SOME ASPECTS OF MATHEMATICAL STATISTICS AS APPLIED TO NON-ISOTHERMAL KINETICS

Part II. Sensitivity of the kinetic parameter calculation method to the form of the kinetic function

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As a numerical characteristic of the sensitivity of the kinetic parameter calculation method to the form of the kinetic function in non-isothermal kinetics, the value of the curvature of the line plotting residual dispersion vs. formal reaction order at the minimum point is suggested. The efficiency of this characteristic is exemplified.

The diversity of the calculation methods in non-isothermal kinetics often makes it difficult to give preference to one or other of them. The difficulty is redoubled because different methods of calculation of the kinetic parameters yield different results. The ambiguity in solving the inverse kinetic problem stems from the insufficient accuracy of the experiment and the low sensitivity of the calculation method to the form of the kinetic function. In the former case, the ambiguity is accounted for by the fact that the differences in the kinetic functions lie within the experimental error. In the latter case, this is due to the low resolution of the calculation method. The experimental error may be expressed numerically. However, there are no sufficiently generalized numerical estimates for the sensitivity of the calculation method in non-isothermal kinetics. The derivation of such a characteristic is the concern of the present study.

Part I [1], by solving a particular problem, we have shown that nonlinear regression analysis, when applied to non-isothermal kinetics, yields less ambiguous kinetic parameters of a solid-phase reaction as compared to the linear anamorphoses. The same situation is considered with the suggested characteristic for the sensitivity of the method of kinetic parameter calculation. The agreement of the results in [1] and in the present study provides evidence for this characteristic, thereby allowing a choice of the calculation approach which would yield more definite results.
Statement

Kinetic parameters are usually estimated through regression analysis. In the most general form this implies that some minimum value be found:

$$S^2 = \frac{1}{K-2} \sum_{i=1}^{K} (g(x_i) - \psi(\beta, T_i))^2$$

where $g(x)$ is the integral form of the kinetic function; $x_i$ is the decomposition degree at temperature $T_i$; $K$ is the number of experimental points; $\beta$ is the heating rate; and $\psi$ and $\varphi$ are some functions in the selected method of kinetic parameter calculation. The function $\psi$ contains one ($E$) or two ($E, \log A$) kinetic parameters, which are found from the condition of minimum (1) at a prescribed value of $n$ (in the case of $g(x) = \frac{1-(1-x)^{1-n}}{1-n}$):

$$\frac{\partial S^2}{\partial E} = 0, \quad \frac{\partial S^2}{\partial \log A} = 0$$

The quantity $S^2$, referred to as the residual dispersion, depends on the form of the kinetic function too, which provides the grounds for choosing the latter relying on the minimum $S^2$. For the case of the kinetic function of the formal reaction order (differential form $f(x) = (1-x)^n$), the dependence of $S^2$ on $n$ is parabolic [1]. The application of different methods of calculating kinetic parameters yields a family of similar curves (Fig. 1). In Fig. 1, curves 1-4 stand for different calculation methods providing accurate values of $n$. In the general case, some of the methods may give under- or overestimated values, but this does not affect the further considerations.

Naturally, the sensitivity of the calculation method is determined by the behaviour of $S^2$ vs. $n$, i.e. the greater the change in $S^2$ due to a given change of $n$, the higher the resolution (sensitivity) of the calculation method (Fig. 2). It is seen from Fig. 1 that the sensitivity is a key factor in the choice of the calculation method.

![Fig. 1 Schematic dependence of $S^2$ on $n$ for different methods of calculating kinetic parameters](image-url)

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