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ERROR IN DETERMINING ACTIVATION ENERGY CAUSED BY THE WRONG CHOICE OF PROCESS MODEL

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ABSTRACT

In this paper we propose an equation which establishes the relation between the relative error in choosing the process model and the absolute error in determining the activation energy. It is demonstrated by model data that even a small error caused by choosing the contracting cylinder equation instead of the contracting sphere equation leads to an error in the activation energy which is essential in further calculations. The conversion of non-isothermal data to the isothermal form is given as an example of a practical calculation. It is shown that the activation energy error caused by the wrong choice of model makes adequate transformation impossible. It is concluded that for practical purposes it is necessary to employ methods which solve the inverse kinetic problem and do not use discrimination.

Errors in determining the activation energy caused by the limited accuracy of the instruments used for kinetic investigations have been estimated before. In particular, cases were considered where inaccuracies in the determination of the activation energy were caused by transformation degree [1] and temperature [2,3] measurement errors. Obviously, these errors, by virtue of their experimental nature, can be reduced to a certain extent, but it is, in principle, impossible to fully avoid them. The aim of our work is to establish the relation between the error in choosing the model of the process and the accuracy of determining the activation energy. This error is methodical (or, more correctly, methodological [4]) in origin, as it is peculiar to the group of methods of solving the inverse problem which use discrimination of formal models, and can therefore be avoided by using an alternative group of non-discrimination methods.

To establish the relation between the error in choosing the process model and the accuracy of determining the activation energy, let us make use of the equation generally accepted in non-isothermal kinetics

$$d\alpha/dT = kf(\alpha)/\beta \qquad (1)$$

where $d\alpha/dT$ is the transformation degree derivative with respect to the absolute temperature, k is the rate constant, β is the heating rate and $f(\alpha)$

is the formal model of the process. According to the linearised form of eqn. (1)

$$\ln k = \ln(\beta\, \mathrm{d}\alpha/\mathrm{d}T) - \ln f(\alpha)$$

the error in ln k caused by the error in choosing $f(\alpha)$ and determined by the approximate formula [5]

$$\delta \ln k \approx \mathrm{d} \ln k/\mathrm{d}f(\alpha)\ \delta f(\alpha)$$

is equal to

$$\delta \ln k \approx -\delta f(\alpha)/f(\alpha) \tag{2}$$

On the other hand

$$\delta \ln k \approx \delta(\ln A - E/RT) \tag{3}$$

Taking into account the apparent compensation dependence [6] between ln A and E, the previous expression is written as

$$\delta \ln k \approx \delta(aE + b - E/RT) = (a - 1/RT)\delta E \tag{4}$$

where $a = 1/R\hat{T}$ ($\hat{T}$ is the isoparametric temperature [6]). Now the error in the activation energy can be found from eqn. (4) taking into account eqn. (2)

$$\delta E \approx [\delta f(\alpha)/f(\alpha)]\, R\hat{T}T/(\hat{T} - T) \tag{5}$$

It follows from eqn. (5) that at temperatures of most heat-stimulated reactions ($T > 330$ K), the absolute error in determining the activation energy (kcal mol^{-1}) is at least an order of magnitude greater than the relative error in choosing the process model. In addition, eqn. (5) indicates the hyperbolic temperature dependence of δE. Hence, when the values of the current and isoparametric temperatures are close, extremely great errors in determining the activation energy are possible, because at the isoparametric temperature the Arrhenius straight lines corresponding to different models intersect and they become indistinguishable whatever the differences in activation energies. As a result, even the smallest error in choosing the model at the isoparametric temperature leads to unpredictable errors in the activation energy. However, we are only interested in the error caused by the wrong choice of the model (the first factor of eqn. (5)). Therefore, for its estimation, temperature values far from the isoparametric one should be used, for example those corresponding to the initial or final stage of the transformation.

To test eqn. (5), we modelled data (T, α, $\mathrm{d}\alpha/\mathrm{d}T$) obeying the contracting sphere model at values $E = 30$ kcal mol^{-1}, $A = 10^{15}$ min^{-1} and $\beta = 10\,^\circ$C min^{-1}. The isoparametric temperature was calculated in terms of the value of the corresponding parameter of the compensation dependence and was equal to 430 K. Model data were used to calculate the kinetic parameters in accordance with different formal models substituted into the equation

$$\ln[\beta/f(\alpha)\ \mathrm{d}\alpha/\mathrm{d}T] = \ln A - E/RT \tag{6}$$

TABLE 1

The values of the median of the relative error in model choice, the activation energy and its absolute error and the ratio of the absolute error of the activation energy to the median of the relative error in model choice, calculated by means of model data for some hypothetical process models

$f(\alpha)$	$\Omega = \text{med}\,\lvert\Delta f(\alpha)/f(\alpha)\rvert$	E (kcal mol^{-1})	$\lvert\Delta E\rvert$ (kcal mol^{-1})	$\lvert\Delta E\rvert/\Omega$ (kcal mol^{-1})
$(1-\alpha)^0$	0.59	21.0	9.0	15.3
$(1-\alpha)^{1/2}$	0.12	27.5	2.5	20.8
$(1-\alpha)^1$	0.21	34.1	4.1	19.5
$(1-\alpha)^2$	0.60	47.2	17.2	28.7
$0.5\,\alpha^{-1}$	1.11	49.4	19.4	17.6

The activation energy values for four reaction-order-type models related to the contracting sphere equation and for a one-dimensional diffusion model are given in Table 1. As the calculation of kinetic parameters was carried out for a wide range of transformation degrees (0.01–0.99), a certain averaged value of the relative error in choosing the model should obviously be used in eqn. (5). And it should be remembered that the relative error in choosing the model exhibits a strongly non-linear dependence on the transformation degree values at the range boundaries when they are close to zero or unity. As a result of this, the mean value of the relative error turns out to be very sensitive to small changes in the boundaries of the transformation degree range used (0.01–0.99). Therefore, we used, as the averaged value of error, the median [7] which is slightly sensitive to the values falling far outside of the range of values being averaged. The corresponding values of the median of the relative error in choosing the model for different models are given in Table 1.

The last column of the table represents the value of the second factor of eqn. (5) which is about 20 kcal mol^{-1} or $10^4 R$ K on average. This proportionality factor is obtained from eqn. (5) provided that $T > 330$ K and $\lvert\hat{T} - T\rvert \approx 30$ K, which corresponds to the conditions used in practice, in thermoanalysis.

Unfortunately, eqn. (5) obtained by us is not suitable for calculation using real data, since the determination of the relative error in choosing the process model presupposes the knowledge of its true model, which is possible for model data only. However, the advantage of eqn. (5) is that it made possible, in general form, the association of the error in choosing the process model inherent in the discrimination methodology [8] with the error in determining the activation energy. Quantitative estimations made on the basis of eqn. (5) and confirmed by calculations on model data suggest the possibility of significant errors in activation energy even in the cases where, instead of the true model, a model similar in physical meaning and mathematical form is chosen.

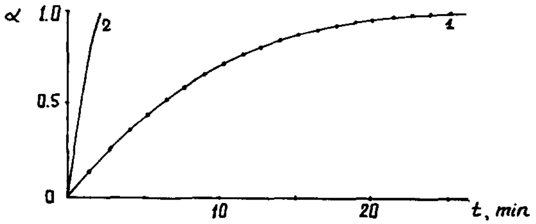

Fig. 1. The model kinetic curve (curve 1), and curves reconstructed as a result of non-isothermal data transformation with respect to eqns. (7) and (8) (curve 2 and points on curve 1, respectively).

A practical example demonstrating the influence of an activation energy error on the results of a calculation can be the previously considered [9] non-isothermal–isothermal conversion of kinetic data. This conversion is readily realised if the invariability of the formal model and kinetic parameters of the process under iso- and non-isothermal conditions is assumed. The isothermal kinetic curve corresponding to the temperature T_{iso} is usually plotted according to

$$t = g(\alpha)/[A \exp(-E/RT_{\mathrm{iso}})] \tag{7}$$

by substituting into it the formal model $g(\alpha)$ and the kinetic parameters A and E, determined from the non-isothermal experiment, and by making use of the available model data whose calculation results are given in the table. Assuming that in solving the inverse kinetic problem, a minimal error in choosing the formal model was made, i.e. the contracting cylinder equation was chosen instead of the contracting sphere equation (the indistinguishability of these equations within the accuracy of conventional kinetic experiment was mentioned in ref. 1). The kinetic curve plotted by substituting the contracting cylinder equation and the corresponding kinetic parameters into eqn. (7) for the temperature $T_{\mathrm{iso}} = 410$ K is given in Fig. 1.

As an alternative to eqn. (7), the use of which is inevitably associated with the discrimination of formal models, we suggest [9] the following conversion

$$t = \int_0^T \exp(-E/RT)\,\mathrm{d}T/[\beta \exp(-E/RT_{\mathrm{iso}})] \tag{8}$$

where t corresponds to the transformation degree for temperature T in the non-isothermal experiment. The obvious advantage of eqn. (8) is the absence of the necessity of choosing the model of the process, which, in the general case, is not unambiguous [8]. Calculation by eqn. (8) requires the knowledge of the reliable value of E obtained by methods which do not use discrimination, e.g. isoconversion [10] or by the method of invariant kinetic parameters [11]. The kinetic curve plotted by substituting the invariant value $E = 30.05$ kcal mol^{-1} into eqn. (8) is given in Fig. 1.

Comparison of the results of calculations by eqns. (7) and (8) with model data shows that even a small error in choosing the process model can lead to an error in activation energy, a value essential in the solution of practical problems; on the other hand, it demonstrates the obvious advantage of non-discrimination methods in solving practical inverse problems.

Thus, the investigation made makes it possible to quantitatively confirm the qualitative results of our earlier work [8] in which we showed that discrimination methodology could not be used to solve the inverse problem of non-isothermal kinetics. As an alternative, we suggest the use of complementary methodology to replace individual formal models by generalised descriptions [4,8]. In this case, errors in determining the kinetic parameters are only caused by the random errors present in the experimental data. Therefore, the methods of calculating kinetic parameters which do not use discrimination of formal models always yield activation energy values which are closer to real ones by at least the value determined by eqn. (5).

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