Thermochimica Acta, 65 (1983) 333–350
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE EFFECTS OF IMPERFECT TEMPERATURE PROGRAMMING ON THE KINETIC EVALUATION OF THERMOANALYTICAL CURVES. PART 3. ERROR BOUNDS FOR THE ACTIVATION ENERGY AND THE FORMAL REACTION ORDER

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(Received 30 December 1982)

ABSTRACT

The difference between the actual and the measured temperature of the sample examined distorts the estimated values of the kinetic parameters. This distortion has been analysed in the instances of simple parameter estimation methods. The results obtained can help to judge the correctness of the kinetic evaluation of the non-isothermal measurements.

NOTATION

A	pre-exponential factor
c, C and C'	constants in approximate equations
E	activation energy
$\mathrm{f}(x)$	function expressing the dependence of $\mathrm{d}x/\mathrm{d}t$ on x
$\mathrm{g}(x)$	integral of $1/\mathrm{f}(x)$ from 0 to x
$\mathrm{G}(x_1,x_2)$	integral of $1/\mathrm{f}(x)$ from x_1 to x_2
h, h' and h''	constants defining the highest deviation between the known and the true temperatures of the sample
$\mathrm{L}(n,x_1,x_2)$	$\ln[\mathrm{g}(x_1)/\mathrm{g}(x_2)]$
R	gas constant
t	time
T	temperature
x	reacted mole fraction
δ	indicates the error of a given quantity
ε	error term in an approximate equation

Superscripted symbols

T^0	the known (measured) temperature of the sample
$x^0(t)$	the solution of the kinetic differential equation when $T \equiv T^0(t)$

0040-6031/83/$03.00

$\delta^0 E$ and $\delta^0 n$	errors caused by the use of T^0 instead of the true temperature in the evaluation

Subscripted symbols

E_{low} and E_{up}	lower and upper bounds of E
t_i $(i = 1,2,...)$	arbitrarily chosen points of time
T_i^0, x_i^0 and x_i	$T^0(t_i)$, $x^0(t_i)$ and $x(t_i)$, respectively
$T_{1/2}^0$	T^0 at the half-life of the sample

INTRODUCTION

The importance of good temperature control in thermal analysis has been judged rather divergently in the literature. Numerous kinetic studies have been based on equipment with poor temperature regulation or sample sizes which were obviously too high for reliable temperature control inside the sample. On the other hand, Arnold et al. claim [1–4] that the kinetic equations are very sensitive to measurement errors and even extremely small errors may make mathematically impossible the calculation of two or three kinetic parameters from a non-isothermal curve. In our opinion, the reality is somewhere between these two extremes.

In a former paper [5] we have formally examined the sensitivity of the kinetic parameters to the experimental errors without discussing the effects of the various sorts of experimental errors. The aim of the present work (which has been published in three parts) is to study a concrete type of experimental error, namely how the difference between the known and the true sample temperature influences the kinetic evaluation. In Part 1 a mathematically simple example has been shown [6]. In Part 2 qualitative results have been deduced [7]. In the present paper, upper and lower bounds will be deduced for the errors in the activation energy and formal reaction order.

Simple estimators based on a few experimental points will be discussed in the paper. Strictly speaking, the results will be error bounds only for these simple estimators. There may be other evaluation methods which are less sensitive to the experimental errors. Great improvements, however, do not seem probable since the estimators treated in the paper are directly connected with the fundamental geometric characteristics of the thermoanalytical curves and any correct evaluation method has to provide some fit between the theoretical and the experimental curves.

A really thorough modelling of the problem would probably lead to a system of partial differential equations which were not suitable for an easy mathematical analysis. To avoid this, simplifying assumptions have been applied. These assumptions, which will be outlined in the next section, are inevitable to keep the complexity of the deductions within reasonable limits.

GENERAL CONSIDERATIONS

Let T^0 stand for the known (experimental) values of the temperature. In thermal analysis, the prescribed temperature program is usually linear. Hence, T^0 is usually close to a linear function of time. This approximate linearity will be assumed everywhere in the paper. The $T^0(t)$ functions to be treated are those for which either the Coats–Redfern type of approximations are applicable [8–10] or the $\ln \int \mathrm{e}^{-E/RT^0}\,\mathrm{d}t$ vs. $1/T^0$ plots are approximately linear [11, 12]. [It can be shown that these approximations are always applicable when $(\mathrm{d}T^0/\mathrm{d}t)^{-1}$ can be approximated by a low order polynomial of T^0 or $1/T^0$ in the given temperature domain.] Note that the non-linearity of $T^0(t)$ itself does not lead to errors at a mathematically correct evaluation. Here the term "correct" refers, among others, to the integration of the kinetic differential equation along the actual $T^0(t)$. Thus the systematic errors of the usual approximations at a non-linear $T^0(t)$ will not be analysed in the present paper. The treatment will be restricted to the errors arising from the difference of the actual and the known temperatures.

The actual temperature in the sample will be assumed to be close to T^0 within a certain error bound. Since the rate constants are simpler functions of T^{-1} than of T, it is worth expressing the closeness of T^0 and the actual temperature through the closeness of their reciprocals.

$$\left|\frac{1}{T^0(t)} - \frac{1}{T(t)}\right| \le h \tag{1}$$

Here h stands for a constant error bound and $T(t)$ may be the temperature of any point in the sample. From a physical point of view, a more natural way seems to be the restriction of either the absolute or the relative error of T^0 by

$$|T(t) - T^0(t)| \le h' \tag{2}$$

or

$$\frac{|T(t) - T^0(t)|}{T(t)} \le h'' \tag{3}$$

where h' and h'' are constant error bounds. These relations will also be applied in the paper. It can be shown however, that (1)–(3) are practically equivalent as far as the kinetic evaluation of a single thermoanalytical curve is concerned. Let us consider that the kinetic evaluation is limited to the temperature domain of the significant reaction rates. On a given non-isothermal thermoanalytical curve, the significant reaction rates belong to a relatively narrow temperature domain where (1)–(3) can mutually be approximated by each other. Denoting the middle point of this temperature domain by T_m and developing (1) into a Taylor series around T_m we get

$$h \approx \frac{h'}{T_\mathrm{m}^2} \quad \text{and} \quad h \approx \frac{h''}{T_\mathrm{m}} \tag{4}$$

In the numerical examples, T_m has been defined as the mean of the temperatures of $x = 0.1$ and $x = 0.9$. (Here x stands for the reacted mole fraction.) In a few instances the temperature of $x = 0.5$ has been used in place of T_m.

Note, that (1) permits smaller temperature errors at lower values of T. Usually this fact does not cause difficulties since the heat effects of the reaction studied are negligible below the domain of the significant reaction rates and in this way the temperature errors are also smaller there. Nevertheless, the temperature domain will be divided into partial intervals during the deductions and in these partial intervals different h values can be applied. This possibility may be used, among others, to obtain a better approximation of (2) or (3) by (1).

Significantly sharper bounds can be obtained for the errors of the kinetic parameters by taking into account that different sorts of temperature errors have different importance in the estimation of the kinetic parameters. As has been mentioned already, the deviation of $T^0(t)$ from linearity does not lead to errors if correct evaluation methods are used. The effects of random errors in temperature measurement can largely be diminished by proper measuring, data collecting and data processing techniques. The systematic errors of the applied thermometers (i.e. the so-called calibration errors) are usually slowly changing functions of the temperature in the domain of a given reaction. Their constant part does not change the width and the asymmetry of the x vs. T or $\mathrm{d}x/\mathrm{d}t$ vs. T curves, hence it has only negligible effects on the estimation of E and n [5]. The linear component of the calibration error–temperature function does not change the asymmetry of the curves, thus it does not disturb the evaluation of n and only slightly influences the evaluation of E.

For the majority of thermoanalytical equipment, the most troublesome contributors to temperature errors seem to be the thermal lag, caused by the non-zero heat capacity of the sample, and the effect of the heat of reaction. If the reaction is endothermic, these errors have the same sign, hence (1)–(3) may be modified to permit only negative $T - T^0$ differences. If the reaction is exothermic and the heat of reaction is much greater than the heat necessary for the non-isothermal heating of the sample, an approximate model can be obtained by assuming $T \geqslant T^0$. These questions will be treated in the section entitled "Sharper Error Bounds".

Now let us regard the mathematical model of the physical or chemical process under study. Following the usual practice of kinetic studies in thermal analysis, an equation of type

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A\,\mathrm{e}^{-E/RT}\mathrm{f}(x) \tag{5}$$

will be assumed, where x is the reacted mole fraction and $f(x)$ is a continuous positive function in the domain $0 \leq x \leq 1$. A few considerations in the present paper are valid at any $f(x)$ at which eqn. (5) has a solution. In the other deductions $f(x) = (1-x)^n$ will be assumed, where n will be called the formal reaction order, regardless of its possible physical meaning.

The validity of eqn. (5) is obviously limited to the simplest type of processes under carefully chosen experimental conditions. For the time being, however, no other simple mathematical model is available to study the effects of the experimental errors in the thermal analysis. It may be worth underlining that x is an overall characteristic of the propagation of the reaction and in this way eqn. (5) is not suitable for the study of the effects of an inhomogeneous temperature distribution. For inhomogeneous distributions, at least two equations would be necessary: one for the change of a local quantity and another for calculation of x from this local quantity. To avoid these complications, we shall look for the most unfavourable homogeneous temperature–time function. This means that the maximum temperature errors permitted by (1) will be assumed to be uniform in the whole sample and only the sign of this error will be changed as a function of time. The procedure applied has a simple physical interpretation if the nature of the given chemical or physical process permits the definition of a local quantity analogous to x. This local quantity will be denoted by x_{loc}. In the case of a first order reaction, for example, x_{loc} is the concentration in a given point of the sample. At the thermal decomposition or phase transition of a powder, x_{loc} may be the reacted mole fraction of the individual grains. At the various points of the sample various $x_{\mathrm{loc}}(t)$ functions arise and the overall $x(t)$ is some average of the $x_{\mathrm{loc}}(t)$ functions. To obtain upper bounds for the errors of the parameters, we shall choose the worst of the possible $x_{\mathrm{loc}}(t)$ functions and suppose that this worst $x_{\mathrm{loc}}(t)$ applies everywhere in the sample. Here the term "worst" means: which has the highest contribution to the errors of the parameters.

ESTIMATION OF THE ACTIVATION ENERGY

In this section we shall examine the estimation of the activation energy in those cases when function $f(x)$ in eqn. (5) does not contain unknown parameters.

Let us substitute the function $T^0(t)$ in eqn. (5) and integrate eqn. (5) in the usual way [5–16].

$$g(x^0) = \int_0^t e^{-E/RT^0} dt \tag{6}$$

Here x^0 is the reacted mole fraction which would arise if the temperature of the sample were exactly $T^0(t)$ and $g(x^0)$ is the integral of $1/f(x^0)$.

Let us choose two points of time, t_1 and t_2, somewhere at the beginning and at the end of the reaction, respectively, and let us denote the corresponding T^0 and x^0 values by subscripts 1 and 2. Eliminating A from eqn. (6) we obtain an equation in which only E is unknown.

$$\frac{g(x_2^0)}{g(x_1^0)} = \frac{\int_0^{t_2} e^{-E/RT^0} dt}{\int_0^{t_1} e^{-E/RT^0} dt} \tag{7}$$

The problem examined in this section is what the error of E would be if we substituted the values of the "worst" $x(t)$ for x_1^0 and x_2^0 in the left-hand side. To obtain a bound for this type of error, we have to find the extrema of $g(x_2)/g(x_1)$ under the validity of (1). Let us write eqn. (7) for a $T(t)$ satisfying (1) and let us rearrange its right-hand side by separating the numerator into the sum of integrals from 0 to t_1 and t_1 to t_2. In this way we get

$$\frac{g(x_2)}{g(x_1)} = 1 + \frac{\int_{t_1}^{t_2} e^{-E/RT} dt}{\int_0^{t_1} e^{-E/RT} dt} \tag{8}$$

To maximize $g(x_2)/g(x_1)$, $T(t)$ must be increased in the numerator and decreased in the denominator. Regarding (1), we obtain

$$\frac{1}{T(t)} = \frac{1}{T^0(t)} - h \qquad \text{if } t_1 < t \leqslant t_2 \tag{9}$$

and

$$\frac{1}{T(t)} = \frac{1}{T^0(t)} + h \qquad \text{if } 0 \leqslant t < t_1$$

Note, that the maximum on the right-hand side of eqn. (8) does not define the value of T at point t_1. This fact does not affect the treatment.

Substituting function (9) into eqn. (8) we get

$$\max \frac{g(x_2)}{g(x_1)} = 1 + \frac{\int_{t_1}^{t_2} e^{hE/R} e^{-E/RT^0} dt}{\int_0^{t_1} e^{-hE/R} e^{-E/RT^0} dt} \tag{10}$$

[Here "max" refers to the maximum of $g(x_2)/g(x_1)$ by $T(t)$.] Taking the constant $e^{hE/R}$ out of the integrals and considering that $e^{2hE/R} > 1$ we obtain

$$\max \frac{g(x_2)}{g(x_1)} < e^{2hE/R} \left(1 + \frac{\int_{t_1}^{t_2} e^{-E/RT^0} dt}{\int_0^{t_1} e^{-E/RT^0} dt} \right)$$

$$= e^{2hE/R} \frac{g(x_2^0)}{g(x_1^0)} \tag{11}$$

In a similar way, the $T(t)$ function minimizing $g(x_2)/g(x_1)$ is

$$\frac{1}{T(t)}=\frac{1}{T^0(t)}+h \qquad \text{if } t_1<t\leqslant t_2 \tag{12}$$

and

$$\frac{1}{T(T)}=\frac{1}{T^0(t)}-h \qquad \text{if } 0\leq t<t_1$$

For the minimum of $g(x_2)/g(x_1)$ we obtain

$$\min\frac{g(x_2)}{g(x_1)}>e^{-2hE/R}\frac{g(x_2^0)}{g(x_1^0)} \tag{13}$$

Inequalities (11) and (13) give bounds to the error of eqn. (7). Now the error of E can be deduced from these relations. If $T^0(t)$ is linear, the $(x^0,\ T^0)$ data can be described, among others, by the Coats–Redfern approximation [8,9,10]

$$\ln g(x^0)=\text{const}-\frac{E}{RT^0}+2\ln T^0 \tag{14}$$

and E can be estimated by the equation

$$\ln g(x_2^0)-\ln g(x_1^0)=\frac{E}{R}\left(\frac{1}{T_1^0}-\frac{1}{T_2^0}\right)+2\ln\left(\frac{T_2^0}{T_1^0}\right) \tag{15}$$

In practice $T^0(t)$ may alter from linearity. In a very correct evaluation, this alteration can be taken into account by the numerical integration of eqn. (5) along $T^0(t)$. Since the study of the numerical integration does not lead to concise results, we shall indicate only formally the error arising from the non-linearity of $T^0(t)$ by ε.

$$\ln g(x_2^0)-\ln g(x_1^0)=\frac{E}{R}\left(\frac{1}{T_1^0}-\frac{1}{T_2^0}\right)+2\ln\left(\frac{T_2^0}{T_1^0}\right)+\varepsilon \tag{16}$$

If x_1^0 and x_2^0 are replaced by x_1 and x_2, respectively, an additional error term, ε^0, will appear.

$$\ln g(x_2)-\ln g(x_1)=\frac{E}{R}\left(\frac{1}{T_1^0}-\frac{1}{T_2^0}\right)+2\ln\left(\frac{T_2^0}{T_1^0}\right)+\varepsilon+\varepsilon^0 \tag{17}$$

Subtracting eqn. (16) from eqn. (17), we get

$$\varepsilon^0=\ln\frac{g(x_2)/g(x_1)}{g(x_2^0)/g(x_1^0)} \tag{18}$$

Comparing the logarithms of relations (11) and (13) with eqn. (18) we obtain

$$-\frac{2hE}{R}<\varepsilon^0<\frac{2hE}{R} \tag{19}$$

When E is calculated from eqn. (17), ε^0 results in an error of E

$$\delta^0 E = \frac{\varepsilon^0 R}{1/T_1^0 - 1/T_2^0} \tag{20}$$

From (19) and (20) we obtain the bound for the relative error of E as given by

$$\frac{|\delta^0 E|}{E} < \frac{2h}{1/T_1^0 - 1/T_2^0} \tag{21}$$

This relation is the result we have been looking for. The denominator on the right-hand side can be interpreted as a measure of the width of the experimental x vs. $1/T^0$ curves. Note, that t_1 and t_2 have been assumed to be somewhere at the beginning and end of the thermoanalytical curve, respectively. In this way the right-hand side can be interpreted as the relative precision of the width of the x vs. $1/T^0$ curves.

NUMERICAL EXAMPLES

To elucidate the meaning of inequality (21), a few numerical examples will be given. In these examples h values have been assumed at which the uncertainty of the sample temperature is about ± 1 K. The values of x_1^0 and x_2^0 have been chosen to be 0.1 and 0.9, respectively. The corresponding T_1^0 and T_2^0 data have been calculated from eqn. (15) at $f(x) = (1-x)^n$, $0 \le n \leqslant 2$. The values of E had to be chosen in such a way that the E/RT ratios should have physically meaningful values in the temperature domain of the supposed reaction. (Note that E is correlated with the temperatures at which the

TABLE 1

Estimation of the relative error of E by inequality (21)
Temperatures given in degrees Kelvin.

$T^0_{1/2}$	h	T_1^0	δT_1^0	T_2^0	δT_2^0	$\delta^0 E/E$
$n = 2$; $E/RT^0_{1/2} = 20$						
500	3.9×10^{-6}	454.4	±0.80	555.2	±1.20	±1.95%
1000	9.7×10^{-7}	908.8	±0.80	1110.4	±1.20	±0.97%
1500	4.3×10^{-7}	1363.3	±0.80	1665.5	±1.20	±0.65%
$n = 0$; $E/RT^0_{1/2} = 40$						
500	4.1×10^{-6}	481.5	±0.95	507.1	±1.05	±7.81%
1000	1.0×10^{-6}	963.1	±0.95	1014.2	±1.05	±3.91%
1500	4.5×10^{-7}	1444.6	±0.95	1521.3	±1.05	±2.60%

given reaction takes place.) This restriction has been taken into account by

$$20 \leq \frac{E}{RT^0_{1/2}} \leq 40 \tag{22}$$

where $T^0_{1/2}$, which may be called the temperature at the half-life, belongs to $x^0 = 0.5$. From these conditions the values of T_1^0, T_2^0 and the right-hand side of (21) have been calculated by a computer. The results are shown in Table 1. Besides the T^0 data, the uncertainties of the corresponding T^0 values are also indicated. [These uncertainties, denoted by δT_1^0 and δT_2^0, are the highest values of $T^0(t) - T(t)$ permitted by eqn. (1).] It can easily be shown, that a difference $1/T_1^0 - 1/T_2^0$, which is characteristic of the width of the given thermoanalytical curve, is an increasing function of n and a decreasing function of E. Hence Table 1 shows the extrema of the error bounds of E in the domain of the conditions outlined.

It may be worth observing, that the values of T_1^0 and T_2^0 are exactly twice as high in the second row and three times higher in the third row than in the first row. This fact is the direct consequence of the invariance of the kinetic differential equation under the simultaneous multiplication of the temperature and the activation energy by the same constant. For a similar reason, the upper bounds listed in the last columns are inversely proportional to the $T^0_{1/2}$ values. If the restrictions on the differences $T^0(t) - T(t)$ were also chosen proportionally to $T^0_{1/2}$, the upper bounds obtained would be independent of the T^0 data. For example, an assumption of ±2 K at $T^0_{1/2} = 1000$ K and ±3 K at $T^0_{1/2} = 1500$ K would result in the same upper bounds as an assumption of ±1 K at $T^0_{1/2} = 500$ K.

ANOTHER APPROACH

The results of the previous sections can also be obtained if the errors in the temperature are restricted by eqn. (2) instead of eqn. (1). Outlining this deduction may be useful to get an overview of the problem.

Let us choose two points of time, t_1 and t_2, in the same way as in the previous sections and let us look for the extrema of the corresponding x_1 and x_2 values under the validity of (2). The $T(t)$ giving the highest x_1 and x_2 under the validity of (2) is $T'(t) \equiv T^0(t) + h'$. The lowest x_1 and x_2 can be obtained at $T''(t) \equiv T^0(t) - h'$. Denoting the solutions of the kinetic differential equation at $T'(t)$ and $T''(t)$ by $x'(t)$ and $x''(t)$, respectively, we can write

$$\max x_1 = x'(t_1) \qquad \max x_2 = x'(t_2) \tag{23}$$
$$\min x_1 = x''(t_1) \qquad \min x_2 = x''(t_2)$$

If $T^0(t)$ is approximately linear, $T'(t)$ and $T''(t)$ will also be approximately linear and we can apply the same approximate equation for the description of data (x^0, T^0), (x', T') and (x'', T''). The simplest approximative equation has been proposed by Doyle [11] and is given by

$$\ln g(x^0) \cong C - \frac{cE}{RT^0} \tag{24}$$

where C and c are constants.

From eqn. (24)

$$E \cong Rc^{-1} \frac{\ln g(x_2^0) - \ln g(x_1^0)}{1/T_1^0 - 1/T_2^0} \tag{25}$$

Applying eqn. (24) for data (x', T') and (x'', T''), we can write eqns. (23) in the form

$$\begin{aligned} \max \ln g(x_1) &\cong C - \frac{cE}{R(T_1^0 + h')} \\ \max \ln g(x_2) &\cong C - \frac{cE}{R(T_2^0 + h')} \\ \min \ln g(x_1) &\cong C - \frac{cE}{R(T_1^0 - h')} \\ \min \ln g(x_2) &\cong C - \frac{cE}{R(T_2^0 - h')} \end{aligned} \tag{26}$$

Note that x_1 and x_2 cannot vary independently in the domain of their extrema since the maximum of x_2 implies the maximum of x_1 and the minimum of x_2 implies the minimum of x_1. Nevertheless, if only upper and lower bounds are deduced, we can formally introduce these extrema into the estimator of E. Denoting the upper and lower bound of E by E_{up} and E_{low}, respectively, eqns. (25) and (26) yield

$$\begin{aligned} \frac{E_{\text{up}}}{E} &\cong \frac{\max \ln g(x_2) - \min \ln g(x_1)}{\ln g(x_2^0) - \ln g(x_1^0)} \\ &\cong \frac{1/(T_1^0 - h') - 1/(T_2^0 + h')}{1/T_1^0 - 1/T_2^0} \end{aligned} \tag{27}$$

and

$$\begin{aligned} \frac{E_{\text{low}}}{E} &\cong \frac{\min \ln g(x_2) - \max \ln g(x_1)}{\ln g(x_2^0) - \ln g(x_1^0)} \\ &\cong \frac{1/(T_1^0 + h') - 1/(T_2^0 - h')}{1/T_1^0 - 1/T_2^0} \end{aligned} \tag{28}$$

The right-hand sides of eqns. (27) and (28) can be interpreted in such a way that the relative error of E is bounded by the relative error of the distances $1/T_1^0 - 1/T_2^0$. Hence eqns. (27) and (28) are practically equivalent to inequality (21). This approximate equivalence can easily be checked with the temperature data of Table 1 at $h' = 1$ K.

As has been mentioned before, eqns. (27) and (28) represent only formal bounds. It may be worth noting that deduction of inequality (21) has also contained formal steps. The right-hand side of eqn. (10) has been formally increased for taking out the $e^{2hE/R}$ factor and a similar decrease has been carried out in the deduction of inequality (13). These mathematical operations have only slight effects on the magnitude of the results if t_1 and t_2 are chosen somewhere at the beginning and the end of the thermoanalytical curves, respectively. If t_1 and t_2 were closer to each other, the formal increases and decreases would result in worse upper and lower bounds.

ESTIMATION OF THE FORMAL REACTION ORDER

In the previous sections, function $f(x)$ has been assumed to be known. However, $f(x)$ may contain unknown parameters and the determination of an unknown parameter of $f(x)$ is a frequent task in non-isothermal reaction kinetics. The most frequently used $f(x)$ with one unknown parameter is $f(x) = (1 - x)^n$. In this section the estimation of n will be discussed. For many reaction types, n can be interpreted physically or chemically. This fact does not affect the analysis of the reliability of the n values estimated.

As is well known, there is a definite correlation between the shape of thermoanalytical curves and the formal reaction order [13–15]. It is also known that the shape of the differential thermoanalytical curves is far more characteristic of n than the shape of the integral curves. From a mathematical point of view, however, the differential and the integral curves are equivalent. This means, that a significant difference between the actual and the known temperature destroys the information content of $dx(t)/dt$ and $x(t)$ to the same extent. Hence we can treat the evaluation of n from $x(t)$, which, from a mathematical point of view, seems to be an easier problem. Let us restrict the treatment to $T^0(t)$ functions at which eqn. (6) can be approximated by an equation of type

$$\ln g(x^0) = C + \frac{C'}{T^0} \tag{29}$$

Here C and C' stand for constants depending on A, E and on the temperature domain of the given reaction [6,11,12]. Note that C' is not necessarily proportional to E [12]. At a hyperbolic $T^0(t)$ eqn. (29) is exact [16]. At a linear $T^0(t)$, eqn. (29) is a good approximation [11,12] but it is not sufficiently good for reliable deduction of such important characteristics as the reacted mole fraction at the peak maximum [6,14]. [Deductions involving the place of the peak maximum require reliable knowledge of the second differential quotient of x and equations of type (29) can hardly provide it.]

However, in the present paper no differential quotient will be used and in the numerical examples of the next section, eqn. (29) has proved equivalent to the more precise Coats–Redfern-type approximations.

If eqn. (29) is written for three or more (x^0,T^0) data pairs, C and C' can be eliminated and an equation can be obtained for n. Let us choose three points of time, t_1, t_2 and t_3, and let us denote the corresponding x^0 and T^0 values by subscripts 1, 2 and 3, respectively. In this way we obtain

$$\frac{\ln \mathrm{g}(x_3^0)-\ln \mathrm{g}(x_2^0)}{\ln \mathrm{g}(x_2^0)-\ln \mathrm{g}(x_1^0)}=\frac{-1/T_3^0+1/T_2^0}{-1/T_2^0+1/T_1^0} \tag{30}$$

The geometric interpretation of this type of equation will be discussed in a separate short communication. The numerical solution of this equation gives the value of n. If data x^0 are replaced by the real x values, an error arises. We shall look for the extrema of this error under the validity of (1).

Let us carry out the integration of the kinetic equation separately in the intervals $0 \le t \le t_1$, $t_1 \le t \le t_2$ and $t_2 \le t \le t_3$. For the sake of compactness, we shall introduce the notation $t_0=0$, $x_0=0$ and we shall speak of intervals $t_i \le t \le t_{i+1}$ and $x_i \le x \le x_{i+1}$ where i may be 0, 1 or 2. Denoting the integral of $1/\mathrm{f}(x)$ in an interval $x_i^0 \le x \le x_{i+1}^0$ by $\mathrm{G}(x_i^0,x_{i+1}^0)$ we get

$$\mathrm{G}(x_i^0,x_{i+1}^0)=\int_{t_i}^{t_{i+1}} \mathrm{e}^{-E/RT^0}\mathrm{d}t \tag{31}$$

Now let us regard the extrema of the quantities $\mathrm{G}(x_i,x_{i+1})$. Under the validity of eqn. (1) their maximum can be obtained when $1/T(t)=1/T^0(t)-h$ in the interval $t_i \le t \le t_{i+1}$, while their minimum belongs to $1/T(t)=1/T^0(t)+h$. Hence

$$\begin{aligned}\max \mathrm{G}(x_i,x_{i+1})&=\mathrm{e}^{hE/R}\mathrm{G}(x_i^0,x_{i+1}^0)\\ \min \mathrm{G}(x_i,x_{i+1})&=\mathrm{e}^{-hE/R}\mathrm{G}(x_i^0,x_{i+1}^0)\end{aligned} \tag{32}$$

Keeping in mind that $\mathrm{g}(x_1)\equiv\mathrm{G}(0,x_1)$, $\mathrm{g}(x_2)\equiv\mathrm{G}(0,x_1)+\mathrm{G}(x_1,x_2)$ and $\mathrm{g}(x_3)\equiv\mathrm{G}(0,x_1)+\mathrm{G}(x_1,x_2)+\mathrm{G}(x_2,x_3)$ we can write

$$\begin{aligned}\frac{\ln \mathrm{g}(x_3)-\ln \mathrm{g}(x_2)}{\ln \mathrm{g}(x_2)-\ln \mathrm{g}(x_1)}&\equiv\frac{\ln[\mathrm{g}(x_3)/\mathrm{g}(x_2)]}{\ln[\mathrm{g}(x_2)/\mathrm{g}(x_1)]}\\ &\equiv\frac{\ln[1+\mathrm{G}(x_2,x_3)/\{\mathrm{G}(0,x_1)+\mathrm{G}(x_1,x_2)\}]}{\ln[1+\mathrm{G}(x_1,x_2)/\mathrm{G}(0,x_1)]}\end{aligned} \tag{33}$$

It can be seen immediately that the right-hand side of this equation is an increasing function of $\mathrm{G}(x_2,x_3)$ and a decreasing function of $\mathrm{G}(x_1,x_2)$. The dependence on $\mathrm{G}(0,x_1)$ is not so obvious, thus the effects of $\mathrm{G}(0,x_1)$ have been studied numerically. [$\mathrm{G}(0,x_1)$ has been stepped between its minimum and maximum by the computer program used for the numerical examples.] In all of the cases studied the right-hand side of eqn. (33) has proved to be an increasing function of $\mathrm{G}(0,x_1)$. Hence the $T(t)$ maximizing the right hand side of eqn. (30) is defined by the equations

$$\begin{aligned}
&\frac{1}{T(t)}=\frac{1}{T^0(t)}-h \qquad &&\text{if } 0 \leq t < t_1\\
&\frac{1}{T(t)}=\frac{1}{T^0(t)}+h \qquad &&\text{if } t_1 < t < t_2\\
&\frac{1}{T(t)}=\frac{1}{T^0(t)}-h \qquad &&\text{if } t_2 < t \leq t_3
\end{aligned} \tag{34}$$

In a similar way, the minimum has been obtained at

$$\begin{aligned}
&\frac{1}{T(t)}=\frac{1}{T^0(t)}+h \qquad &&\text{if } 0 \leq t < t_1\\
&\frac{1}{T(t)}=\frac{1}{T^0(t)}-h \qquad &&\text{if } t_1 < t < t_2\\
&\frac{1}{T(t)}=\frac{1}{T^0(t)}+h \qquad &&\text{if } t_2 < t \leq t_3
\end{aligned} \tag{35}$$

The considerations outlined readily give expressions for the maximum and minimum of the right-hand side of eqn. (30). The corresponding maximal and minimal values of n need to be calculated numerically.

NUMERICAL EXAMPLES

For the application of eqn. (30) three points need to be chosen on the experimental x vs. T^0 curve. Accordingly, in the construction of numerical examples we need to choose three x^0 values. From a mathematical point of view, any choice of x_1^0, x_2^0 and x_3^0 is acceptable. Obviously, we want the error bounds to be as sharp as possible. Test calculations have shown that this can be achieved if x_1 and x_3 are chosen at the very beginning and end of the thermoanalytical curves and x_2 is close to x_3. Such a choice, however, looks somehow irrelevant to the modelling of a real evaluation process. Thus, as a compromise, the values of $x_1^0 = 0.1$, $x_2^0 = 0.6$ and $x_3^0 = 0.9$ have been chosen.

The errors of n are obviously dependent on the errors in the temperature. In the numerical examples the relative precision of the temperature has been assumed to be about 0.1%. At low temperatures this would correspond to a rather tight restriction. At room temperature, for example, this would correspond to an uncertainty of ± 0.3 K. However, in the domain studied the errors in n are roughly proportional to the errors in T^0, thus the error bounds relating to a precision of 0.2 or 0.3% can readily be obtained by multiplying the listed data by 2 or 3, respectively.

For the choice of E, we have assumed that $20 \leq E/RT_m \leq 40$, where T_m is the middle point of the temperature domain of the given reaction. Since the

TABLE 2

Error bounds for the estimation of n by eqn. (30)
[$T^0 - T \cong \pm T/1000$; $x_1^0 = 0.1$; $x_2^0 = 0.6$; $x_3^0 = 0.9$; $E/RT_m = 20$ (I) and 40 (II).]

n	I	II
0	±0.07	±0.13
0.50	±0.07	±0.14
1.00	±0.07	±0.15
1.50	±0.07	±0.15
2.00	±0.08	±0.17

relative precision of T^0 is about hT_m [see eqns. (4)], the assumptions on the relative precision of T^0 and the values of E can be summarized as $0.02 \leq hE/R \leq 0.04$. Table 2 contains the bounds obtained for n at $hE/R = 0.02$ and $hE/R = 0.04$. These values show that the experimental determination of the finer details of the mechanism, e.g. the distinction of a mechanism of $n = 1/2$ from a mechanism of $n = 2/3$, may be problematic if the temperature errors are higher than 0.1%. However, the magnitude of the kinetic parameters is not destroyed by the assumed errors of T. It may be worth emphasizing that the activation energy only slightly inherits the errors of n. For example, an error of $n = 0.25$ causes an error of only 8–10% in the estimation of E [5].

ALTERNATIVE EQUATIONS

The deductions of the previous two sections could also have been carried out using Coats–Redfern-type approximations, which have better precision [10]. In the Coats–Redfern type of approximations, $\ln[g(x)/T^2]$ is expressed as a linear function of $1/T$. Hence eqn. (30) would be replaced by

$$\frac{\ln g(x_3^0) - \ln g(x_2^0) - 2\ln(T_3^0/T_2^0)}{\ln g(x_2^0) - \ln g(x_1^0) - 2\ln(T_2^0/T_1^0)} \cong \frac{-1/T_3^0 + 1/T_2^0}{-1/T_2^0 + 1/T_1^0} \tag{36}$$

The right-hand sides of eqns. (30) and (36) are identical. The deviation of their left-hand sides depends on the range in which the values of T^0 vary. Hence this deviation is higher at low values of E. (Low activation energies result in wide thermoanalytical curves.) Table 3 shows the values of the left-hand sides of eqns. (30) and (36). The error bounds of n calculated from eqn. (36) have proved identical with the data in Table 2.

Another approach is to use more than three points in the calculation of n. Test calculations have been carried out on up to 12 points but the error bounds obtained have not been significantly different from the data in Table 2. This is not surprising, since the increase in the number of experi-

TABLE 3

The values of the left-hand sides of eqns. (30) and (36)
[$x_1^0 = 0.1$; $x_2^0 = 0.6$; $x_3^0 = 0.9$; $20 \leq E/RT_{1/2} \leq 40$.]

n	Eqn. (30)	Eqn. (36)
0	0.226	0.225–0.226
0.50	0.315	0.314–0.315
1.00	0.426	0.423–0.425
1.50	0.553	0.549–0.552
2.00	0.688	0.682–0.687

TABLE 4

Error bounds for the estimation of n by eqn. (37)
[$T^0 - T \cong \pm T/1000$; $x_1^0 = 0.1$; $x_2^0 = 0.3$; $x_3^0 = 0.6$; $x_4^0 = 0.9$; $E/RT_m = 20$ (I) and 40 (II).]

n	I	II
0	±0.06	±0.12
0.50	±0.06	±0.13
1.00	±0.07	±0.14
1.50	±0.07	±0.15
2.00	±0.08	±0.17

mental points can decrease only the random errors while in this paper systematic errors have been studied. As an illustration, the results obtained at four points will be shown here. If eqn. (29) is written for four (x^0, T^0) points, we get

$$\frac{\ln g(x_4^0) - \ln g(x_3^0)}{\ln g(x_2^0) - \ln g(x_1^0)} \cong \frac{-1/T_4^0 + 1/T_3^0}{-1/T_2^0 + 1/T_1^0} \tag{37}$$

This equation is analogous to eqn. (30) and it can be analysed by the same mathematical methods. The results at $x_1^0 = 0.1$, $x_2^0 = 0.3$, $x_3^0 = 0.7$ and $x_4^0 = 0.9$ are shown in Table 4. These error bounds are a little bit sharper than the data of Table 2.

SHARPER ERROR BOUNDS

As has been outlined in the beginning of the paper, the most troublesome temperature error seems to be caused by the enthalpy change of the reaction. (In our opinion the effects of the other temperature errors on the kinetic parameters are usually far smaller.) Thus the treatment may frequently be confined to the "self heating" and "self coloing" caused by the positive or negative heat of reaction. For endothermic reactions, the differences $1/T^0 - 1/T$, $T - T^0$ and $(T - T^0)/T$ may be restricted to intervals $[-h,0]$, $[-h',0]$, and $[-h'',0]$ while for endothermic reactions these intervals would be $[0,h]$, $[0,h']$ and $[0,h'']$, respectively. In this way eqn. (21) may be replaced by

$$\frac{|\delta^0 E|}{E} < \frac{h}{1/T_1^0 - 1/T_2^0} \tag{38}$$

For endothermic reactions, eqns. (27) and (28) give

$$\frac{E_{\text{up}}}{E} \cong \frac{1/(T_1^0 - h') - 1/T_2^0}{1/T_1^0 - 1/T_2^0} \tag{39}$$

and

$$\frac{E_{\text{low}}}{E} \cong \frac{1/T_1^0 - 1/(T_2^0 - h')}{1/T_1^0 - 1/T_2^0} \tag{40}$$

while for exothermic reactions we get

$$\frac{E_{\text{up}}}{E} \cong \frac{1/T_1^0 - 1/(T_2^0 + h')}{1/T_1^0 - 1/T_2^0} \tag{41}$$

and

$$\frac{E_{\text{low}}}{E} \cong \frac{1/(T_1^0 + h') - 1/T_2^0}{1/T_1^0 - 1/T_2^0} \tag{42}$$

Table 5 contains error bounds for n. These data have been calculated from eqn. (37) with the same values of x^0 and hE/R as Table 4.

Equations (38)–(42) and Table 5 show that the exclusion of the positive or negative temperature errors diminishes the error bounds of E and n by a factor of about 0.5.

TABLE 5

Error bounds for the estimation of n by eqn. (37) when $T^0 \geqslant T$
[$\max(T^0 - T) \cong T/1000$; $x_1^0 = 0.1$; $x_2^0 = 0.3$; $x_3^0 = 0.6$; $x_4^0 = 0.9$; $E/RT_{\text{m}} = 20$ (I) and 40 (II).]

n	I	II
0	±0.03	±0.06
0.50	±0.03	±0.06
1.00	±0.03	±0.07
1.50	±0.04	±0.07
2.00	±0.04	±0.08

ESTIMATION OF E AND n

When $f(x) = (1-x)^n$, the estimation of E from a single non-isothermal measurement requires knowledge of n. If n is determined from experimental data, E inherits the errors of n to a certain extent. As eqn. (25) shows, E is roughly proportional to quantities of type $\ln[g(x_1)/g(x_2)]$. To express the dependence of E on n explicitly, let us introduce the notation

$$L(n,x_1,x_2) \equiv \ln[g(x_1)/g(x_2)] \tag{43}$$

and let us apply the 15th eqn. of ref. 5 in the form

$$\frac{\partial}{\partial n} L(n,x_1,x_2) \approx 0.33\ L(n,x_1,x_2) \tag{44}$$

Let n and n^{obs} stand for the true and the experimentally obtained values of n, respectively, and let us combine eqn. (44) with a first order Taylor series

$$\begin{aligned} L(n^{\text{obs}},x_1,x_2) &\cong L(n,x_1,x_2) + (n^{\text{obs}} - n)\frac{\partial L}{\partial n} \\ &\cong L(n,x_1,x_2)\left[1 + 0.33(n^{\text{obs}} - n)\right] \end{aligned} \tag{45}$$

In the section entitled "Another approach", upper and lower bounds have been deduced for E by eqns. (27) and (28). Substituting n^{obs} for n in terms $\ln[g(x_1)/g(x_2)]$ and applying notation (43) and eqn. (45) we get

$$\begin{aligned} \frac{E_{\text{up}}}{E} &\cong \frac{\max L(n^{\text{obs}},x_1,x_2)}{L(n,x_1^0,x_2^0)} \\ &\cong (1 + 0.33|n^{\text{obs}} - n|)\frac{1/(T_1^0 - h') - 1/(T_2^0 + h')}{1/T_1^0 - 1/T_2^0} \end{aligned} \tag{46}$$

and

$$\begin{aligned} \frac{E_{\text{low}}}{E} &\cong \frac{\min L(n^{\text{obs}},x_1,x_2)}{L(n,x_1^0,x_2^0)} \\ &\cong (1 - 0.33|n^{\text{obs}} - n|)\frac{1/(T_1^0 + h') - 1/(T_2^0 - h')}{1/T_1^0 - 1/T_2^0} \end{aligned} \tag{47}$$

Substituting the data of Table 4 for $|n^{\text{obs}} - n|$, we find that an additional error term of about 2–6% is added to the right-hand side of eqns. (27) and (28). Regarding the temperature data of Table 1, we find that the assumption of temperature errors of about ±0.1% leads to relative error bounds of between 3 and 10%. It should be noted, however, that substitution of the data in Table 4 for $|n^{\text{obs}} - n|$ is only a formal operation which leads to an over-estimation of the errors of E. In reality, the $T(t)$ maximizing the errors of n does not maximize the errors of E and vice versa.

CONCLUSIONS

The considerations outlined show that the difference between the actual and the known temperature of the sample can result in signifcant errors in the kinetic parameters. As has been underlined, the non-linearity of the heating program itself does not disturb a mathematically correct parameter estimation. The really troublesome errors are the non-linear components of the difference between the actual and the known temperature–time function. These errors can deform the shape of the thermoanalytical curves and in this way distort the estimated values of n and E. Their effects cannot be eliminated by mathematical means since any good evaluation method has to result in a good fit between the observed and the theoretically calculated shape of the thermoanalytical curves. The good quality of the up-to-date measuring equipment, however, permits the use of sufficiently small samples in which the thermal gradient is negligible at low or moderate heating rates. Regarding the measurement of temperature, such systematic errors which are a quickly changing function of the temperature can probably be avoided with some care. [As has been underlined earlier, the slowly changing or constant systematic errors of $T^0(t)$ have only slight effects on the value of n and E.]

ACKNOWLEDGEMENTS

The author thanks Prof. Gy. Varsányi and Dr. F. Till for their help and advice.

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