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Building and statistical interpretation of non-isothermal kinetic models

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Abstract

Main features of building non-isothermal kinetic models are discussed. The possibilities of evaluation of kinetic and temperature terms are described. Statistical methods for parameter estimation under more realistic assumptions about the nature of data are presented.

INTRODUCTION

The treatment of non-isothermal thermoanalytical data is a widely discussed topic in thermal analysis.

Many techniques exist for thermokinetic model building and estimation of parameters (especially activation energy). Linearizations and graphically oriented approximate techniques converting the non-linear optimization problem to a linear one are very attractive methods [1]. These methods lead to some parameter estimates, but without physical meaning.

The methods based on non-linear optimization lead to incorrectly stated problems with difficult solutions. The parameter estimates are often not physically acceptable, either. For a correct statement of the optimization target function (regression criterion), various statistical questions (i.e. model of measurements, statistical nature of errors, etc.) must be answered [1].

In this paper selected problems of building non-isothermal kinetic models and evaluating their parameters are presented. The corresponding statistical problems associated with the formulation of the regression criterion for parameter estimation are also discussed.

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Dedicated to Professor H. Flynn in honour of his 70th birthday.

BASIC APPROACH

A simplified thermodynamical description of chemical kinetics is based on a constitutive system of equations defining the relations between the rate of conversion $\dot{\alpha}$, the rate of temperature changes $\dot{T}$ and the state of the investigated system represented by variables (α, T). Two main relations can be defined

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \dot{\alpha} = f_{\alpha}(\alpha, T) \tag{1a}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \dot{T} = f_{T}(\alpha, T) \tag{1b}$$

Equation (1b) is obviously replaced by the time–temperature program which controls the surrounding temperature. For isothermal conditions

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \dot{T} = 0 \tag{2}$$

applies and for linear non-isothermal conditions

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \dot{T} = \Phi \tag{3}$$

applies. Here Φ means the rate of heating or cooling.

Real sample temperature, as a combination of the surrounding temperature and enthalpy changes during the reaction, is indicated in the case of DTA only. This temperature is obviously not used for computations.

For non-isothermal thermoanalytical data treatment eqn. (1a) is often factorized to

$$\dot{\alpha} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T, \boldsymbol{\beta}) f(\alpha, \boldsymbol{\delta}) \tag{4}$$

In eqn. (4) α denotes the degree of conversion $(0 \leqslant \alpha \leqslant 1)$ and t is the corresponding time of reaction.

The temperature term $k(T, \boldsymbol{\beta})$ is dependent on the temperature only. Model parameters $\boldsymbol{\beta}$ are thermodynamical characteristics of the investigated reaction (activation energy, entropy, etc.).

The kinetic term $f(\alpha, \boldsymbol{\delta})$ id dependent on the degree of conversion only. Model parameters $\boldsymbol{\delta}$ are connected with the kinetic model of the investigated reaction.

Equation (4) is based on the formal assumption that temperature dependence in the non-isothermal kinetic model appears in the rate constant only.

Based on eqn. (3), the temperature is a linear function of the time of reaction

$$T(t) = T_0 + \Phi t \tag{5}$$

where T_0 is the starting temperature.

From the results of thermoanalytical measurements it is often possible to obtain information about α, $\dot{\alpha}$ and T simultaneously, i.e. the data $(\dot{\alpha}_i, \alpha_i, T_i)$ for $(i = 1, \ldots N)$ are determined.

For non-isothermal model building it is then possible to use eqn. (4) directly. If only integral data (α_i, T_i) $(i = 1, \ldots N)$ are available, the formal integration of eqn. (4) is adopted. The resulting relation has the form

$$g(\alpha, \boldsymbol{\delta}) = F(t, \boldsymbol{\beta}) \tag{6}$$

where

$$g(\alpha, \boldsymbol{\delta}) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha, \boldsymbol{\delta})}; F(t, \boldsymbol{\beta}) = \int_0^t k[T(t), \boldsymbol{\beta}]\, \mathrm{d}t$$

The degree of conversion α can be simply determined from eqn. (6)

$$\alpha = g^{-1}[\boldsymbol{\delta}, F(t, \boldsymbol{\beta})] \tag{7}$$

Equation (7) is an integral model of non-isothermal kinetics. In some cases the $g^{-1}(.)$ can be expressed in explicit form. The term $F(t, \boldsymbol{\beta})$ cannot be analytically integrated: various analytical approximations of $F(t, \boldsymbol{\beta})$ have been proposed [6].

In eqn. (7) the model parameters $\boldsymbol{\beta}$ and $\boldsymbol{\delta}$ can be estimated on the basis of experimental data. This task is often called the inverse kinetical problem (IKP). In practice, the more important parameters are $\boldsymbol{\beta}$, characterizing the thermodynamics of the reaction being investigated.

In thermal analysis a number of possible non-isothermal kinetic models obviously exist and the selection of a suitable one is very difficult. The main problem lies in the fact that computed thermodynamical parameters (activation energy) are also dependent on the kinetic model used (see Example I).

NON-ISOTHERMAL MODEL BUILDING

The main problems of non-isothermal kinetic model building are discussed in refs. 1 and 2. Some uncertainties about the IKP solution are thoroughly described in ref. 3.

Two limiting situations (A and B) exist.

(A) Based on theory and hypothesis, the theoretical models $k(T, \boldsymbol{\beta})$ and $f(\alpha, \boldsymbol{\delta})$ can be specified.

(B) The models $k(T, \boldsymbol{\beta})$ and $f(\alpha, \boldsymbol{\delta})$ can be examined on the basis of experimental data only (this problem has no general unique solution).

In practical situations some preliminary information is available. The art of modelling lies in combining preliminary information with information extracted from data, to create a suitable non-isothermal model. The basic models for temperature terms and kinetic terms are presented below.

Temperature term models

In thermal analysis the simple exponential relation for describing the temperature dependence of the rate constant is widely used

$$k(T, \boldsymbol{\beta}) = \beta_1 T^{\beta_2} \exp(-\beta_3/RT) \tag{8}$$

Here R is the gas constant, β_1 is the pre-exponentia factor (connected with activation entropy) and β_3 is the activation energy (usually denoted as E). Commonly $\beta_2 = 0$, when eqn. (8) becomes the well-known Arrhenius model. The Arrhenius model is based on the so-called reaction isochora, in which the activation energy is defined by

$$E = RT^2 \frac{\partial \ln k(T)}{\partial T} \tag{9}$$

When E is temperature independent, the integration of eqn. (9) leads to eqn. (8) for $\beta_2 = 0$. It follows from the theory of unimolecular reactions that $\beta_2 = 1$; for bimolecular reactions (solid/gas) $\beta_2 = 0.5$.

The well-known Eyring equation, based on the theory of absolute reaction rates (or the activated-complex theory) is a special case of eqn. (8) for $\beta_2 = 1$ [4]. In these theories the activation energy is not constant but temperature dependent.

The rate of a reaction being investigated is often dependent on diffusion processes. In polymeric systems diffusion processes are controlled by the segmental mobility of polymeric chains. The temperature dependence of these processes can be described by the Williams–Landel–Ferry (WLF) model

$$k(T, \boldsymbol{\beta}) = \beta_1 \exp\left[-\frac{\beta_2 (T - T_D)}{\beta_3 + T - T_D} \right] \tag{10}$$

Here T_D is the transition temperature defining the temperature of sudden increase of segmental mobility. For amorphous polymers β_2 and β_3 are universal constants: $\beta_2 = -17.4$ K; $\beta_3 = 51.6$ K. The main difference between eqn. (10) and eqn. (8) lies in fact that for eqn. (10) the activation energy defined by eqn. (9) is a decreasing function of temperature

$$E = -RT \left[\frac{\beta_2 \beta_3 T}{(\beta_3 + T - T_D)^2} - 1 \right] \tag{11}$$

For viscoelastic relaxation in semicrystalic polymers it has been shown that the activation energy is an increasing function of temperature of the form [5]

$$E = RT^2 \beta_2 \tag{12}$$

This can be explained by assuming cooperative segmental mobility of polymeric chains.

After substitution from eqn. (12) into eqn. (9) and integration, the temperature term

$$k(T, \boldsymbol{\beta}) = \beta_1 \exp(\beta_2 T) \tag{13}$$

results.

Based on these models, it can be stated that the activation energy defined by eqn. (9) is not generally constant and can be either a decreasing or an increasing function of temperature. The classical Arrhenius model is based on the idealized assumption of a constant activation energy.

Solution of the IKP requires the integration of the temperature term. For the case of eqns. (8) and (10), various approximate equations can be used. A simple and precise approximation of the temperature term has the form [7]

$$\int \exp(-E/RT)\, \mathrm{d}T \approx \frac{RT^2}{E}\left[\frac{1-2(RT/E)}{1-5(RT/E)}\right]\exp(-E/RT) \tag{14}$$

The relative error of approximate eqn. (14) is below 1% for $E/RT \geqslant 7$. The integral of eqn. (13) can be derived analytically.

Kinetic term models

Based on various kinetic or empirical assumptions, a number of kinetic terms are available. The most widely used can be described by the generalized equation

$$f(\alpha, \boldsymbol{\delta}) = \alpha^{\delta_1}(1-\alpha)^{\delta_2}[-\ln(1-\alpha)]^{\delta_3} \tag{15}$$

When $\delta_1 = \delta_3 = 0$ eqn. (15) is equal to the nth order kinetic model (RO), where $n = \delta_2$. When $\delta_1 = 0$ and $\delta_2 = 1$ the well-known Johnson–Mehl–Avrami (JMA) model results. The empirical Šesták–Berggren (SB) model is also a special case of eqn. (15) for $\delta_3 = 0$.

Some kinetic models have only limited validity (e.g. the first stages of diffusion processes). For kinetic terms it is obviously required that [8]

$$\lim_{t\to 0} g^{-1}(t) = 0 \qquad \lim_{t\to\infty} g^{-1}(t) = 1 \tag{16}$$

For empirical kinetic terms $g(\alpha)$ the conditions of eqn. (16) are necessary, especially when the $f(\alpha, \boldsymbol{\delta})$ term cannot be derived. For example, the generalized JMA model suitable for description of kinetic processes controlled by diffusion has the form

$$g^{-1}(t) = \left\{1 - \exp\left[-F(t, \boldsymbol{\beta})^{\delta_1}\right]\right\}^{\delta_2} \tag{17}$$

It is possible to simply evaluate the validity of the conditions defined by eqn. (16) for the model by eqn. (17), but the form $f(\alpha, \boldsymbol{\delta})$ is very complicated.

TABLE 1

Results of non-linear regression for data generated from RO model

Model	E (kJ mol^{-1})	$s(E)$ (kJ mol^{-1})	RSC
RO	100.01	0.012	2.4×10^{-8}
JMA	−171.86	4.480	1.6×10^{-4}
SB	100.08	0.266	2.4×10^{-8}

TABLE 2

Results of non-linear regression for data generated from JMA model

Model	E (kJ mol^{-1})	$s(E)$ (kJ mol^{-1})	RSC
RO	46.510	0.0234	5.8×10^{-8}
JMA	101.050	2.8500	3.0×10^{-8}
SB	44.263	0.4600	3.2×10^{-8}

TABLE 3

Results of non-linear regression for data generated from SB model

Model	E (kJ mol^{-1})	$s(E)$ (kJ mol^{-1})	RSC
RO	290.82	1.750	2.4×10^{-4}
JMA	−399.17	19.790	1.5×10^{-3}
SB	100.16	0.334	3.2×10^{-8}

In eqn. (17) parameters δ_1 and δ_2 are empirical constants (often $\delta_2 = 0.5$).

Parameters $\boldsymbol{\delta}$ are generally not so important as parameters $\boldsymbol{\beta}$. The kinetic term, however, influences estimation of the $\boldsymbol{\beta}$ parameters (and therefore influences activation energy). Incorrect specification of $g(\alpha\sigma)$ leads to incorrect evaluation of activation parameters [2]. From the statistical viewpoint the correct and incorrect models are often indistinguishable.

Example I

For demonstrating the influence of incorrect kinetic terms on the estimation of activation energy and the statistical precision of data approximation, the simulated samples were prepared. The 30 points ($\dot{\alpha}_i$, α_i, T_i) were generated from RO ($\delta_2 = 0.5$), JMA ($\delta_3 = 3$) and SB ($\delta_1 = 0.7$ and $\delta_2 = 0.5$) models. For the temperature term, the Arrhenius model was chosen. The same activation parameters were used (activation energy $E = 100$ kJ mol^{-1}).

In Tables 1, 2 and 3 the activation energy E, the standard deviation of the activation energy values $s(E)$ and the residual sum of squares (RSC), computed for RO, SB and JMA models by non-linear regression are summarized. The kinetic terms used in non-linear regression models are in the first columns of Tables 1, 2 and 3. A full description of this simulation study is given in ref. 13. From Tables 1, 2 and 3 it is possible to draw the following main conclusions.

(1) Data generated by using the RO model (Table 1) can be approximated by using the SB model with the same correct activation energy. Note that the RO model is a special case of the SB model for $\delta_1 = 0$. The JMA model cannot approximate these data precisely.

(2) Data generated by using the JMA model (Table 2) can be very precisely approximated by using incorrect RO and SB kinetic terms. The approximation is very good but the corresponding activation energies are very low.

(3) Data generated by using the SB model cannot be precisely approximated by incorrect RO and JMA models.

This example shows that good approximation of data by non-isothermal models can lead to quite incorrect activation energy estimates. In practice this problem is more complicated, owing to the presence of measurement errors and the complex nature of the kinetic processes being investigated.

Specification of temperature and kinetic terms

For specification of kinetic $f(\alpha, \boldsymbol{\delta})$ and temperature $k(T, \boldsymbol{\beta})$ terms, the series of isothermal kinetic curves at various temperatures can be used. After specification of these terms for a particular system, the non-isothermal experiments can be simply processed.

Very often this approach cannot be used and it is possible to investigate only the data from non-isothermal experiments: for specification of $k(.)$ and $f(.)$, partial regression graphs combined with a broad spectrum of possible models can be used.

Very often the models defined by eqn. (8) and eqn. (15) can be combined. The resulting kinetic model has the form

$$\frac{d\alpha}{dt} = \beta_1 T^{\beta_2} \exp(-\beta_3/RT)\alpha^{\delta_1}(1-\alpha)^{\delta_2}[-\ln(1-\alpha)]^{\delta_3} \tag{18}$$

Let the error of $\dot{\alpha}_i$ or α_i measurements be multiplicative (see eqn. (25)). Then eqn. (18) can be correctly logarithmically transformed into the linear regression model

$$y_i = A_0 + \sum_{j=1}^{5} A_j x_{ij} \tag{19}$$

where $y_i = \ln(\dot{\alpha}_i)$; $x_{i1} = \ln(T_i)$; $x_{i2} = 1/T_i$; $x_{i3} = \ln(\alpha_i)$; $x_{i4} = \ln(1-\alpha_i)$; $x_{i5} = \ln[-\ln(1-\alpha_i)]$. Parameters $A_0, \ldots A_5$ are transformed parameters $\beta_1, \ldots \beta_3$ and $\delta_1, \ldots \delta_3$.

Substitution into eqn. (19) for $i = 1, \ldots N$, produces a set of N linear equations with six unknowns. In matrix notation this set has the form

$$y = XA \tag{20}$$

where y is an $(N \times 1)$ vector, X is an $(N \times 6)$ matrix and A is a (6×1) unknown vector.

The theory of linear regression states that parameters A can be obtained by orthogonal projection of y into the space spanned by the columns of matrix X.

For investigation of partial linearity between y and the jth column X_j of matrix X, the projection into space L orthogonal to the space defined by the columns of matrix $X_{[j]}$ is used. Matrix $X_{[j]}$ is created by dropping the jth column x_j from matrix X.

The corresponding projection matrix into space L has the form

$$P_{[j]} = E - X_{[j]}\left(X_{[j]}^{\mathrm{T}} X_{[j]}\right)^{-1} X_{[j]}^{\mathrm{T}} \tag{21}$$

Let $u = P_{[j]}y$ and $v = P_{[j]}x_j$. The partial regression graph is then the dependence of vector u on vector v [9]. If the term x_j is correctly specified, the partial regression graph forms a straight line. Systematic non-linearity is an indication of incorrect specification of x_j and a random pattern shows the unimportance of x_j for explaining the variability of y.

It is possible in practice by selecting β_2, δ_1, δ_2 and δ_3, to specify a particular kinetic model. From the partial regression graph it is then

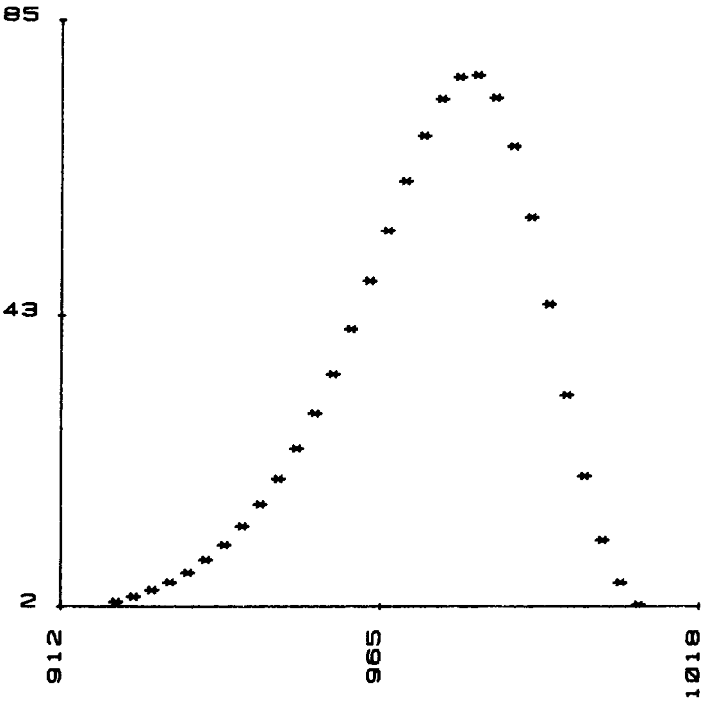

Fig. 1. Simulated peak (Example I).

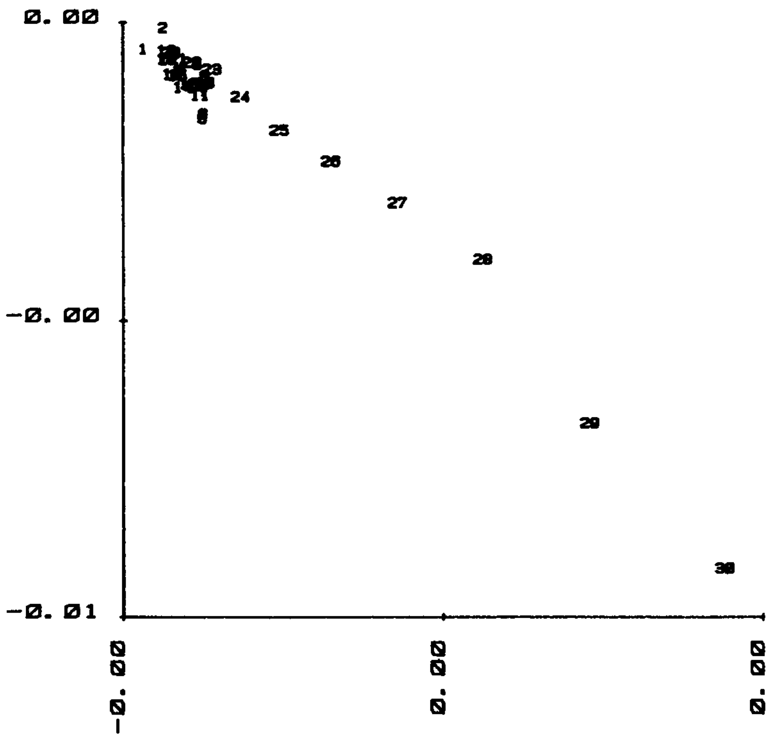

Fig. 2. Partial regression graph for data from Example I and correct Arrhenius term (1/*T*).

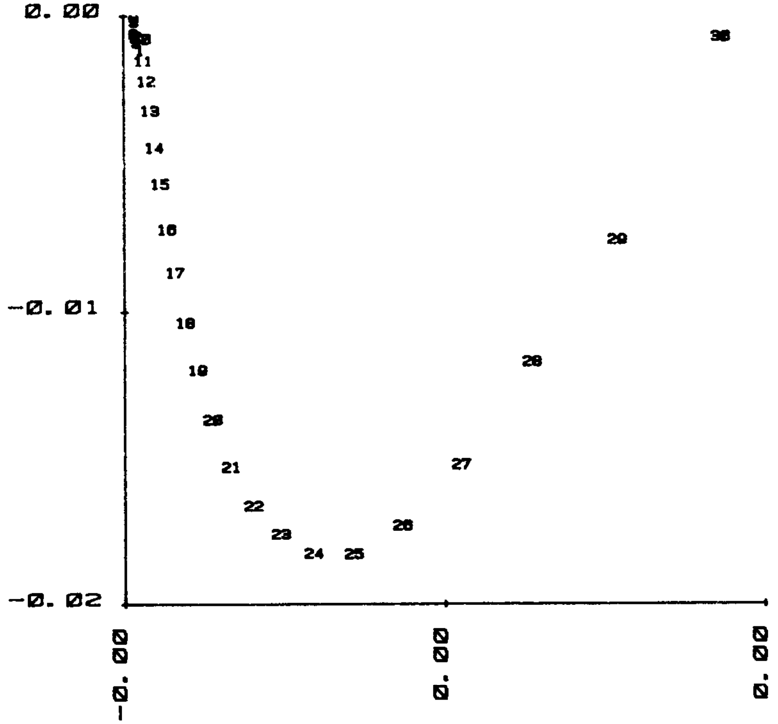

Fig. 3. Partial regression graph for data from Example I and incorrect simple exponential term (*T*) (see eqn. (13)).

possible to investigate its correctness. This approach has been applied for simulated data in Example II.

Example II

In ref. 2 the partial regression graphs for simulated data (a combination of an Arrhenius term with ln $\beta_1 = 23.03$; $\beta_2 = 0$; $\beta_3 = 200$ kJ mol^{-1}, and a JMA term with $\delta_1 = 0$; $\delta_2 = 1$ and $\delta_3 = 0.5$) have been presented. Simulated data are shown in Fig. 1. These simulated data have been used for investigating the effect of incorrect specification of the temperature term on the shape of the corresponding partial regression graphs. In the correct case, a combination of the JMA kinetic term and the Arrhenius term was used for creation of the partial regression graph. In the incorrect case, the Arrhenius term was replaced by the simple exponential term defined by eqn. (13).

The partial regression graph for the correct case and the variable x_2 ($1/T$) in eqn. (19) is shown in Fig. 2. The corresponding partial regression graph for the incorrect case is shown in Fig. 3. It is evident that incorrect specification of the temperature term also leads to pronounced non-linearity in the partial regression graphs.

SOLUTION OF THE INVERSE KINETIC PROBLEM

The final stage in non-isothermal kinetic modelling is parameter estimation for known integral model $g^{-1}(t)$ or the differential model defined by eqn. (4), and evaluation of its corresponding statistical characteristics.

Let us concentrate in this section to the integral model

$$g^{-1}(t) = g^{-1}(F(t), p) \tag{22}$$

which contains the unknown estimable parameter vector $p = (\boldsymbol{\beta}, \boldsymbol{\delta})$. For this case the commonly used least squares (LS) criterion has the form

$$S(p) = \sum_{i=1}^{n} \left[\alpha_i - g^{-1}(F(t_i), p)\right]^2 \tag{23}$$

Parameter estimates p can be obtained by minimizing $S(p)$. The LS criterion is not generally applicable and its effectivness is dependent on very strong assumptions about the measured variable α and errors in measurements. Basic assumptions are as follows.

(1) Measured degree of conversion α_i corresponds to additive model of measurements in the form

$$\alpha_i = g^{-1}(F(t_i), p) + \varepsilon_i \tag{24}$$

where ε_i are identically distributed random variables (errors) whose mean value equals zero ($E(\varepsilon_i) = 0$), with a unimodal probability density function.

(2) Errors of measurements have constant variance ($D(\varepsilon_i) = \sigma^2$).

(3) Errors of measurements are mutually independent, i.e. they are uncorrelated ($E(\varepsilon_i \cdot \varepsilon_j) = 0$; $i \neq j$). Then the measured quantities α_i and α_j are also independent.

In the thermal analysis assumptions (1)–(3) are often not acceptable, as follows.

(1) The model of measurements defined by eqn. (24) has some constraints. The main problem lies in the fact that for continuous errors ε_i on the whole real line, the α_i can with non-zero probability be negative. This physically impossible situation can be overcome by use of the multiplicative measurement model

$$\alpha_i = g^{-1}(F(t_i), p) \exp(\varepsilon_i) \tag{25}$$

In eqn. (25) the errors ε_i have the same properties as in eqn. (24). The statistical technique for discrimination between additive (eqn. (24)) and multiplicative (eqn. (25)) measurement models have been proposed in ref. 10.

(2) Variance-constancy in measured variables can be achieved over a small range only. Ranges of measured α_i are often 10^{-4} to 0.99. Therefore the relative measurement error is commonly constant and error variance $D(\varepsilon_i)$ is an increasing function of the measured quantity α. A dependence of this type also follows from the multiplicative measurement model of eqn. (25).

(3) Independence of measurements in non-isothermal kinetic experiments cannot be generally accepted. Owing to special experimental arrangements (measuring on one system only) the errors caused by process conditions variation (e.g. thermal fluctuations) are cumulative [11]. The total error ε_i is then composed of the measuring device error d_i and cumulative process fluctuations u_i

$$\varepsilon_i = d_i + \sum_{j=1}^{i} u_j \tag{26}$$

The regression criterion for estimation of parameters p is dependent on the magnitude of individual terms in eqn. (26).

For a precise measurement device (d_i small), the LS criterion must be replaced by a difference form

$$S_D = \sum_{i=2}^{N} \left\{ (\alpha_i - \alpha_{i-1}) - \left[g^{-1}(F(t_i), p) - g^{-1}(F(t_{i-1}, p)) \right] \right\}^2 \tag{27}$$

Full derivation of S_D and other special variants of the regression criteria for ε_i defined by eqn. (26) are given in ref. 11.

It can be concluded that the more realistic assumptions about data and their origin lead to more general estimation problems [9,11]. For effective solution of these problems, non-linear optimization methods can be used.

A serious numerical and statistical problem is the strong multicollinearity between parameters, especially of temperature terms. The practical consequence of this multicollinearity is that a small change in the regression criterion value leads to very large changes in parameters **β** (e.g. activation energy *E*). This leads to the activation energy appearing to be dependent on the quality of the software used. It has been verified that the classical statistical software packages (BMDP, SYSTAT, SAS, STATGRAPHICS, SPSS and others) are unsuitable for solution of the IKP [12]. Based on our tests, the best system is the statistical system ADSTAT [14]. ADSTAT enables full statistical analysis of the IKP from the point and interval estimates, computing to the expression of model quality and finally to the influential points and sensitivity analysis.

CONCLUSIONS

The solution of the IKP is generally very complicated and the resulting estimates are often unacceptable from a physical viewpoint. It is necessary to analyse experimental data with great care and to compare the adopted assumptions with experiment. For solution of the IKP, it is necessary to have suitable software. Statistical analysis of the IKP often avoids the use of incorrect models and parameters. In the age of computers it is possible to replace some approximate graphically oriented techniques for the IKP by more correct methods based on finer assumptions about data and the process studied.

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