

REACTION KINETICS IN THERMAL ANALYSIS. PART 1. THE SENSITIVITY OF KINETIC EQUATIONS TO EXPERIMENTAL ERRORS. A MATHEMATICAL ANALYSIS

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(Received 26 January 1982)

ABSTRACT

The frequent publication of contradicting or meaningless kinetic parameters and the resulting criticism of the “ill-conditioned nature” of non-isothermal reaction kinetics led the authors to an examination of the sensitivity of kinetic parameters to experimental errors. Using simple mathematical deductions, conditions were given at which about 10% precision of the kinetic parameters can easily be achieved. To obtain a graphic picture about the information content of a thermoanalytical curve and the effect of the systematic measurement errors, mathematical relationships were deduced to show the dependence of the kinetic parameters on the formal (geometric) characteristics of the thermoanalytical curves.

NOTATION

a	Heating rate
A	Pre-exponential factor
E	Energy of activation
n	formal reaction order
r	A shape index characterizing the degree of asymmetry of a thermoanalytical curve
R	Gas constant
t	Time
T	Temperature
T_p	Temperature at the peak maximum
x	Reacted mole fraction
x_p	Reacted mole fraction at the peak maximum
$f(x)$	Function describing the dependence of dx/dt on x
$g(x)$	Integral of $1/f(x)$
$q(E/RT)$	A function approximately equal to $(L/RT + 1)/(E/RT + 3)$
δ	Indicates measurement errors or small finite differences
$\langle \rangle$	Indicates average quantities
\cong	Indicates approximations with precision better than 1%
\approx	Indicates approximations with precision worse than 1%

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INTRODUCTION

In the field of thermal analysis, about 25% of the publications deal with reaction kinetics or contain reaction kinetic evaluation [1]. The overwhelming majority of these works is based on equations of the type

$$dx/dt = A e^{-E/RT} f(x) \quad (1)$$

where x is the reacted mole fraction, A is the pre-exponential factor, and E is either the true or the formal energy of activation. The actual form of function $f(x)$ depends on the type and mechanism of the reaction. From a mathematical point of view, $f(x)$ may be any continuous function with positive values in the interval $0 \leq x < 1$.

The validity of eqn. (1) is limited to the simplest type of processes [2–5], including

(i) evaporation, sublimation, desorption and one part of the phase transitions;

(ii) simple diffusion processes;

(iii) chemically simple one-step reactions and surface reactions;

(iv) a few multistep reactions, e.g. a few polymer decompositions;

(v) elementary steps in complex physical or chemical processes.

The direct application of eqn. (1) in thermal analysis requires special care in the choice of proper samples and experimental conditions. In other cases, eqn. (1) can only be applied as part of a more complex mathematical model. For example, if a chemical reaction is not sufficiently far from chemical equilibrium, the backward reaction also has to be taken into consideration. If diffusion control arises, the equations of the forward and backward reactions have to be combined with an equation or approximate expression describing the diffusion, etc. At this time, however, only the direct application of eqn. (1) is usual in thermal analysis.

Unfortunately, many researchers have applied eqn. (1) outside the domain of applicability outlined above. In this way, a huge but incoherent set of kinetic parameters has been accumulated in the literature. Seeing the contradicting (and sometimes even physically meaningless) kinetic data, researchers have begun to suspect that the source of the problem is in the mathematical properties of eqn. (1). The most explicit attack against the use of eqn. (1) was carried out by Arnold et al. [6,7], who stated [6]: “the measured data should be known with an error not greater than 0.0001% in order to ensure that the uncertainty of the parameters should not be greater than 10%”.

The criticism that has arisen in connection with eqn. (1) has shown that the basic mathematical and numerical properties of equations of this type have not been fully revealed or proven. In this paper, we examine three problems strongly correlated with each other:

(i) how the experimental errors change the parameters obtained in the

evaluation of thermoanalytical curves;

(ii) what experimental precision is required for kinetic evaluation;

(iii) what may be the mathematical reliability of the kinetic data published in the literature of thermal analysis.

Although we cannot give definite and final answers to these questions, we shall try to show that a 10–20% precision can easily be achieved in the evaluation of the kinetic parameters, and the kinetic compensation effects described in the literature are not a consequence of the “ill-conditioned nature” of eqn. (1). We do not state that higher precision cannot be achieved; we only list arguments to show that at least 10–20% precision can be achieved.

EVALUATION FROM ISOTHERMAL CURVES

Classical reaction kinetics are based on the evaluation of isothermal measurements. This method is also widely used in thermal analysis. Its fundamental assumption is that the kinetic parameters (E , $\log A$, etc.) do not depend on the size, shape and lattice error distribution of the measured samples, or these properties do not vary from measurement to measurement. This assumption is always implied if more than one thermoanalytical curve is *described by exactly the same values of the kinetic parameters*. Unfortunately, this assumption is frequently not applicable in the practice of thermal analysis.

The error propagation in the evaluation methods of classical reaction kinetics is beyond the scope of the present work, thus only an extremely simple example will be treated here in order to make comparisons with the non-isothermal methods.

Let us introduce the usual notation

$$g(x) = \int_0^x \frac{dx'}{f(x')} \quad (2)$$

and integrate eqn. (1) in the isothermal section of the heating program

$$g(x) = A e^{-E/RT} t + C \quad (3)$$

where C is an integration constant connected to the amount of sample reacted during the heating until the isothermal section of the heating program. [If we denote the reacted mole fraction at the starting point of the isothermal section by x_0 , then $C = g(x_0)$.] To eliminate C , eqn. (3) is written at two fixed conversions, say at $x = 0.2$ and $x = 0.8$, and the corresponding changes of $g(x)$ and t are denoted by Δg and Δt , respectively

$$\Delta g = A e^{-E/RT} \Delta t \quad (4)$$

Now let us consider two isothermal curves at temperatures T_1 and T_2 and

denote the values of Δt belonging to the same conversions by Δt_1 and Δt_2 , respectively. Using eqn. (4) at T_1 and T_2 , we can eliminate A and get a simple estimator of E

$$\frac{E}{R} = \frac{\ln(\Delta t_1/\Delta t_2)}{1/T_1 - 1/T_2} \quad (5)$$

Similar formulae for the evaluation of E are widely used in thermal analysis as well as in other areas of chemistry.

In eqn. (5) only $\Delta t_1/\Delta t_2$ will be regarded as a measured quantity. Note that T_1 and T_2 are the values set on the instrument. If the actual temperatures differ from the set values, $\Delta t_1/\Delta t_2$ "inherits" some error. (Note that a constant or quasi constant error in the temperature calibration only slightly changes $\Delta t_1/\Delta t_2$). The sensitivity of eqn. (5) to the measurement errors depends on the value of $\Delta t_1/\Delta t_2$. If this ratio is far from unity, eqn. (5) is not sensitive to measurement errors.

A numerical example

In the case of normal chemical reactions, a temperature increase of 30–40 K results in an approximately 10-fold increase of the reaction rates. Let us suppose that the true value of $\Delta t_1/\Delta t_2$ is just 10 and its uncertainty is as much as 20%. Now the numerator in eqn. (5) is 2.3 ± 0.2 , thus the corresponding error of E is less than 10%. This example shows that even a poor measurement precision can be sufficient to estimate kinetic parameters, provided that eqn. (1) is valid, there is no diffusion control, and the kinetic parameters do not vary from measurement to measurement. Finally, we should like to underline that eqn. (5) serves only for illustration. Obviously better estimators can be deduced if more than two curves are used and more than two points on a curve are used.

CALCULATIONS FROM TWO NON-ISOTHERMAL THERMOANALYTICAL CURVES

If thermoanalytical measurements are carried out at various heating rates, the temperatures of the characteristic points of the curves show strong correlation with the heating rate and energy of activation. The mathematical description of this phenomenon yields simple and easily applicable estimators for the energy of activation. In this section we shall treat the simplest of this type of evaluation technique, i.e., when two measurements of heating rates a_1 and a_2 are available and the temperatures of points $x = 0.5$ are used in the calculation. These temperatures will be denoted by T_1 and T_2 , respectively.

In the case of the usual linear heating programs, the solution of eqn. (1)

has to be approximated. Two simple approximations are frequently used in the literature [8,9]

$$\ln g(x) \cong \text{const} - E/RT - \ln a \quad (6)$$

and

$$\ln[g(x)/T^2] \cong \text{const} - E/RT - \ln a \quad (7)$$

It can be shown [10] that eqn. (7) is a significantly better approximation, provided that the constant term is properly chosen. In this paper we shall use eqn. (7) in a slightly rearranged form

$$\ln g(x) \cong \text{const} - E/RT - \ln a + 2 \ln T$$

and we shall neglect the term $2 \ln T$ only when rough approximations are deduced.

Considering points $x = 0.5$ at two different heating rates, we get

$$\frac{E}{R}(1/T_1 - 1/T_2) \cong \ln(a_2/a_1) - 2 \ln(T_2/T_1) \quad (8)$$

In eqn. (8), the measured quantities are T_1 and T_2 . The heating rates on the right-hand side are the values set on the instrument. If the actual heating programs differ from the preset ones, the temperatures of points $x = 0.5$ will be changed.

If T_1 is close to T_2 , eqn. (8) is quite sensitive to experimental errors. However, if a_2/a_1 is at least 10, the difference of T_1 and T_2 is about 50–100 K for normal chemical reactions and eqn. (8) becomes suitable for the estimation of E . To illustrate this, let us consider that on the right-hand side, $2 \ln(T_2/T_1)$ is small compared to $\ln(a_2/a_1)$ and its sensitivity is negligible. Thus the relative precision of E is approximately equal to the relative precision of the difference $(1/T_1 - 1/T_2)$. If both T_1 and T_2 are changed by the same magnitude of errors in the same direction, $(1/T_1 - 1/T_2)$ changes only slightly and the error of E is small. For other types of experimental errors, the relative precision of $(1/T_1 - 1/T_2)$ is roughly equal to the relative precision of $(T_2 - T_1)$. Thus if $(T_2 - T_1)$ is about 50–100 K, estimation of E with a relative precision of 10% requires a precision of 5–10 K of $(T_2 - T_1)$. In our opinion, modern instruments of high precision can give smaller errors for $(T_2 - T_1)$, provided that the kinetic parameters themselves do not vary from measurement to measurement.

A numerical example

Let T_1 and T_2 be 770 and 840 K, respectively. These values correspond to $E = 163.5 \text{ kJ mole}^{-1}$ at $a_1 = 1 \text{ K min}^{-1}$ and $a_2 = 10 \text{ K min}^{-1}$. If the errors of T_1 and T_2 are $\pm 3 \text{ K}$, the relative error of $1/T_1 - 1/T_2$ is less than 9%

$$0.91 \leq \frac{1/(770 \pm 3) - 1/(840 \pm 3)}{1/770 - 1/840} \leq 1.09$$

If there is a constant error of 5 K besides the random error of ± 3 K, the relative error will be less than 10%

$$0.90 \leq \frac{1/(770 + 5 \pm 3) - 1/(840 + 5 \pm 3)}{1/770 - 1/840} \leq 1.07$$

$$0.93 \leq \frac{1/(770 - 5 \pm 3) - 1/(840 - 5 \pm 3)}{1/770 - 1/840} \leq 1.10$$

The relative error of the right-hand side of eqn. (8) is negligible (less than 0.7% in both cases).

As in the previous sections, we should like to emphasize that eqn. (8) serves only to show that a 10% precision can be achieved in the estimation of E . Higher precisions may also be achieved if more than two curves are measured and more than one point is used on a curve. However, analysis of the errors in that case seems difficult, since no general assumptions can be made on the randomness or independence of the errors. For example, the errors of the temperatures corresponding to points $x = 0.1$, $x = 0.2$, $x = 0.3$, etc., of a given curve cannot be regarded random or independent, thus the usual considerations of mathematical statistics cannot be applied.

EVALUATION OF E FROM A SINGLE NON-ISOTHERMAL THERMOANALYTICAL CURVE

In many cases it is advantageous to evaluate each measured curve separately and later compare or average the parameters obtained from the different measurements. Thus in many kinetic investigations two or three parameters are calculated from a single thermoanalytical curve. Usually these parameters are the energy of activation, the pre-exponential factor and the formal reaction order, n . In the following sections we shall briefly show that it is a mathematically correct practice: the information content of a non-isothermal thermoanalytical curve is sufficient for the unique determination of at least three parameters. In the present section we shall start with the simplest case: when function $f(x)$ is known and we want to estimate only E .

Let us choose two points on a given thermoanalytical curve, for example, points $x = 0.2$ and $x = 0.8$, and denote the corresponding temperatures by T_1 and T_2 , respectively. As in the previous section, we shall use eqn. (7) which immediately gives

$$E/R(1/T_1 - 1/T_2) \cong \ln[g(x_2)/g(x_1)] - 2 \ln(T_2/T_1) \quad (9)$$

Here the measured data are T_1 and T_2 . (x_1 and x_2 on the right-hand side are arbitrarily chosen values.)

Formally, eqn. (9) is analogous to eqn. (8), thus the same considerations can be applied: the relative precision of E is approximately equal to the relative precision of $(1/T_1 - 1/T_2)$ which is roughly equal to the relative

precision of $(T_2 - T_1)$. To show this more clearly, let us expand $(1/T_1 - 1/T_2)$ and $\ln(T_2/T_1)$ into a Taylor series around the temperature of the peak maximum, T_p

$$\left(\frac{E}{R} + 2T_p\right)(T_2 - T_1)/T_p^2 \approx \ln[g(x_2)/g(x_1)] \quad (10)$$

Experience shows that E/R is considerably larger (usually at least 10-times larger) than $2T_p$. (Note that from the point of view of reaction kinetics, the heating rates applied in thermal analysis are slow, thus a sample can hardly survive until a temperature where the thermal energy of the molecules is comparable with the bond energies.) Thus, if only a rough estimation of the error of E is required, the term $2T_p$ can be neglected. Forming the differential of the logarithm of eqn. (10), we immediately get the following relationship between the errors of E , T_p and $(T_2 - T_1)$

$$\frac{\delta E}{E} \approx 2 \frac{\delta T_p}{T_p} - \frac{\delta(T_2 - T_1)}{T_2 - T_1} \quad (11)$$

Since $2 \delta T_p/T_p$ is small (usually it is not more than 0.01 – 0.02), the relative error of E is roughly equal to the relative error of $(T_2 - T_1)$.

The drawback of eqn. (9) is that only two points, (x_1, T_1) and (x_2, T_2) , are used in the evaluation. However, we can write eqn. (9) by several (x_1, T_1) and (x_2, T_2) pairs of points and can form the average of these equations. If we indicate the averages by angular brackets, we get

$$(E/R)\langle 1/T_1 - 1/T_2 \rangle \cong \langle \ln[g(x_2)/g(x_1)] \rangle - 2\langle \ln(T_2/T_1) \rangle \quad (12)$$

Note that eqn. (12) stands at any type of averaging, thus the angular brackets may also indicate weighted averages. Using the same considerations as before, we get

$$\left(\frac{E}{R} + 2T_p\right)\langle T_2 - T_1 \rangle / T_p^2 \approx \langle \ln[g(x_2)/g(x_1)] \rangle \quad (13)$$

and

$$\frac{\delta E}{E} \approx 2 \frac{\delta T_p}{T_p} - \frac{\delta \langle T_2 - T_1 \rangle}{\langle T_2 - T_1 \rangle} \quad (14)$$

If points (x_1, T_1) fall on the first half of the curve and points (x_2, T_2) fall on the second half, $\langle T_2 - T_1 \rangle$ can be regarded as a measure of the average width of a thermoanalytical curve. Obviously, the width of a thermoanalytical curve can be characterized in an endless number of ways. We prefer quantities of the type $\langle T_2 - T_1 \rangle$ for the simplicity of the corresponding mathematical considerations. We should like to underline that $\langle T_2 - T_1 \rangle$ may be the simple average of differences $\langle T_2 - T_1 \rangle$ as well as any weighted average deduced by statistical considerations.

Regarding $\langle T_2 - T_1 \rangle$ as a measure of the average width, eqn. (14) shows a strong correlation between E and the width of the thermoanalytical curves.

Thus, if an experimental error widens the curves, the calculated energy of activation is lower than the true one, while if any factor sharpens a thermoanalytical curve, the apparent energy of activation increases. The relative precision of E is roughly equal to the relative precision of $\langle T_2 - T_1 \rangle$.

ESTIMATION OF E WHEN $f(x)$ IS ONLY APPROXIMATELY KNOWN

In the previous section, the function $f(x)$ was supposed to be known exactly. In practice, however, this assumption is never satisfied. Usually we have only an approximation of the true $f(x)$. We shall denote the true $f(x)$ by $f^0(x)$ and its approximation by $f(x)$. Their difference [i.e. the error of $f(x)$] will be denoted by $\delta f(x)$. A part of $\delta f(x)$ arises from simplification of theoretical considerations. Usually, the mathematical approximation of $f^0(x)$ contains adjustable parameters, for example, the formal reaction order, n . These adjustable parameters have to be determined from experimental data, thus $\delta f(x)$ will be increased by the effect of the experimental errors.

Regarding the previously treated estimation method, $\delta f(x)$ changes $\ln[g(x_2)/g(x_1)]$ on the right-hand side of eqns. (9) and (12) and in this way an additional error term is added to the errors of E . Obviously, this additional error term will be small if $f(x)$ approximates $f^0(x)$ in such a way that $g(x)$ is close to $g^0(x)$. [Here $g^0(x)$ is the integral of $1/f^0(x)$.] From a mathematical point of view, it is quite simple to get such approximations from isothermal thermoanalytical curves. The thermoanalyst, however, might be more interested in the answer to the following type of question: "What will be the error of the energy of activation if a thermoanalytical curve of a contracting sphere mechanism ($n = 2/3$) is evaluated by first order kinetics?"

TABLE I

Dependence of $\ln[g(x_2)/g(x_1)]$ on the formal reaction order

n	$\ln \frac{g(0.6)}{g(0.4)}$	$\ln \frac{g(0.8)}{g(0.2)}$	$\ln \frac{g(0.95)}{g(0.05)}$
0.00	0.41	1.39	2.94
0.25	0.45	1.52	3.17
0.50	0.49	1.67	3.42
0.75	0.54	1.81	3.72
1.00	0.58	1.98	4.07
1.25	0.64	2.16	4.46
1.50	0.69	2.35	4.90
1.75	0.75	2.56	5.37
2.00	0.81	2.77	5.89
2.25	0.88	3.00	6.44
2.50	0.94	3.24	7.01

To answer this, we have shown in Table I how $\ln[g(x_2)/g(x_1)]$ depends on n if $f(x) = (1-x)^n$. Three representative pairs of x_1 and x_2 were chosen. It may be interesting to observe that a change of n by 0.25 changes $\ln[g(x_2)/g(x_1)]$ by only 8–10%. Thus even an error of 0.25 of n adds only an error of 8–10% to the value of E .

To obtain an explicit relationship for the error of E , we have calculated the differential quotient of $\ln[g(x_2)/g(x_1)]$ at nine representative pairs of x_1 and x_2 in the range $0 \leq n \leq 3$. (The pairs of x_1 and x_2 were: 0.45 and 0.55, 0.40 and 0.60, 0.35 and 0.65, 0.30 and 0.70, 0.25 and 0.75, 0.20 and 0.80, 0.15 and 0.85, 0.10 and 0.90, 0.05 and 0.95.) From these data, the following rough approximation is obtained

$$\frac{d}{dn} \ln[g(x_1)/g(x_2)] \approx 0.33 \ln[g(x_1)/g(x_2)] \quad (15)$$

Using approximations (15) and (13), we can estimate the relative error of E by

$$\frac{\delta E}{E} \approx 2 \frac{\delta T_p}{T_p} - \frac{\delta(T_2 - T_1)}{T_2 - T_1} + 0.33 \delta n \quad (16)$$

THE DEGREE OF ASYMMETRY OF THE THERMOANALYTICAL CURVES

In 1957, Kissinger [11] studied the properties of

$$dx/dt = A e^{-E/RT}(1-x)^n \quad (17)$$

and showed that n can be estimated from the degree of asymmetry of the thermoanalytical curves. His results, in a slightly modified form, have been re-established by other authors and are used today [12]. Kissinger characterized the degree of asymmetry of a curve $(dx/dt)(t)$ by the "absolute value of the ratio of the slopes of tangents to the curve at the inflection points". Regarding the corresponding mathematical deductions, however, a mathematically simpler definition can be given if we divide curve $(dx/dt)(t)$ into two parts at the peak maximum and characterize the degree of asymmetry by the ratio of the areas of the parts right and left from the peak maximum [17]. We shall denote this ratio by r . At symmetric peaks the value of r is obviously one. The area of the part left of the peak maximum is the reacted mole fraction at the peak maximum, x_p , while the area of the part right of the peak maximum is $(1 - x_p)$. In this way we can write

$$r = (1 - x_p)/x_p \quad (18)$$

Rearrangement of eqn. (18) gives

$$x_p = 1/(r + 1) \quad (19)$$

This type of characterization is based on the work of Horowitz and Metzger

[13]. They showed that, approximately, x_p is a function of only n and in this way n can be estimated from the experimental value of x_p .

In the present section we shall examine to what extent the degree of asymmetry depends on the formal reaction order and to what extent it depends on the other parameters of eqn. (17). First, we shall deduce a general relationship between x_p , E , T_p and the adjustable parameters of any function $f(x)$ at which eqn. (1) has a solution. Let us begin this deduction by writing the condition of the maximum of dx/dt , $d^2x/dt^2 = 0$. Differentiating eqn. (1) and rendering it equal to zero gives

$$f(x_p) \frac{dE}{RT_p^2} + \frac{df}{dx}(x_p) \left(\frac{dx}{dt} \right)_p = 0 \quad (20)$$

(Here subscript "p" indicates that the corresponding quantities belong to the point of the peak maximum.) Now we have to eliminate $(dx/dt)_p$ from eqn. (20) without reintroducing $e^{-E/RT}$. To achieve this, we shall combine eqn. (1) with its integrated form. As is known from the literature, the integrated form of eqn. (1) can be written as

$$g(x) = \int A e^{-E/RT} dt = \frac{RT^2}{aE} A e^{-E/RT} q(E/RT) \quad (21)$$

where $q(E/RT)$ denotes a slowly changing (nearly constant) function [10.11.8.3]. Combining eqns. (1) and (21) gives

$$g(x)f(x) = \frac{RT^2}{aE} q(E/RT) dx/dt \quad (22)$$

Using eqn. (22), we can eliminate $(dx/dt)_p$ from eqn. (20)

$$\frac{df}{dx}(x_p)g(x_p) = -q(E/RT_p) \quad (23)$$

Equation (23) is the desired relationship. If $f(x) = (1-x)^n$ and $n > 0$, the following algebraic solution can be deduced

$$\begin{aligned} x_p &= 1 - \left[(1/n - 1)q(E/RT_p) + 1 \right]^{1/n-1} & n \neq 1 \\ x_p &= 1 - e^{-q(E/RT_p)} & n = 1 \end{aligned} \quad (24)$$

From a mathematical point of view, dx/dt has no maximum if $n = 0$. From a physical point of view, $x_p = 1$ if $n = 0$. Equation (24) also gives $x_p = 1$ as a limit when $n \rightarrow 0$.

It follows from eqn. (24) that r is a function of n and E/RT_p . We shall denote this function by $r(n, E/RT_p)$; a general overview of it is given in Table 2. Note that at the usual heating rates of thermal analysis, E/RT_p varies within a limited range, i.e. there is some correlation between E and T_p . Thus we found it sufficient to study $r(n, E/RT_p)$ only in the domain $20 \leq E/RT_p \leq 40$. Table 2 shows that the dependence of r on E/RT_p is slight: a rough estimation of n can always be obtained by the assumption of

TABLE 2

The degree of asymmetry at $E/RT_p = 20, 30$ and 40

n	$r(n, 20)$	$r(n, 30)$	$r(n, 40)$
0	0	0	0
0.25	0.21	0.20	0.20
0.50	0.38	0.36	0.36
0.75	0.53	0.51	0.50
1.00	0.67	0.64	0.63
1.25	0.81	0.77	0.75
1.50	0.94	0.89	0.87
1.75	1.07	1.01	0.98
2.00	1.19	1.13	1.10
2.25	1.31	1.24	1.21
2.50	1.43	1.35	1.31

$E/RT_p = 30$. At small values of n (at $n < 0.5$), the dependence of r on E/RT_p is negligible. At higher values of n we have found that a 100% change of E/RT_p corresponds to about a 10% change of n . This is illustrated in Table 3. Thus $r(0.9, 20) \approx r(1.0, 40)$, $r(1.0, 20) \approx r(1.1, 40)$, $r(2.25, 20) \approx r(2.50, 40)$ and $r(2.50, 20) \approx r(2.75, 40)$.

Although it is possible to estimate n without the estimation of E , it is obviously better to estimate n and E together. This does not require actual simultaneous calculations. For example, we can get a first estimation of n by assuming $E/RT_p = 30$, then we can use this value of n to calculate a first approximation of E and with this E we can get a better approximation of n ,

TABLE 3

The dependence of the degree of asymmetry on r and E/RT_p

n	$r(n, 20)$	$r(n, 40)$
0.90	0.62	0.57
1.00	0.67	0.63
1.10	0.73	0.68
1.35	0.86	0.80
1.50	0.94	0.87
1.65	1.02	0.94
1.80	1.09	1.01
2.00	1.19	1.10
2.20	1.29	1.18
2.25	1.31	1.21
2.50	1.43	1.31
2.75	1.56	1.42

and so on. In consequence of the slight dependence of r on E/RT_p , this simple iteration rapidly converges and the final value of n only slightly "inherits" the errors of the calculated value of E .

The sensitivity of n on the experimental errors of r can be seen from Tables 2 and 3. In this way, we can estimate the sensitivity of E on the experimental errors of r . In the previous section, we showed that an error of 0.25 of n results in an error of 8–10% of E . Table 2 shows that an error of $\delta n = 0.25$ is caused by an experimental error of $\delta r \approx 0.10$ – 0.14 in the range $0.75 < n < 2.5$, and at smaller values of n the sensitivity is more favorable.

ESTIMATION OF THREE PARAMETERS FROM A SINGLE NON-ISOTHERMAL THERMOANALYTICAL CURVE

In this section, we shall briefly show that the information content of a non-isothermal thermoanalytical curve is sufficient for the unique determination of parameters E , $\log A$ and n . We shall also deal with the information content of a thermoanalytical curve in the case of a general $f(x)$ function in eqn. (1).

First, let us consider that the simple geometric characterization of a thermoanalytical curve requires at least three independent parameters which, among others may correspond to the following three independent geometric properties: (i) the position of the peak; (ii) the width of the peak; and (iii) the degree of asymmetry. (Here we do not make distinction between integral and differential thermoanalytical curves. Geometric properties (i)–(iii) can be defined in both cases.) In the case of a good fit, the fundamental geometric characteristics must be approximately the same on the measured curve and its mathematical approximation. Thus if a mathematical model can provide good approximations of thermoanalytical curves in a wide range of position, width and degree of asymmetry, it must have at least three independent adjustable parameters.

Besides the theoretical independence, however, we have to examine whether the parameters are sufficiently independent for the actual parameter estimations. In other words, we have to show that the change of the value of a given kinetic parameter cannot be "compensated" by the proper adjustment of the other kinetic parameters without a considerable change of at least one of the fundamental geometric characteristics.

The considerations of the preceding section, especially eqn. (21), show that the degree of asymmetry is almost entirely determined by function $f(x)$. Thus if a function $f(x)$ is suitable to describe thermoanalytical curves in a wide range of degree of asymmetry, it must have at least one adjustable parameter correlated with the degree of asymmetry. The strong correlation between the formal reaction order and the degree of asymmetry is well known. For example, an experienced researcher can distinguish a first order

and a contracting sphere ($n = 2/3$) reaction by a quick glance at the measured non-isothermal curve.

The correlation between E and the geometric properties can be deduced from eqn. (13). If $f(x)$ does not contain variable parameters, eqn. (13) shows that any change of E is accompanied by the change of the width, $\langle T_2 - T_1 \rangle$, or (and) by the position of the peak, T_p . If $f(x)$ contains variable parameters, a change of E may be compensated by the change of $\langle \ln[g(x_2)/g(x_1)] \rangle$. From a mathematical point of view, one may construct such $f(x)$ functions at which $\ln[g(x_2)/g(x_1)]$ can vary without considerable variation of the shape of the corresponding curve $\frac{dx}{dt}(t)$. However, we do not believe that such functions may arise in the case of a useful mathematical model of thermoanalytical curves.

In the previous sections we have shown that if $f(x) = (1 - x)^n$, then the value of $\ln[g(x_2)/g(x_1)]$ cannot be changed considerably without a considerable change of the degree of asymmetry. Using the data of Tables 1 and 2, we could formulate this relationship by the following rough approximation

$$\frac{d}{dr} \ln[g(x_2)/g(x_1)] \approx 0.65 \ln[g(x_2)/g(x_1)] \quad (25)$$

Using this approximation we get the following approximation from eqn. (13)

$$\frac{\delta E}{E} \approx 2 \frac{\delta T_p}{T_p} - \frac{\delta \langle T_2 - T_1 \rangle}{T_2 - T_1} + 0.65 \delta r \quad (26)$$

Equation (26) shows that a change of the value of E cannot be compensated by the proper adjustment of the other kinetic parameters ($\log A$ and n) without a considerable change of at least one of the geometric properties.

Finally, we shall briefly deal with the estimation of the third parameter, $\log A$, in the case of $f(x) = (1 - x)^n$. Let us take the logarithm of eqn. (21) at the point of the peak maximum

$$\begin{aligned} \log g(x_p) = \log A - 0.434(E/RT_p) - \log(E/RT_p) \\ + \log(T_p/a) + \log q(E/RT_p) \end{aligned} \quad (27)$$

Calculating the numeric values of x_p , we found that $\log g(x_p)$ is between 0 and -0.1 if $E/RT_p \geq 20$ and $n \leq 2.5$. Thus $\log g(x_p)$ can be neglected. In a similar way, $\log q(E/RT_p)$ can also be omitted and we get

$$\log A \approx 0.434(E/RT_p) + \log(E/RT_p) - \log(T_p/a) \quad (28)$$

Equation (28) shows that, in a good approximation, $\log A$ is the function of only E , T_p and the heating rate, a . Since a significant change of E is always accompanied by a considerable change of at least one of the geometric parameters, no significant change of $\log A$ can be compensated by the proper adjustment of E and n without a considerable change of at least one of the geometric parameters.

The correlation between $\log A$ and the fundamental geometric parameters can be explicitly expressed as follows. Since the logarithmic terms vary only slightly with E/RT_p and T_p

$$\delta \log A \approx 0.434 \delta(E/RT_p) \quad (29)$$

Taking the differential of (E/RT_p) gives

$$d(E/RT_p) = (E/RT_p)(dE/E - dT_p/T_p) \quad (30)$$

Combining eqns. (26), (29) and (30) we get the relationship between $\delta \log A$ and the geometric parameters

$$\delta \log A \approx 0.434(E/RT_p)(0.65 \delta r + \delta T_p/T_p - \delta \langle T_2 - T_1 \rangle / \langle T_2 - T_1 \rangle) \quad (31)$$

Keeping in mind that E/RT_p is usually between 20 and 40, we can read from eqn. (31) that the value of $\log A$ cannot be changed significantly without the considerable change of at least one of the geometric parameters. For example, a change of $\delta \log A = 1$ may correspond to

- (i) an increase of 6–12% of T_p
- (ii) a decrease of 6–12% of $\langle T_2 - T_1 \rangle$
- (iii) an increase of r by 0.09–0.18

HYPERBOLIC TEMPERATURE PROGRAMS

The considerations of the present paper remain valid at hyperbolic $T(t)$. The deductions, however, are simpler in that case, since terms $2 \ln T$ and $2 \ln(T_2/T_1)$ do not arise in eqns. (7)–(9). Thus eqn. (13) also becomes simpler

$$(E/R) \langle T_2 - T_1 \rangle / T_p^2 \approx \langle \ln[g(x_2)/g(x_1)] \rangle \quad (32)$$

In the case of hyperbolic heating programs, function $q(E/RT)$ in eqns. (21–24) must be replaced by unity, thus the degree of asymmetry depends entirely on the parameters of function $f(x)$.

CONCLUSIONS

We have briefly dealt with the frequently used types of kinetic evaluation methods thermal analysis:

- (i) evaluation from isothermal curves;
- (ii) evaluation from non-isothermal curves of different heating rates;
- (iii) evaluation of two parameters from a non-isothermal curve; and
- (iv) evaluation of three parameters from a non-isothermal curve.

We do not rank these types of evaluation; each has its own merits and drawbacks and the nature of the examined samples determines which type of

evaluation is the most favorable. Thus the methods based on the simultaneous evaluation of more than one curve require that the kinetic parameters themselves do not vary from measurement to measurement, i.e., they require that the distribution of the lattice errors, impurities and the geometric parameters of the samples do not vary from measurement to measurement or do not influence the kinetic parameters. On the other hand, the separate evaluation of the curves requires that neither side reactions nor the errors of the temperature program could distort the shape of the thermoanalytical curves. Although there may exist such materials at which none of the available kinetic evaluation methods is applicable, we firmly believe that a 10% precision of the kinetic parameters is usually an attainable goal, provided that eqn. (1) describes well the reaction. The actual conditions of this precision can be found in the discussion of the corresponding equations and tables. However, we do not state that better precision cannot be achieved.

From the considerations of this paper it follows that the kinetic compensation effects are not the necessary consequences of the "ill-conditioned nature" of eqn. (1). Although "ill-conditioned" (non-correct) evaluation methods are frequently used in thermal analysis, correct, well-conditioned techniques are also available and, as we have shown here, the correct methods are not necessarily more complicated than the non-correct ones. (Regarding the observed kinetic compensation effects, however, we cannot exclude the influence of the frequently used non-correct methods.)

We have also dealt here with the correlation between kinetic parameters E , n , $\log A$ and the geometric characteristics of the thermoanalytical curves. These considerations can be directly applied in the least squares curve fitting of kinetic equations to the thermoanalytical curves [14]. We should like to emphasize here again that the determination of three kinetic parameters from a thermoanalytical curve always requires agreement between the fundamental geometric characteristics of the calculated and observed thermoanalytical curves. If this agreement is not checked, one of the parameters may appear redundant. (This may be the cause of the non-correctness of an evaluation method.) However, one of the kinetic parameters may actually be redundant if only a short section of the measured curve is evaluated. The evaluated section of the thermoanalytical curve should have at least three independent geometric characteristics in order to determine three kinetic parameters.

Finally, we should like to underline that the evaluation of partially overlapping thermoanalytical peaks can yield more than three kinetic parameters, provided that the geometric properties of the individual peaks are not concealed completely [14–16].

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