T\Big/\int_{T_0}^{T_\mathrm{p}}\mathrm{e}^{-E/RT}\mathrm{d}T \tag{9}$$

In this average, $\mathrm{e}^{-E/RT}$ is a weight function. The numerator is the integral of the right-hand side of eqn. (8). Using this definition, eqn. (8) can formally be written as

$$g(x_p) = A\langle dt/dT\rangle \int_{T_0}^{T_p} e^{-E/RT} dT \tag{10}$$

As is well known, the integral of $e^{-E/RT}$ by $T$ can be written in the form

$$\int_{T_0}^{T_p} e^{-E/RT} dT \cong \int_{0}^{T_p} e^{-E/RT} dT =$$

$$= E^{-1} RT_p^2 e^{-E/RT_p} q(E/RT_p) \tag{11}$$

where $q(E/RT_p)$ is a slowly changing (nearly constant) function [4,11,12]. (For a critical review on function q and its approximations see, for example, ref. 12.)

Using eqns. (1), (10) and (11) $dx(t_p)/dt$ can be expressed in the form

$$\frac{dx}{dt}(t_p) = \frac{E}{RT_p^2} \frac{g(x_p)f(x_p)}{\langle dt/dT\rangle q(E/RT_p)} \tag{12}$$

Introducing this expression into eqn. (7), a relationship is obtained between $x_p$ and the characteristics of the temperature program

$$-\frac{df}{dx}(x_p)g(x_p) = q(E/RT_p)\langle dt/dT\rangle \frac{dT}{dt}(t_p) \tag{13}$$

Equation (13) will now be examined. Let us start the analysis at the right-hand side. According to the mean value theorem of the integral calculus [13], there is a $t'$ point in the interval $0 < t' < t_p$ where $\langle dt/dT\rangle$ is equal to $dt(t')/dT$. Thus

$$\left.\begin{array}{ll} \langle dt/dT\rangle \frac{dT}{dt}(t_p) > 1 & \text{if } dT/dt \text{ is increasing} \\ \langle dt/dT\rangle \frac{dT}{dt} t_p = 1 & \text{if } dT/dt \text{ is constant} \\ \text{and} & \\ \langle dt/dT\rangle \frac{dT}{dt}(t_p) < 1 & \text{if } dT/dt \text{ is decreasing} \end{array}\right\} \tag{14}$$

in the interval $0 < t < t_p$

Regarding function $q(E/RT_p)$, note that its values fall between 0.90 and 0.96, provided that $E/RT_p$ is in the usual interval between 20 and 50. Thus at linear $T(t)$ the right-hand side of eqn. (13) is a nearly constant quantity between 0.90 and 0.96. It is interesting to note, that the right-hand side of eqn. (13) is exactly equal to one at hyperbolic $T(t)$ functions [10].

Let us consider how the equality is reached in eqn. (13) at a hyperbolic $T(t)$. Function $-df(x)/dx g(x)$, arising on the left-hand side of eqn. (13), is zero at $x = 0$ since $g(0) = 0$. It may have a minimum if $df(x)/dx$ has a positive section and, finally, it has to rise until one in order to reach the equality of the two sides. This means that in the vicinity of $x_p$,

$-\mathrm{d}f(x)/\mathrm{d}x g(x)$ has to be an increasing function. (If it fails to increase until the value of the right-hand side, $\mathrm{d}x/\mathrm{d}t$ will not have maximum in the interval $0 < x < 1$.)

The situation is similar at linear $T(t)$ functions though, from a purely mathematical point of view, one can imagine such $f(x)$ functions at which the left-hand side stops increasing before $x_\mathrm{p}$ and the equality is reached by the very slow decrease of function $q(E/RT)$ on the right-hand side. However, this type of situation can be excluded if the treatment is restricted to such $f(x)$ functions at which

(i) there is one, and only one, maximum of the calculated $(\mathrm{d}x/\mathrm{d}t)(t)$ curves at any positive heating rate and at any physically meaningful value of $E$; and

(ii) the temperature of the peak maximum, $T_\mathrm{p}$, changes continuously with the heating rate.

It is easy to show that these conditions can only be fulfilled if $-\mathrm{d}f(x)/\mathrm{d}x g(x)$ is an increasing function of $x$ around $x_\mathrm{p}$. Note that $-\mathrm{d}f(x)/\mathrm{d}x g(x)$ is an increasing function in the whole domain of $0 < x < 1$ if $f(x) = (1-x)^n$ and $n > 0$.

These considerations lead to the following interpretation of relations (14). If a linear $T(t)$ is changed to a concave $T(t)$, the maximum of $\mathrm{d}x/\mathrm{d}t$ is shifted to a higher value of $x_\mathrm{p}$. If a linear $T(t)$ is changed to a convex $T(t)$, the maximum of $\mathrm{d}x/\mathrm{d}t$ is shifted to a lower $x_\mathrm{p}$. The extent of the shift is determined by the alteration of $\langle \mathrm{d}t/\mathrm{d}T \rangle \mathrm{d}T(t_\mathrm{p})/\mathrm{d}t$ from unity. Of course, these statements are valid only for small changes of $T(t)$. Here the meaning of the term "small" depends on the type of function $f(x)$. If $f(x) = (1-x)^n$, and $n > 0$, then $-\mathrm{d}f(x)/\mathrm{d}x g(x)$ is an increasing function in the whole domain of $0 < x < 1$, thus the only limiting factor lies in the fact that a very high change of $T(t)$ may result in a shift of $T_\mathrm{p}$ by more than 50–100 K, and in this way the change of $q(E/RT_\mathrm{p})$ may partially compensate the change of $\langle \mathrm{d}t/\mathrm{d}T \rangle \mathrm{d}T(t_\mathrm{p})/\mathrm{d}t$.

Regarding the definition of $\langle \mathrm{d}t/\mathrm{d}T \rangle$ by eqn. (9), we can immediately see that

(i) the shift of $x_\mathrm{p}$ depends on the deviation of $(\mathrm{d}T/\mathrm{d}t)^{-1}$ at the peak maximum from an average value of $(\mathrm{d}T/\mathrm{d}t)^{-1}$;

(ii) the values of $(\mathrm{d}T/\mathrm{d}t)^{-1}$ around the peak maximum play a far more important role than the values in the previous part of the domain. Note that the increase of the weight function in eqn. (9) can roughly be estimated by the old empirical rule which states that a 10 K rise of $T$ roughly doubles $\mathrm{e}^{-E/RT}$;

(iii) if $T(t)$ contains convex and concave sections, too, the convex and concave sections partially compensate each other in the formation of $\langle \mathrm{d}t/\mathrm{d}T \rangle$.

## ESTIMATION OF THE ACTIVATION ENERGY AND THE FORMAL REACTION ORDER

Let us suppose that parameters $E$, $n$ and $A$ are evaluated through equations deduced for linear temperature programs. At $f(x) = (1-x)^n$, eqn. (13) can easily be solved for $x_p$. (The solution is a simple modification of the formulae deduced in refs. 3, 7 and 9.) In this way it can be shown that a concave curvature of $T(t)$ decreases $n$ while a convex curvature increases it. The errors of $n$ also influence the determination of $E$ [3]. It is interesting to note that the error of $E$ arising from the error of $n$ has the same sign as the error arising from the application of eqn. (3) at a concave or convex $T(t)$. In other words, the two types of error treated in this paper cumulate in the evaluation of $E$.

Finally we should like to emphasize that the errors treated in the paper arise at any evaluation methods provided that

(i) its deduction involves the integration of eqn. (1) at a linear $T(t)$;

(ii) it uses explicitly or implicitly the information contained by such fundamental properties of the experimental curves as the reacted mole fraction at the peak maximum or the average width of plots $x$ vs. $1/T$.

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