"Model-free" kinetic analysis?

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Abstract

All kinetic analyses aim to determine a sufficient number of kinetic parameters, usually at least an apparent Arrhenius activation energy and pre-exponential factor, and a conversion function or kinetic model (making up a 'kinetic triplet'), so that accurate extrapolations of kinetic behaviour can be made. "Model-free" methods of kinetic analysis postpone the problem of identifying a suitable kinetic model until an estimate of the activation energy has been made. A major reason for doing this is that misidentification of the kinetic model has a marked effect on the values obtained for the Arrhenius parameters in both isothermal and non-isothermal kinetic analyses. Some aspects of this problem are discussed.

The non-parametric kinetics (NPK) method [1,2] is a "model-free" method of kinetic analysis that does not seem to have received the attention that it deserves. This is probably because of its mathematical sophistication and the fact that the matrix and non-linear regression calculations involved are not readily automated. The principle of the method appears to be that of "forcing" a set of non-isothermal data into the set which should have been obtained if the experiments had been carried out isothermally. The method deserves wider testing and also raises some interesting aspects of the philosophy behind non-isothermal kinetic analysis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Non-parametric kinetics; Kinetic compensation effect; Model-free methods

1. Introduction

Although, the description "model-free" for an approach to kinetic analysis is an unfortunate choice and the alternative of "isoconversional" methods [3,4] is more precise and less misleading, this misnomer does focus attention on an important aspect of kinetic analysis, namely the influence that the choice of kinetic model has on the derivation of the Arrhenius parameters, E and A, for a rate process. The objection to the description "model-free" is that it tends to imply that knowledge of the kinetic model (or more precisely, the conversion function, $g(\alpha)$ or $f(\alpha)$, where α is the extent of conversion), that best describes the process being investigated, however complicated this may be, is not an essential piece of information in the kinetic analysis. That this is not true has been illustrated repeatedly by Maciejewski [5], and Maciejewski and Reller [6]. Without knowledge of all three of the components labelled the "kinetic triplet", the conversion function and the Arrhenius parameters, E and A, no accurate predictions of kinetic behaviour beyond the conditions of time and temperature used in the original experiments are possible. The "model-free" approach does, however, postpone, with some advantages, the consideration of the conversion function until after estimates have been made of the Arrhenius parameters. In many of the methods, overmuch attention

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is focussed on the estimation of only the activation energy, E.

The non-parametric kinetics (NPK) method of kinetic analysis, proposed by Serra et al. [1,2], is an interesting example of a "model-free" method that uses a system of submatrices derived from a set of non-isothermal experiments at different heating rates, to find the Arrhenius parameters, without any prior knowledge of the conversion function. Although, the method is rather complicated and time-consuming, and hence may not gain widespread use, it raises some interesting aspects of the philosophy behind non-isothermal kinetic analysis. Ever since the early discussions about the possibilities of extracting of kinetic information from programmed temperature experiments in general and thermal analysis results in particular, there have been "heated" debates [7] about the reliability of such kinetic parameters relative to those same parameters evaluated using the more-traditional isothermal approach. The division between these two approaches has gradually begun to lessen as more rational discussions have pointed out that both approaches have their advantages and their limitations [8]. The NPK method has the distinction of both making the claim to be "model-free" and contributing to the blurring of the division between isothermal and non-isothermal kinetic analyses, as is discussed in detail below.

2. Misidentification of the kinetic model

2.1. Kinetic models and conversion functions

A set of conversion functions, $g(\alpha)$ or $f(\alpha)$, derived for a variety of kinetic models [9,10], has been in use for many years for the kinetic analysis of solid-state reactions. This set has been criticised [11] for being too limited and, hence, for forcing researchers to pick the statistically best model (or even a limited group of statistically-equivalent models) from this set to describe their experimental results instead, perhaps, of exploring the possible applicability of some more-complicated model. This is a valid criticism, but it tends to ignore the practical difficulties of distinguishing between the applicability of the existing models [12]. Experimental data have to be highly reproducible before the additional effort required in exploring

greater complexity is warranted. Describing experimental data by some conversion function with an increased number of adjustable parameters is of little value unless these parameters can be given some physical significance [13]. Amongst the many excellent contributions to kinetic analysis made by Vyazovkin and Wight [14], is a discussion of the statistical background to identifying which model, or group of models, best describes a rate process. Because of the idealised nature of the models, real processes can often be described equally well by more than one model. An example would be a real process, such as decomposition of an asymmetric crystal, described by a contracting-geometry model with dimensions between 2 and 3.

2.2. Reduced-time plots

It is fairly generally accepted that attempts to identify the kinetic model are simplified if the results of isothermal experiments are available for analysis. The results of a series of experiments at different isothermal temperatures can be converted to a composite reduced-time plot [9,10,15]. The real-time values in each experiment are converted to reduced-time values by setting the time, t_α, required for the extent of conversion, α, to reach some reference value usually, but not necessarily [15], $\alpha = 0.50$ as unit reduced-time and then all other real times are converted to reduced times by division by the same factor (t_α). If the curves are superimposable (within the limits of the reproducibility at individual temperatures), the conversion function does not change with temperature and the kinetic model may be temporarily eliminated from consideration while the Arrhenius parameters are determined from the scaling factors used to convert the real times to reduced times [9,10,15]. Such an approach is thus the equivalent of the non-isothermal approaches that have been labelled "model free" or "isoconversional". If the conversion function does change with temperature, the composite plots are not superimposable and the Arrhenius parameters would be found to depend upon α. From a superimposable plot (or for any individual isothermal plot), the kinetic model, or models, that come closest to describing the experimental results can be determined by quantitative comparison of the experimental results with the predicted reduced-time curves for the models [9,10,15].

2.3. Non-isothermal isoconversional methods

A series of programmed temperature experiments at different heating rates provides an alternative (or additional) means of estimating the activation energy, E, and any dependence of E on the extent of conversion, α, [3,4], by temporary elimination of the conversion function and the pre-exponential factor, A, during the solution of simultaneous equations. The subsequent identification of the conversion function and any dependence upon temperature is not as straightforward [16]. In both isothermal and non-isothermal approaches, a dependence of one or both of the Arrhenius parameters on the extent of reaction, α, is a warning of complexity that must be examined further [14]. An additional complication, always hovering in the background, is the interdependence of the Arrhenius parameters through the so-called "kinetic compensation effect" [17,18].

2.4. Misidentification of the model during isothermal kinetic analysis

Assume that, for a particular isothermal process, the rate equation is

$$g(\alpha) = kt = At \exp\left(-\frac{E}{RT}\right)$$

so

$$E = RT\left(-\ln\left[\frac{g(\alpha)}{At}\right]\right)$$

If the true conversion function $g(\alpha)$ is misidentified as some other model, $g^*(\alpha)$, say, then there will obviously be an error in E that will vary with α, because of the differences between $g(\alpha)$ and $g^*(\alpha)$.

$$g^*(\alpha) = k^* t = At \exp\left(-\frac{E^*}{RT}\right)$$

$$E^* = RT\left(-\ln\left[\frac{g^*(\alpha)}{At}\right]\right)$$

Alternatively, the error could be regarded as arising in the pre-exponential factor, A. The differences in the conversion functions, $g(\alpha)$, with extent of reaction, α, for the well-known sigmoidal group of JMAEK models [9,10], with different values of the exponent n, are shown in Fig. 1. Vyazovkin and Wight [16] have given
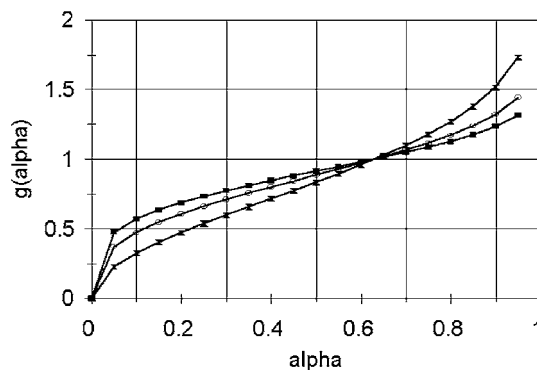

Fig. 1. The differences in the conversion functions, $g(\alpha)$, with extent of reaction, α, for the sigmoidal group of JMAEK models An: (circles) A3; (rectangles) A4; and (crosses) A2.

a plot containing a wider range of the models. In Fig. 2, the consequences of misidentifying the "true" A3 model (with "true" E set at 100 kJ mol^{-1} and "true" $A = 4.0 \times 10^8$ min^{-1}, so as to give $\alpha = 0.95$ at $t = 100$ min at 500 K) as A4 or A2 are shown as a dependence of E upon α.

Similar results for a deceleratory group of models that are difficult to distinguish are shown in Fig. 3, where the F1 kinetic model (with E set at 100 kJ mol^{-1} and A as 8.4×10^8 min^{-1}) has been misidentified as R2 and R3, and in Fig. 4, where the F1 kinetic model has been misidentified as F2 and F3. In Fig. 5, the R3 kinetic model (with E set at 100 kJ mol^{-1} and A as 1.8×10^8 min^{-1}) has been misidentified as R2 and F1.
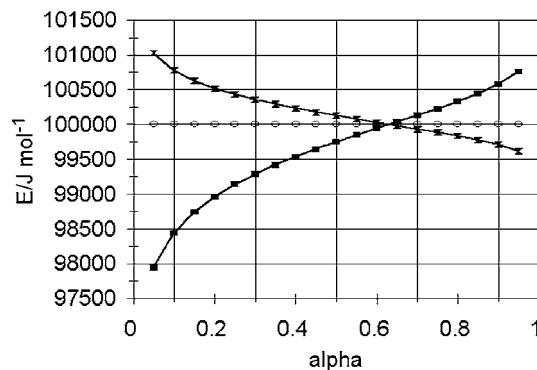

Fig. 2. The consequences of misidentifying the "true" (circles) A3 model (with "true" E set at 100 kJ mol^{-1} and "true" $A = 4.0 \times 10^8$ min^{-1}) as (crosses) A4 or (rectangles) A2 are shown as a dependence of E upon α.
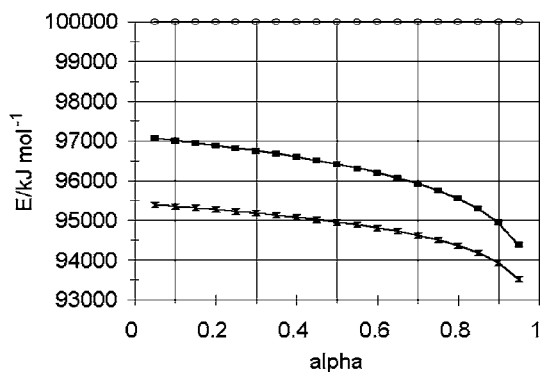
Fig. 3. The F1 kinetic model (circles) (with E set at 100 kJ mol^{-1} and A as 8.4×10^8 min^{-1}) has been misidentified as (rectangles) R2 and (crosses) R3.

The results illustrated here refer to those groups of models that are notoriously difficult to distinguish [12]. If all the possible combinations were explored entirely mechanically, without regard for the most likely misidentifications, the differences in the apparent Arrhenius parameters would be even greater.

2.5. Misidentification of the model during non-isothermal kinetic analysis

An early method of kinetic analysis suggested by Piloyan et al. [19] starts from

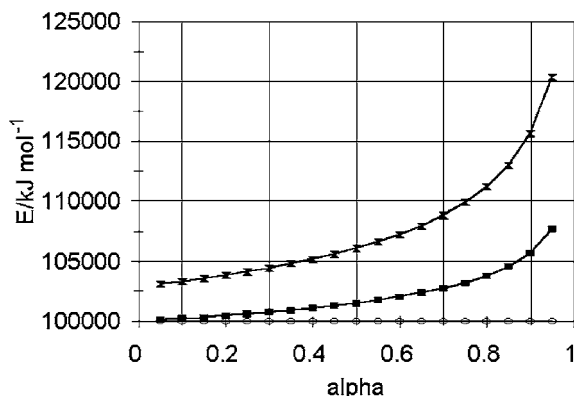$$\frac{d\alpha}{dt} = Af(\alpha) \exp\left(-\frac{E}{RT}\right)$$

Fig. 4. The F1 kinetic model (circles) (with E set at 100 kJ mol^{-1} and A as 8.4×10^8 min^{-1}) has been misidentified as (rectangles) F2 and (crosses) F3.
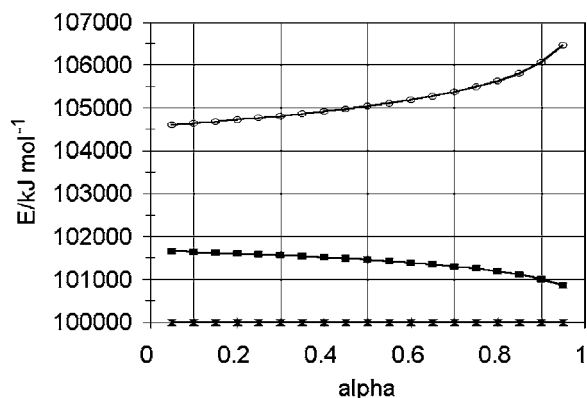

Fig. 5. The (crosses) R3 kinetic model (with E set at 100 kJ mol^{-1} and A as 1.8×10^8 min^{-1}) has been misidentified as (rectangles) R2 and (circles) F1.

and hence

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + \ln[f(\alpha)] - \frac{E}{RT} \quad (1)$$

They proposed that the term $\ln[f(\alpha)]$ could be neglected and the value of E (and $\ln A$) estimated from a plot of $\ln(d\alpha/dt)$ against $1/T$. They stated [19] that the error in E values estimated in this way could be of the order of 15–20%. Although, this method falls into the now discredited group of methods which attempt to obtain the kinetic triplet from a single programmed temperature experiment, Criado and Ortega [20] have also pointed out that this limitation has often been overlooked and they have published detailed calculations of the errors in E resulting from this assumption. The derivative and integral conversion functions, $f(\alpha)$ and $g(\alpha)$, respectively are related through

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \left(\frac{AE}{\beta R}\right) p(x)$$

where $x = E/RT$ and $p(x)$ is the temperature integral. Hence,

$$\ln g(\alpha) = \ln\left(\frac{AE}{\beta R}\right) + \ln p(x)$$

They then used the Doyle approximation [21]:

$$\ln p(x) = -5.331 - 1.052x$$

to obtain

$$\ln g(\alpha) = \ln\left(\frac{AE}{\beta r}\right) - 5.33 - 1.05\left(\frac{E}{RT}\right) \quad (2)$$

From Eqs. (1) and (2):

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[f(\alpha)g(\alpha)^{1/1.05}] + \text{constant}$$

If it is assumed that the following relationship holds:

$$\ln[f(\alpha)g(\alpha)^{1/1.05}] = a\ln g(\alpha) + b \quad (3)$$

where a and b are constants, then

$$\ln\left(\frac{d\alpha}{dt}\right) = -1.05a\left(\frac{E}{RT}\right) + \text{constant}$$

Thus, the slope of a plot of $\ln(d\alpha/dt)$ against $1/T$ would give an apparent activation energy, $E^* = 1.05aE$. The percentage error in the activation energy is then:

$$\varepsilon = 100\frac{E^* - E}{E} = 100(1.05a - 1)$$

Eq. (3) was found [20] to apply to the standard models with values of a ranging from 0.35 (D3 model) to 2.25 (A3 model) and, hence, neglect of the model in the Piloyan method could lead to errors in the activation energy of from -62% (D3 model) to $+142\%$ (A3 model).

Koga et al. [22] have discussed the distortion of the Arrhenius parameters caused by the selection of an inappropriate kinetic model in non-isothermal kinetic analyses based on measurements of the temperature, T_p, and conversion, α_p, at which the conversion rate is a maximum. The distortion in the values of E is given by

$$\frac{E^*}{E} = \frac{[f(\alpha_p)f^{*\prime}(\alpha_p)]}{[f^\prime(\alpha_p)f^*(\alpha_p)]}$$

where $f(\ )$ and $f^\prime(\ )$ are the derivative and second derivative conversion functions, respectively, and * labels the misidentified function, as used above.

The distortion in the value of $\ln(A)$ is given by [22]:

$$\ln\left(\frac{A^*}{A}\right) = \left(\frac{E}{RT_p}\right)\left\{\frac{(f(\alpha_p)f^{*\prime}(\alpha_p) - f^\prime(\alpha_p)f^*(\alpha_p)}{f^\prime(\alpha_p)f^*(\alpha_p)}\right\}$$
$$+ \ln\left(\frac{f(\alpha_p)}{f^*(\alpha_p)}\right)$$

Using various combinations of true and misidentified functions, they obtained values of E^*/E ranging from 0.46 to 4.23 and of $\ln(A^*/A)$ from -12.8 to $+80.7$.

Málek [23] extended this approach and related the apparent activation energy, E^*, to the the true activation energy, E, by a multiplicative factor, q:

$$E^* = qE$$

where the value of q is characteristic of the true kinetic model [23].

3. The NPK method of kinetic analysis

In brief, and hopefully fair summary, the NPK method [1,2] involves the following. The basic rate equation is assumed to be able to be written as

$$\text{rate} = \frac{d\alpha}{dt} = f(\alpha)h(T) \quad (1)$$

where $f(\alpha)$ is the derivative form of the conversion function (the corresponding integral form is $g(\alpha)$ as used above) and the temperature-dependent function, $h(T)$, is usually the Arrhenius equation:

$$h(T) = k = A\exp\left(-\frac{E}{RT}\right)$$

The rate, $d\alpha/dt$, can thus be expressed as a three-dimensional surface determined by the temperature, T, and the degree of conversion, α. Serra et al. [1,2] suggested that this surface should be discretised as an $(n \times m)$ matrix $\boldsymbol{A}$ of which the elements of the rows are rates at constant α, but varying temperatures, and the elements of the columns are rates at constant temperature, but varying α.

$$\boldsymbol{A} = \begin{matrix} f(\alpha_1)h(T_1) & f(\alpha_1)h(T_2) & f(\alpha_1)h(T_3) & \dots & f(\alpha_1)h(T_m) \\ f(\alpha_2)h(T_1) & f(\alpha_2)h(T_2) & f(\alpha_2)h(T_3) & \dots & f(\alpha_2)h(T_m) \\ \dots & \dots & \dots & & \dots \\ \dots & \dots & \dots & & \dots \\ f(\alpha_n)h(T_1) & f(\alpha_n)h(T_2) & f(\alpha_n)h(T_3) & \dots & f(\alpha_n)h(T_m) \end{matrix}$$

The matrix A can be written as the product of two vectors:

$$A = fh^{\mathrm{T}}$$

where

$$f^{\mathrm{T}} = [f(\alpha_1)f(\alpha_2)f(\alpha_3) \cdots f(\alpha_n)]$$

$$h^{\mathrm{T}} = [h(T_1)h(T_2)h(T_3) \cdots h(T_m)]$$

Applying the mathematical procedure known as singular value decomposition (SVD) to matrix A, provides the vectors f and h, without any prior assumptions about the forms of the conversion function, $f(\alpha)$, or the temperature-dependent function, $h(T)$. From these two vectors, plots of $f(\alpha)$ against α and of $h(T)$ against T are immediately available and the nature of the functions $f(\alpha)$ and $h(T)$ can be determined. Plots of the calculated values of $f(\alpha)$ against α for most of the models have been published [24,25]. If, as is almost always the case, the Arrhenius equation describes the temperature dependence, the parameters, A and E, for the process can be calculated.

Amidst the mathematical complexity, the principle of the method may be easily overlooked. Sets of non-isothermal data (reaction rate against temperature) obtained at different heating rates, β, are being "forced" into the sets which would have been obtained if the experiments had been carried out isothermally, that is, each column of the matrix is a set of rate against alpha data at a constant temperature.

How does this differ in principle from what have been named isoconversional methods [3,4]? The general principle of isoconversional methods is that for sets of non-isothermal data (alpha or reaction rate against temperature) obtained at different heating rates, β, sets of values of temperatures against β obtained at constant values of alpha (isoconversion) are used, with the major assumption that the form of the conversion function, $f(\alpha)$, does not change with either temperature or α, so that it can be (temporarily) eliminated from calculation of the Arrhenius parameters (on the further, but usually well-grounded, assumption that the Arrhenius equation applies). It is also usually assumed that the pre-exponential factor, A, is independent of temperature and alpha.

Fig. 6 shows four α–temperature curves simulated for a first-order reaction ($E = 110 \text{ kJ mol}^{-1}$ and $A = 1 \times 10^{12} \text{ s}^{-1}$) at different heating rates, β of 2,
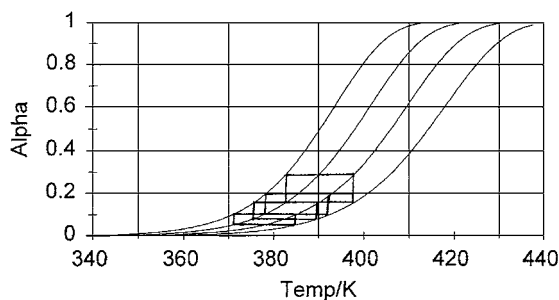

Fig. 6. Four α–temperature curves simulated for a first-order reaction ($E = 10 \text{kJ mol}^{-1}$ and $A = 1 \times 10^{12} \text{ s}^{-1}$) at different heating rates, β of 2, 4, 8 and 16 K min^{-1}. The rectangles define suggested overlapping submatrices.

4, 8 and 16 K min^{-1}. In actual practice it is not possible to find all the elements of matrix A for a sufficient range of alpha values and temperatures and hence the thermal analysis curves must be subdivided into submatrices. The rectangles shown indicate the submatrices.

If q submatrices are formed, SVD on each will produce q matrices U_i, S_i and W_i, respectively, of which only the first columns will be used.

$$A_i = u_i s_i w_i^{\mathrm{T}}$$

Each u_i and w_i will have to be multiplied by some factor to combine the u_i's to form one continuous vector u and the w_i's to form one continuous vector w, i.e.

$$u^{\mathrm{T}} = [a_1 u_1 a_2 u_2 \cdots a_q u_q]$$

$$w^{\mathrm{T}} = \left[\left(\frac{s_1}{a_1}\right) w_1 \left(\frac{s_2}{a_2}\right) v_2 \cdots \left(\frac{s_q}{a_q}\right) w_q \right]$$

where s_i is the first singular value of submatrix A_i.

Submatrices are compiled [1,2] choosing constant alpha values, (i.e. moving horizontally across Fig. 1, this is the isoconversional aspect of the method) and determining the rates at different temperatures, by numerical differentiation of the α–temperature data. The rate against temperature data for alpha values ranging from the minimum to the maximum alpha values accessible in each submatrix are obtained. The more difficult part is attempting to fill in the submatrices by estimating rates at the alpha values corresponding to vertical movement (constant temperature) in Fig. 6. This can be done using non-linear regression.

For example, for one of the rectangles in Fig. 6, the temperatures corresponding to the intersections of the curves with minimum and maximum alpha values are found. For the four curves at different heating rates, normally only three intersections are within the rectangle for any constant alpha value.

For alpha values between the maximum and minimum, the values of the intersection temperatures are different each time, so that non-linear regression has to be done using the measured rates and temperatures at constant alpha values, to determine the rates at the required temperatures. It is important to use the highest possible numerical precision in the regression. For example, alpha values of 0.061, 0.072 and 0.082 were chosen to fit between $\alpha = 0.050$ and 0.098. At $\alpha = 0.061$, the temperatures and corresponding rates from the original data were as follows:

T (K)	366	372.8	379.6	386.8
Rate	0.000204	0.000394	0.000745	0.001423

Applying the non-linear regression software NLREG [26] to these values, gave, for a second-order regression:

$$\text{rate} = a + bT + cT^2$$

where

$a = 0.320457643$, $b = -0.00175783659$ and $c = 2.41214177 \times 10^{-6}$, and for a third-order regression:

$$\text{rate} = a + bT + cT^2 + dT^3$$

where

$a = -3.00539992$, $b = 0.0247634833$,
$c = -6.80676071 \times 10^{-5}$, $d = 6.24182082 \times 10^{-8}$.

The third-order regression gave a far better fit, so this was used and the rates at temperatures of 370.8, 377.6 and 384.8 K and alpha values of 0.061, 0.072 and 0.082, respectively were then calculated to give the second row of the submatrix as: 0.000327, 0.000618, 0.001195 (values calculated from the second-order polynomial were 0.000304, 0.000626, 0.00120).

Care must be taken that overlapping submatrices contain at least one common alpha value, and that submatrices that have one side in common, also have at least one temperature in common. This becomes necessary for scaling the vectors later on Serra et al. [1,2] have suggested that the maximum alpha of one
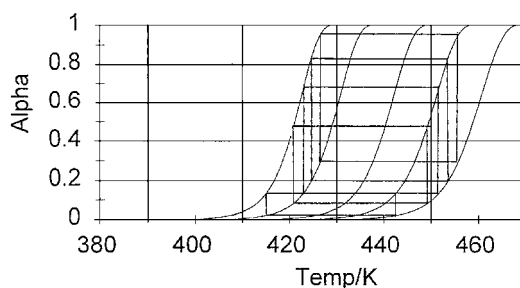

Fig. 7. The α–temperature curves simulated for a reaction following the JMAEK model [9,10] with $n = 3$ ($E = 120\,\text{kJ mol}^{-1}$ and $A = 1 \times 10^{12}\,\text{s}^{-1}$) at heating rates, β of 1, 2, 5, 10 and 20 K min^{-1}. The rectangles define suggested overlapping submatrices.

submatrix be the minimum of an alternate submatrix. This is not always very practical, as illustrated (Fig. 7) by the differently shaped α–temperature curves simulated for a reaction following the JMAEK model [9,10] with $n = 3$ ($E = 120\,\text{kJ mol}^{-1}$ and $A = 1 \times 10^{12}\,\text{s}^{-1}$) at heating rates, β of 1, 2, 5, 10 and 20 K min^{-1}. Submatrices thus have to be chosen to give as good a range of α and temperature values as possible.

SVD (using MATLAB [27] for example) of each of the submatrices produces the vectors $\boldsymbol{u}_i$ and $\boldsymbol{w}_i$, from which plots of the elements of vector $\boldsymbol{u}_i$ against the corresponding alpha values and the elements of vector $\boldsymbol{w}_i$ against the corresponding temperatures can be constructed for each submatrix $\boldsymbol{A}_i$. To get one continuous graph instead of the several separate graphs, the ordinates of the individual submatrices are scaled, using the fact that the submatrices overlap. One continuous plot can thus be formed for vector $\boldsymbol{u}$ against alpha and another for vector $\boldsymbol{w}$ against temperature.

The plots of the $f(\alpha)$ values from the compiled vector $\boldsymbol{u}$ against alpha give characteristic shapes from which the form of $f(\alpha)$ can be determined [24,25]. For example, for a first-order model, $f(\alpha) = (1-\alpha)$, so the plot is linear with unit negative slope. If a general order-of-reaction model, $f(\alpha) = (1-\alpha)^n$, applies, a plot of $\ln[f(\alpha)]$ against $\ln(\alpha)$ should be linear with the slope providing the value of the order, n. The characteristic shape of the plot for the JMAEK model with $n = 3$ is shown in Fig. 8. An alternative means of identifying the form of the conversion function is to plot the $f(\alpha)$ values against those calculated from the corresponding α values for the various reaction models [24]. These plots are linear for correct identification of
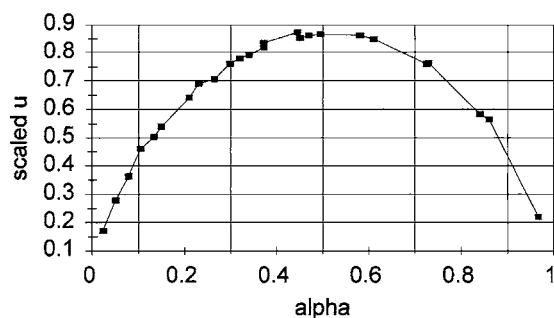
Fig. 8. A plot of $f(\alpha)$ against α for a reaction following the JMAEK model [9,10] with $n = 3$. $E = 12$ kJ mol^{-1} and $A = 1 \times 10^{12}$ s^{-1}) at heating rates, b of 1, 2, 5, 10 and 20 K min^{-1}.

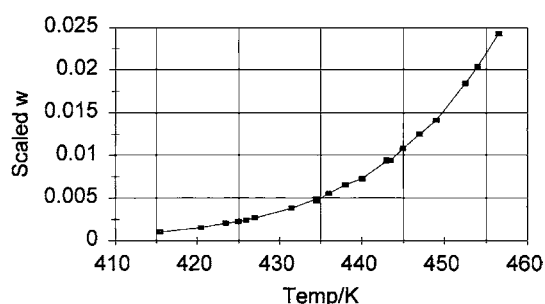Fig. 9. A plot of $h(T)$ against T for a reaction following the JMAEK model [9,10] with $n = 3$. ($E = 120$ kJ mol^{-1} and $A = 1 \times 10^{12}$ s^{-1}). An Arrhenius plot of the data shown gave an activation energy of 121.7 ± 0.5 kJ mol^{-1} and $A = (2.05 \pm 0.04) \times 10^{12}$ s^{-1}; $R^2 = 0.9997$.

the model and have characteristic shapes when the wrong model is chosen [24].

The plot of the $h(T)$ values ($k = \text{rate}/f(\alpha)$) from the vector w against temperature usually gives a typical exponential curve (Fig. 9) as expected for applicability of the Arrhenius equation. An Arrhenius plot of $\ln[h(T)]$ against $1/T$ should give a straight line with slope $= -E/R$ and intercept (as so often happens) picking up any constants (arising from scaling) in addition to A.

4. Conclusions

The distortion of Arrhenius parameters caused by misidentification of the kinetic model, using either isothermal or non-isothermal kinetic analyses, is a

good reason for postponing this problem until an estimate of the activation energy has been made using an isoconversional method [3,4]. It is important, though, to heed Maciejewski's advice that the problem is only postponed and is not avoided [5,6].

The recently proposed NPK method [1,2] has not received the attention that it probably deserves. The method does involve a large amount of calculation and the types of calculation do not lend themselves to automation, mainly due to the selection of submatrices and the calculation of missing values. The principle of the method is, however, very interesting because it appears to "force" a set of non-isothermal data into the set which should have been obtained if the experiments had been carried out isothermally, that is, each column of the matrix is a set of rate against alpha data at a constant temperature. When a set of simulated isothermal data was processed using the NPK method, the procedure recovered the input parameters.

The main assumption that the NPK method relies on is that the conversion function, $f(\alpha)$, and the temperature-dependent function, $h(T)$ can be regarded as independent of each other. Unusual results are expected if the conversion function is different over different temperature ranges and/or the Arrhenius parameters vary with extent of reaction [16]. The method has been shown [28] to be able to deal very successfully with concurrent first-order reactions.

Unlike some of the other methods labelled as "model-free" all the kinetic information is available in the two vectors. In this sense, the NPK method is similar in principle to the reduced-time method used in isothermal kinetic analysis [9,10]. In this method, the influence of temperature is temporarily eliminated to enable a check to be made on the constancy of the form of the conversion function, $f(\alpha)$ or $g(\alpha)$, over the range of isothermal temperatures used.

Maciejewski [5], and Maciejewski and Reller [6] have demonstrated very clearly the absolute necessity of describing a reaction by its complete kinetic triplet ($f(\alpha)$ or $g(\alpha)$, A and E) and has shown how predicted behaviour can be way off the mark if any one of these three factors is not known, so no kinetic method should be regarded as being more than temporarily "model-free".

Many researchers, for example Flynn and Wall [3] and Criado et al. [29], have demonstrated equally clearly the impossibility of obtaining a unique kinetic

triplet from experiments at a single heating rate. Vyazovkin and Wight [30], and Vyazovkin [31] has shown, by numerous examples, the advantages of isoconversional methods and the necessity of testing Arrhenius parameters for dependence upon extent of reaction. Such a dependence usually indicates some inadequacy in the kinetic model that is assumed to apply.

Galwey and Brown [17] have sounded repeated warnings on the apparent relationships observed between the Arrhenius parameters, E and A, known as the kinetic compensation effect. Maciejewski [5], Vyazovkin [11], Burnham and Braun [32,33] have emphasized the need for proceeding beyond the present oversimplified kinetic models of solid-state decompositions, and the NPK method [1,2], used to its full potential, appears to be a step in the right direction. It is interesting that, in principle, the method blurs the once unbridgeable gap between non-isothermal and isothermal techniques.

Acknowledgements

References

[1] R. Serra, R. Nomen, J. Sempere, Thermochim. Acta 316 (1998) 37.
[2] R. Serra, R. Nomen, J. Sempere, J. Therm. Anal. 52 (1998) 933.
[3] J.H. Flynn, L.A. Wall, J. Res. Nat. Bur. Standards 70A (1966) 487.
[4] J.H. Flynn, J. Therm. Anal. 27 (1983) 95.
[5] M. Maciejewski, Thermochim. Acta 355 (2000) 145.
[6] M. Maciejewski, A. Reller, Thermochim. Acta 110 (1987) 145.
[7] M.E. Brown, J. Therm. Anal. 49 (1997) 17.
[8] K.N. Ninan, J. Therm. Anal. 35 (1989) 1267.
[9] M.E. Brown, D. Dollimore, A.K. Galwey, Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
[10] A.K. Galwey, M.E. Brown, Thermal Decomposition of Ionic Solids, Elsevier, Amsterdam, 1999.
[11] S. Vyazovkin, Thermochim. Acta 355 (2000) 155.
[12] M.E. Brown, A.K. Galwey, Thermochim. Acta 29 (1979) 129.
[13] S.W. Churchill, The Interpretation and Use of Rate Data: The Rate Concept, McGraw-Hill, New York, 1974.
[14] S. Vyazovkin, C.A. Wight, Int. Rev. Phys. Chem. 17 (1998) 407.
[15] S. Vyazovkin, A.I. Lesnikovich, E.A. Gunin, V.G. Guslev, Thermochim. Acta 130 (1988) 269.
[16] S. Vyazovkin, C.A. Wight, Ann. Rev. Phys. Chem. 48 (1997) 125.
[17] A.K. Galwey, M.E. Brown, Thermochim. Acta 300 (1997) 107.
[18] M.E. Brown, A.K. Galwey, Thermochim. Acta 387 (2002) 175.
[19] G.O. Piloyan, I.D. Ryabchikov, O.S. Novikova, Nature 212 (1966) 1229.
[20] J.M. Criado, A. Ortega, J. Therm. Anal. 29 (1984) 1075.
[21] C.D. Doyle, J. Appl. Polym. Sci. 6 (1962) 639.
[22] N. Koga, J. Šesták, J. Málek, Thermochim. Acta 188 (1991) 333.
[23] J. Málek, Thermochim. Acta 200 (1992) 257.
[24] A.K. Galwey, M.E. Brown, Thermochim. Acta 269/270 (1995) 1.
[25] J. Málek, Thermochim. Acta 138 (1989) 337.
[26] NLREG—Nonlinear statistical regression analysis program. Phillip H. Sherrod, 6430 Annandale Cove, Brentwood, TN 615-309-8087, USA.
[27] MATLAB, The MathWorks Inc., 24 Prime Park Way, Natick, MA 01760, USA. www.mathworks.com.
[28] M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Desseyn, C.-R. Li, T.B. Tang, B. Roduit, J. Malek, T. Mitsuhashi, Thermochim. Acta 355 (2000) 125.
[29] J.M. Criado, A. Ortega, F. Gotor, Thermochim. Acta 157 (1990) 171.
[30] S. Vyazovkin, C.A. Wight, Thermochim. Acta 340/341 (1999) 53.
[31] S.V. Vyazovkin, J. Comput. Chem. 22 (2001) 178.
[32] A. Burnham, Thermochim. Acta 355 (2000) 165.
[33] A. Burnham, R.L. Braun, Energy Fuels 11 (1997) 88.