PARAMETER DISTORTION BY UNAPPROPRIATE NONISOTHERMAL TREATMENT

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The aim of this contribution is to draw attention to the following problems:
(i) boundary conditions of kinetic models,
(ii) distortion of kinetic data by cutting-off the peak ends,
(iii) regression analysis involved in the evaluation of kinetic data.

For the mathematical treatment of DSC/DTA experimental data the factorized kinetic equation

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{1}$$

is obviously applied. The temperature term $k(T)$ bears usually the Arrhenius exponential form

$$k(T) = A \exp(-E/RT) \tag{2}$$

The symbols α, A and E have the usual meaning of the degree of conversion (obtained upon integration), pre-exponential factor and activation energy, respectively. The rate of conversion $d\alpha/dt = \dot{\alpha}$ can be simply obtained as a result of DTA analysis. The form of the kinetic term $f(\alpha)$ can be dependent on a proposed kinetic mechanism but often it is chosen empirically. This term can be written in generalized form [1, 2] as follows:

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \tag{3}$$

The most common kinetic models which are special forms of Eq. (3) are shown in Table 1.

Table 1 Kinetic models based on Eq. (3)

Model	Symbol	Parameters involved
Reaction order	RO	n
Johnson–Mehl–Avrami–Yerofeev–Kolmogorov	JMAYK	$n = 1, p$
Šesták–Berggren	SB	n, m

For the chosen type of kinetic term the activation parameters E and A can be determined on the basis of data $\{\dot{\alpha}_i, \alpha_i, T_i\}\, i = 1, \ldots, N$ by the method of nonlinear regression. For the case of integral data (α_i, T_i) and linear heating

$$T = T_0 + \phi t \tag{4}$$

the integration of Eq. (1) within the limits $\langle 0, \alpha \rangle$ and $\langle 0, t \rangle$ leads to the expression

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t k(T_0 + \phi t)\, dt \tag{5}$$

Here T_0 and ϕ are the starting temperature and rate of heating, respectively. Eq. (5) can be formally rewritten in the form

$$g(\alpha) = F(t) \tag{6}$$

or

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

One of the main problems is that the term $F(t)$ cannot be expressed in closed form. For estimation purposes both numerical integration and various approximations can be applied.

Boundary conditions of kinetic terms

The solution of Eq. (5) in the isothermal case ($\phi = 0$) gives

$$g(\alpha) = k(T_0)t \tag{8}$$

or in inverted form

$$\alpha = g^{-1}[k(T_0)t] \tag{9}$$

It is evident that the following boundary conditions for the $g(\alpha)$ function must be fulfilled

$$\lim_{\alpha \to 0} g(\alpha) = 0 \qquad \lim_{t \to 0} g^{-1}(t) = 0 \tag{10a}$$

$$\lim_{\alpha \to 1} g(\alpha) = \infty \qquad \lim_{t \to \infty} g^{-1}(t) = 1 \tag{10b}$$

It seems to be surprising that these two elementary classical kinetical conditions are not valid for several $g(\alpha)$ functions which are used for kinetic parameter calculation from thermoanalytical data.

For the simple RO model conditions (10a) and (10b) are fulfilled for $n \geqslant 1$ only. In cases where $n < 1$, condition (10b) yields

$$\lim_{\alpha \to 1} g(\alpha) = n/(1-n) \tag{11}$$

so that the use of popular models of shrinking core particles is in question because condition (10b) is not valid. However, it can be shown that JMAYK model fulfils both conditions mentioned above. For the third class of $f(\alpha)$ functions called SB the $g(\alpha)$ function cannot be obtained in analytical form. It can be proved that the SB class of functions also hardly fulfils the condition (10b).

The question arises to what extent these incorrectnesses influence the estimation of the activation parameters E and A.

Distortion of kinetic data by cutting-off the peak ends

It is known from previous experiences with experimental data treatment that the activation parameters E and A are sensitive to the inclusion of enough points at the beginning and end of peaks, i.e. at the level of the peak baseline representing boundary conditions [5].

For many peaks the inflection points are very close to the low values of $\dot{\alpha}$. Unsensitive cut-off of the peak tails can considerably decrease the information content of experimental data necessary for correct analysis. For illustration we have used the JMAYK model from Table 1 with parameters: $p = 0.5$, $\ln A = 23.03$ and $E = 200 \text{ kJ} \cdot \text{mol}^{-1}$. After simulation of the theoretical $\dot{\alpha}$ versus T curve the random centered normally distributed errors were added to $\dot{\alpha}$. The standard deviation of this noise was 0.044.

For each curve 30 points were created for the preselected temperature interval (T_{min}, T_{max}) corresponding to the individual position of the base line (cutting-off the peak ends).

The activation parameters were estimated from simulated data by the nonlinear least squares. Results are summarized in Table 2.

Table 2 Effect of cutting-off peak ends of the activation parameters

T_{min}, K	T_{max}, K	$\ln(A)$	E, kJ $\cdot$ mol^{-1}
918	1008	23.64	198.53
958	998	534.40	4319.70

It is evident that the cut-off of the both peak ends, often assumed as negligible compared to the rest of peak, may lead to catastrophic results.

Statistical aspects of nonisothermal kinetics

The estimation of activation and kinetic parameters from experimental data leads to solution of nonlinear regression problems [6, 7]. The suitable regression criterion (loss function) depends on the statistical assumptions about the nature of experimental data [8]. Let us concentrate in this section on the integral model (7). For this model the commonly used least squares (LS) criterion has the form

$$S(E, K, n, m, p) = \sum_{i=1}^{n} \{\alpha_i - g^{-1}[F(t_i)]\}^2 \qquad (12)$$

The application of criterion (12) leads from the statistical point of view to effective parameter estimates as long as the *additive measurement model*

$$\alpha_i = g^{-1}[F(t_i)] + \varepsilon_i \qquad (13)$$

is valid.

Necessary conditions for effective estimations by LS are based on two basic groups of assumptions about random errors ε_i.

I. Errors ε_i have identical symmetric unimodal distribution with zero mean $E(\varepsilon_i) = 0$ and constant variance $E(\varepsilon_i^2) = \sigma^2$.

II. Measurements are mutually independent. Then errors are uncorrelated and $E(\varepsilon_i \varepsilon_j) = 0$ for $i \neq j$.

These assumptions are only rarely fulfilled for thermoanalytical measurements.

The additive measurement model (13) has serious restrictions. Due to the nature of ε_i (random errors defined on the whole real line $\langle -\infty, \infty \rangle$) the values α_i are not restricted to physically accepted positive values. The important problem often met in practice is that the error variance increases with rising true values of $g^{-1}[F(t_i)]$.

Errors due to measurement devices have often constant coefficient of variation and therefore the variance σ_i^2 is a quadratic function of the true values of the conversion degree.

Due to special experimental arrangements (measuring on one system only) the errors ε_i caused by process conditions variation are *cumulative* [8, 9]. It means that

$$\varepsilon_i = \sum_{j=1}^{i} \mu_j \qquad (14)$$

where μ_j are independent identically distributed random quantities with constant variance.

In paper [12] a more general case is solved, where both *process* (cumulative) errors and *measuring device* errors (with nonconstant variance) are considered. One of the frequent alternatives to the additive measurement model is the multiplicative measurement model. In this case the relationship

$$\alpha_i = g^{-1}[F(t_i)] \exp{(\varepsilon_i)} \tag{15}$$

is valid. Among the main advantages of the multiplicative model the following can be stated [13]:

— measured values α_i are always positive,

— variances of errors are not constant but they represent an increasing function of the true values $g^{-1}[F(t_i)]$.

Moreover, provided that this measurement model is valid, logarithmic transformation (leading obviously to linearization) is correct (see [10]).

One general method that enables to find suitable measurement model type with simultaneous determination of activation and kinetic parameter estimates is described in paper [10].

The errors ε_i have often the short or long tailed distribution. In these cases the L_p regression criterion leads to maximum likelihood estimators of parameters. The L_p criterion is a generalization of LS where in Eq. (12) power two is replaced by power p $(1 \leqslant p < \infty)$ [14].

It can be concluded that the more realistic assumptions about data and their origin lead to the more general estimation problems [8].

For effective solution of these problems nonlinear optimization methods can be used. It is evident that the incorrect statistical or numerical treatment of nonlinear regression leads often to unacceptable parameter estimates.

An independent problem of this type is the special form of Eq. (7). Due to double integration (across time and degree of conversion) it is possible to obtain the good approximation of experimental data also by using incorrect kinetic models. It leads to a situation where the values of activation energy differ strongly in spite of using different relatively good models.

For demonstrating this phenomena a small simulation study was realized. Data $\{\dot{\alpha}_i, \alpha_i, t_i\}$ were generated by JMAYK model with parameters $p = 0.5$, $\ln{(A)} = 23.03$ and $E = 200$ kJ·mol^{-1}. Values α_i were corrupted by additive normal errors with zero mean and variance $\sigma^2 = 0.0016$. The model defined by Eq. (1) and kinetic terms (3) with prechosen constant from Table 1 were used for the description of the data. Parameters were estimated by nonlinear LS after logaritmic transformation (multiplicative measurement model). The results are summarized in Table 3.

In all cases the simulated data were well approximated by the model.

Table 3 Results of a small simulation study

Model	T_{max}, K*	T_{min}, K*	ln (A)	E, kJ·mol^{-1}	n	m	p
JMA	1008	918	29.65	198.53	1	—	0.502
RO			71.40	539.10	1.04	—	—
SB			35.14	243.06	0.44	0.88	—

* Initial and final temperature used in the simulation.

On the basis of these limited simulation experiments it is possible to claim that

(i) it will be difficult to determine correct estimates of activation parameters E and A from one nonisothermal experiment only. This is a direct consequence of a strong multicollinearity between estimates of E and ln (A);

(ii) incorrect kinetic models can be successfully used for modelling nonisothermal data, too.

The corresponding estimates of activation parameters are then obviously far from the true values.

Specification of the kinetic term

As it is shown in Table 3, the correct specification of the kinetic term is very important. Let us suppose that we have experimental data $\{\dot{\alpha}_i, \alpha_i, t_i\}$ $i = 1, \ldots N$ from DTA. Substitution of Eqs (2) and (3) into model (1) and logarithmic transformation (correct for multiplicative measurement model) leads to the linear regression model

$$y_i = A_0 + A_1 x_{1i} + A_2 x_{2i} + A_3 x_{3i} + A_4 x_{4i} \tag{16}$$

In this equation new variables are

$$y_i = \ln \dot{\alpha}_i \quad x_{1i} = 1/T_i \quad x_{2i} = \ln(1-\alpha_i) \quad x_{3i} = \ln \alpha_i$$

$$x_{4i} = \ln[-\ln(1-\alpha_i)]$$

and new parameters are

$$A_0 = \ln A \quad A_1 = -E/R \quad A_2 = n \quad A_3 = m \quad A_4 = p$$

The problem of correct specification of the kinetic term is converted to the problem of judging partial linearity between y_i and x_{ji} $(j = 2, \ldots 4)$. Variables x_{ji} $(j = 1, \ldots 4)$ are mutually highly correlated. In paper [8] there is a survey of methods for graphical estimation of the partial dependence between y and x_j in cases of multicollinearity.

Partial regression graphs belong to the simplest ones. Let us consider a linear regression model in the matrix form

$$y = \ast A + \varepsilon \tag{17}$$

where y is an $(N \times 1)$ vector of dependent variables, A is an $(m \times 1)$ vector of regression constant, $\ast$ is an $(N \times m)$ matrix of explanatory variables and ε is an $(N \times 1)$ vector of random errors.

Linear model (17) can be resolved to terms

$$y = \ast_{[j]} A^* + x_j c + \varepsilon \tag{18}$$

Here $\ast_{[j]}$ is matrix $\ast$ without the jth column x_j and A^*, c are regression constants. By using projection matrix $IP_{[j]} = IE - \ast_{[j]}(\ast_{[j]}^T \ast_{[j]})^{-1} \ast_{[j]}^T$ it is possible to rewrite Eq. (18) into a form

$$IP_{[j]} y = IP_{[j]} \ast_{[j]} A^* + IP_{[j]} x_j c + IP_{[j]} \varepsilon \tag{19}$$

In view of the fact that $IP_{[j]}$ is a projection into a subspace orthogonal to the column of $\ast_{[j]}$, Eq. (19) can be simplified to the final relation

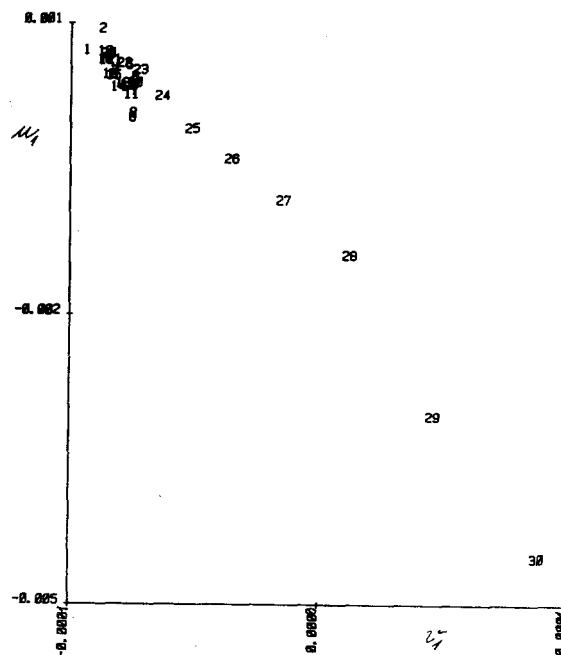$$u_j = c v_j + IP_{[j]} \varepsilon \tag{20}$$

Fig. 1a Partial regression graph for proving the correctness of the JMAYK model (partial dependence of $\ln \dot{\alpha}_i$ on $1/T_i$)
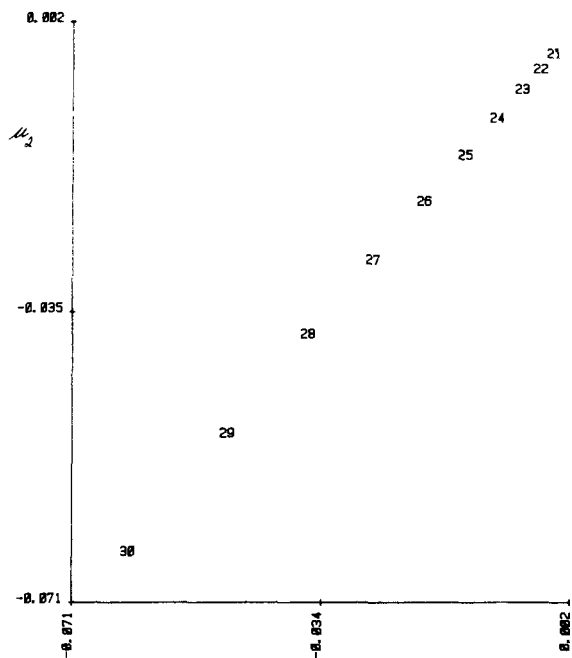
Fig. 1b Partial regression graph for proving the correctness of the JMAYK model (partial dependence of $\ln \dot{\alpha}_i$ on $\ln (1 - \alpha_i)$)
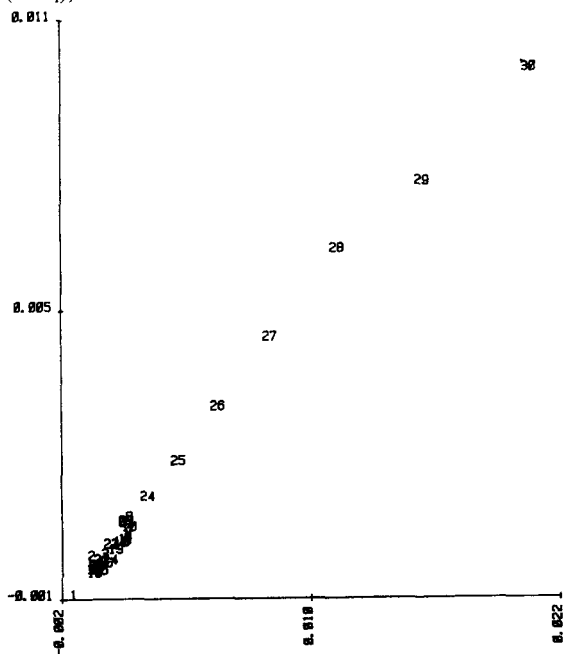

Fig. 1c Partial regression graph for proving the correctness of the JMAYK model (partial dependence of $\ln \dot{\alpha}_i$ on $\ln (-\ln (1 - \alpha_i))$)
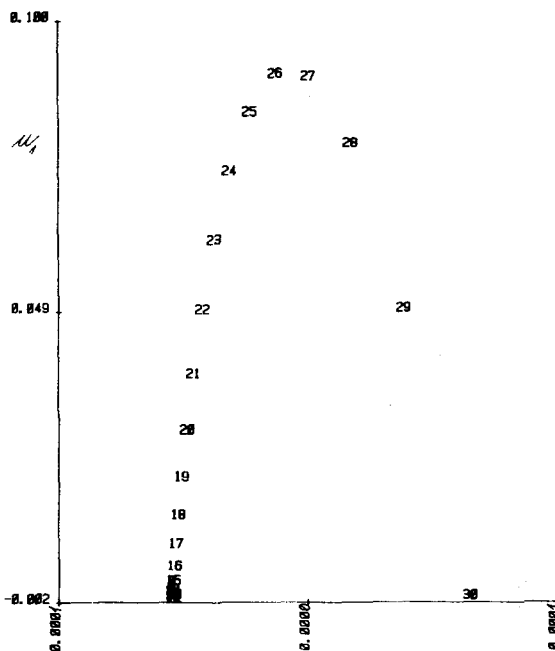
Fig. 2a Partial regression graph for proving the correctness of the SB model (partial dependence of ln $\dot{\alpha}_i$ on $1/T_i$)
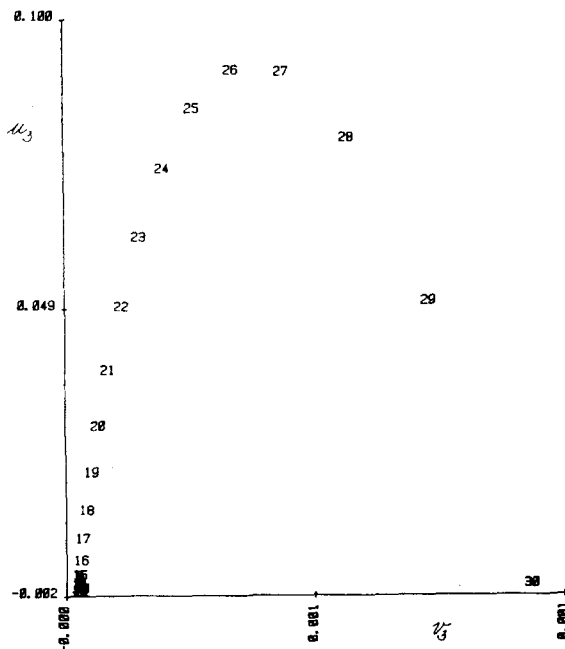

Fig. 2b Partial regression graph for proving the correctness of the SB model (partial dependence of ln $\dot{\alpha}_i$ on ln α_i)

It follows from the theory of linear regression that u_j are residual of the regression y on columns $\divideontimes_{[j]}$ and v_j are residuals of the regression x_j on columns of $\divideontimes_{[j]}$. By using mean value operator on Eq. (20) we easy find out that the dependence of residuals u_j on residuals v_j is linear with zero intercept and slope $C \equiv A_j$. This dependence is denoted the *partial regression graph*. The properties of this graph are summarized in work [8].

For the purpose of kinetic term selection it is important that for the partial linear dependence between y and x_j the corresponding partial regression graph must be *linear*. Nonlinear trends on this graph clearly indicate the incorrectness of the model used.

From data generated by the JMAYK model in our small simulation study the partial regression graphs corresponding to JMAYK model $(A_2 = 1, A_3 = 0)$ are shown in Fig. 1a, b, c and the partial regression graphs corresponding to SB model $(A_4 = 0)$ in Fig. 2a, b.

It is evident that for correct JMAYK model all the partial regression graphs are practically linear. For incorrect SB model the partial regression graphs are strongly nonlinear. As it follows from this and our simulated experiments the partial regression graphs are sufficiently sensitive to using incorrect kinetic terms. They are able to comprehend also the presence of outliers and nonconstant error variance.

Conclusion

The modelling of nonisothermal kinetic processes in thermal analysis is still rather an art than a serious science [3]. It is necessary to analyze experimental data with great care and to compare the adopted assumptions with reality. In this contribution only selected problems connected with nonisothermal kinetic data treatment are discussed. Other problems were open in the paper [11].

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Zusammenfassung – Ziel dieser Betrachtung ist, auf folgende Problemstellungen aufmerksam zu machen:

    (i) Randbedingungen in kinetischen Modellen

    (ii) Verzerrung kinetischer Daten durch Abschneiden der Peakenden

    (iii) Regressionsanalyse bei der Auswertung kinetischer Daten

Резюме — Целью представленной статьи обратить внимание на следующие проблемы: и) пограничные условия кинетических моделей, ии) искажение кинетических данных при отрезании концов пиков, иии) введение регрессионного анализа при оценке кинетических данных.