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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.

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Statement

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

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

where $g(\alpha)$ is the integral form of the kinetic function; α_i is the decomposition degree at temperature T_i; K is the number of experimental points; β is the heating rate; and ψ and ϱ are some functions in the selected method of kinetic parameter calculation. The function ψ 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 $g(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n}$):

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

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 $f(\alpha) = (1-\alpha)^n$), 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

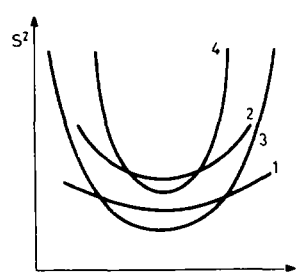

Fig. 1 Schematic dependence of S^2 on n for different methods of calculating kinetic parameters

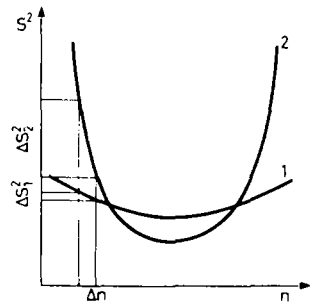

Fig. 2 Comparative steepness for two dependences of S^2 on n

Fig. 2 that calculation method 2 with a steeper S^2 *vs.* n curve is more sensitive than method 1 with a gentle S^2 *vs.* n curve. Thus, the curvature of the line $S^2 = \xi(n)$ characterizes the sensitivity of the calculation method to the form of the kinetic function. The line curvature may be estimated via the formula [2]:

$$C = \left|\frac{\partial^2 S^2}{\partial n^2}\right| \left(\left(1 + \left(\frac{\partial S^2}{\partial n}\right)^2\right)^{-1.5}\right. \tag{3}$$

It should be noted that C depends on the absolute value of S^2. It is therefore more reasonable to replace S^2 by a relative value:

$$F = \frac{S^2}{S^2_{min}} \tag{4}$$

As C also depends on n, the curvature calculated at the minimum point:

$$\frac{\partial S^2}{\partial n} = 0 \tag{5}$$

may be used to characterize the sensitivity of the calculation method.

Considering (5) and (4), (3) assumes the form:

$$C_m = \left|\frac{\partial^2 F}{\partial n^2}\right| n = n_m \tag{6}$$

The calculation of (6) may be replaced by a polynomial approximation:

$$F = \sum_{j=0}^{L} a_j n^j \tag{7}$$

Varying the polynomial power L may result in a fine approximation of F vs. n. Approximation (7) yields a new curvature expression:

$$C_m = \sum_{j=2}^{L} j(j-1)a_j n_m^{j-2} \tag{8}$$

The value of n_m is found from the condition:

$$\frac{\partial F}{\partial n} = 0 \tag{9}$$

where F is calculated from (7). Equation (9), depending on L, may be solved analytically or numerically. The value of n_m is substituted into (8) to find the curvature of the line for F vs. n. Since F obeys the Fisher distribution (cf. (4)) with $K-2$ degrees of freedom, the critical tabulated Fisher criterion is substituted into the LHS of expression (7). In this case, the solution of Eq. (7) yields the boundary values of the n range with an insignificant difference in the kinetic functions (Fig. 3).

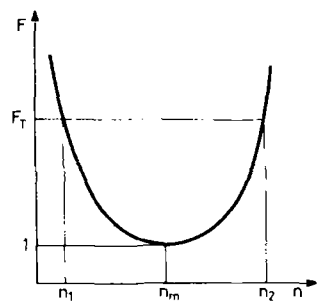

Fig. 3 Determination of boundary values of n (confidence interval)

Verification of the efficiency of the suggested characteristic

The suggested characteristic is used to compare the sensitivities of the linear and nonlinear versions of the Coats–Redfern approach [3]. The linear version uses the expression [3]:

$$\log \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \log \frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right) - \frac{E}{2.3RT} \tag{10}$$

The residual squared sum is found following expression (1). In the nonlinear version suggested in [1], the residual squared sum is related as:

$$S^2 = \frac{1}{K-2}\sum_{i=1}^{K}(\alpha_i^* - \alpha_i)^2 \tag{11}$$

where α_i^* is defined from Eq. (10); and α_i is the experimental transformation degree. We have calculated S^2 vs. n from the data of [4] to construct the parabola

$S^2 = A \cdot n^2 + B \cdot n + C$. For linear version (10):

$$S^2 = 0.00279n^2 - 0.00979n + 0.00884 \tag{12}$$

For nonlinear version (11) [1]:

$$S^2 = 0.00052n^2 - 0.00181n + 0.00159 \tag{13}$$

The values of S^2_{min} calculated with the parabola coefficients are $0.2518 \cdot 10^{-3}$ for (12) and $0.2399 \cdot 10^{-4}$ for (13). The values of F estimated with (4) are listed in Table 1 for different n. Following (8), the parabola curvature is $2a_2$ (at $L = 2$), i.e. double the parabola coefficient for n^2 in (7). Curvatures (8) for (10) and (11) are $C_m = 22.18$ and $C_m = 43.60$, respectively. It may be concluded that the nonlinear version of the

Table 1 Alteration of F-value (4) for linear and nonlinear versions of Coats–Redfern method

n	Linear version	Nonlinear version
	$F = S^2/S^2_{min}$	$F = S^2/S^2_{min}$
1.4	2.40	3.45
1.5	1.77	2.07
1.6	1.32	1.29
1.7	1.07	1.02
1.8	1.05	1.16
1.9	1.26	1.68
2.0	1.74	2.50

Coats Redfern method possesses in this case a higher sensitivity to the form of the kinetic function as compared to the linear version. In [1] we have therefore succeeded in choosing a statistically substantiated reaction order out of the two possible ones which are characterized by the same correlation coefficient in linear anamorphoses.

Conclusion

The value of the curvature (8) we have suggested for characterizing the sensitivity of the calculation to the form of the kinetic function makes it possible to choose an approach which would yield the most nonambiguous solution to the inverse kinetic problem in each particular case.

It should also be noted that value (8) characterizes the sensitivity of the kinetic parameter calculation method to the form of any kinetic function, the formal-order function being chosen for simpler calculation.

References

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Zusammenfassung — Der Wert der Krümmung der beim Auftragen der residuellen Dispersion gegen die formale Reaktionsordnung beim Minimumspunkt erhaltenen Kurve wird als eine numerische Kenngröße der Empfindlichkeit der Berechnung kinetischer Parameter auf die Form der kinetischen Funktion bei nicht-isothermer Versuchsausführung vorgeschlagen. Die Brauchbarkeit dieser Kenngröße wird an Beispielen gezeigt.

Резюме — Значение кривизны линии в точке минимума на графике в координатах остаточная дисперсия — формальный порядок реакции предложено использовать в качестве численной характеристики чувствительности метода вычисления кинетического параметра в форме кинетической функции в неизотермической кинетике. Эффективность этой характеристики показана на ряде примере.