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THE USE OF NON-LINEAR STATISTIC METHODS FOR DETERMINATION OF KINETIC PARAMETERS AND KINETIC FUNCTIONS CHOISE ACCORDING TO THERMOGRAVIMETRIC DATA

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ABSTRACT

The work deals with the defects of the use of the linearized forms of the main equation of the non-isothermic kinetics, shows the possibilities of their liquidation with the help of the use of the non-linear regression analysis.

INTRODUCTION

The linearized form of the main equation of the non-isothermic kinetics is used, as rule, in the methods of determination the kinetic parameters (KP), e.g., in the method of Coats-Redfern [1], Achar [2], and others [3].

The choise of the type of the kinetic functions (KF) and of the corresponding KP is realized according either to the maximum value of the absolute magnitude of the correlation coefficient (R_i) or the minimum value of the residual sum of squares (S_i^2).

Nevertheless, such a variant has some defects. The first defect is such that the values of the confidence intervals for the KP ($\log A^o, E^o$) corresponding to the minimum S_i^2 or the maximum $|R_i|$ are too diminished. Really because of the KP correlation (compensation effect) the confidence range for both the KP (ellipse) is much bigger than the confidence interval for the $\log A^o$ and E^o (rectangle).

Fig.1 schematically shows that the real bounds of the change of the KP $E_1''-E_2''$, $\log A_1''-\log A_2''$ is wider than the corresponding bounds for E^o and $\log A^o$ ($E_1'-E_2'$; $\log A_1'-\log A_2'$). A similar situation is characteristic for the solving of the inverse kinetic problems, in general, and in the non-isothermic kinetics, in particular. For defining the real bounds of the change of the KP besides the KF corresponding to the minimum S_i^2 or the maximum $|R_i|$, the KF insignificantly differing in the value S_i^2 from the minimum or $|R_i|$ from the maximum value should be taken into consideration.

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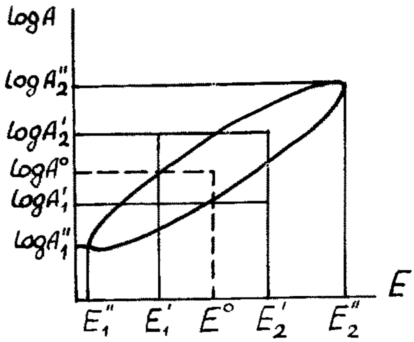

Fig.1 Bounds for KP

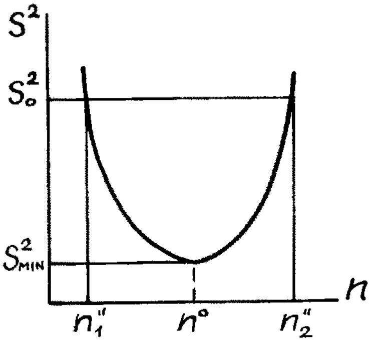

Fig.2 Dependence S^2 on n

APPLICATION OF NON-LINEAR STATISTICS

When using the kinetic function of the type $f(\alpha)=(1-\alpha)^n$ the dependence S_i^2 on n is as shown on Fig.2. This is the section of the surface of the residual sum of squares by the plane perpendicular to the plane (logA, E) and going through the big axe of the ellipse.

It is possible to obtain the real bounds of the change of the KP by defining the upper bound for S^2_{min} with the help of the Fisher dispersion relation

$$S_o^2=S^2_{min}F_p \tag{1}$$

Then n_1'' and n_2'' are as the abscisses of the points of the intersection of the line $S^2=f(n)$ with the straight line $S^2=S_o^2$; and the bound values of the KP may be found with the help of the bound values n. The use of the (1) makes it possible to overcome the mentioned defect in the limits of the linear regression analysis.

The second defect of the methods using the linearized form of the main equation of the non-isothermic kinetics is connected with their poor sensitivity to the type of the KF because the lenght of the big axe of the ellipse (Fig.1) significantly depends just on this sensitivity. Turning back to Fig.2 let's make it clear that the sensitivity of the method of calculation to the type KF as we understand it is the steepness of the dependence of S^2 on n. It's natural that the steeper this dependence, the narrower this interval and accordingly the interval of the KP.

Practice shows that in general all the methods of calculation of the KP using the linearized form of equation of the non-isothermal kinetics are similar in their sensitivity. Nevertheless, if we don't use the forsed linearization in the methods of calculation of **KP**, then it is possible to increase the sensitivity of these methods to the type of the KF.

For the integral method of Coats-Redfern [1] the defining of the KP is, really, the finding of the minimum of the value

$$(K-2)S_i^2 = \sum_j^K \left(g_i(\alpha_j) - \frac{A_i R T_j^2}{\beta E_i}\left(1 - \frac{2RT_j}{E_i}\right)\exp\left(-\frac{E_i}{RT_j}\right)\right)^2 \qquad (2)$$

and for the differential method of Achar [2] - the corresponding minimum

$$(K-2)S_i^2 = \sum_j^K \left(\frac{d\alpha_j}{f_i(\alpha_j)dT_j} - \frac{A_i}{\beta}\exp\left(-\frac{E_i}{RT_j}\right)\right)^2 \qquad (3)$$

Minimum S_i^2 can be found with the help of the gradient methods, that is, with the help of solving the system of equations of the general type

$$\begin{cases} \dfrac{\partial S_i^2}{\partial E} = 0 \\ \dfrac{\partial S_i^2}{\partial \log A} = 0 \end{cases} \qquad (4)$$

for each KF.

The bounds of the change of the KP are defined taking into consideration (1) as

$$S_o^2 = S_{i\ min}^2 F_{p_2} \qquad (5)$$

The value S_o^2 obtained with the help of (5) gives in the section of the surface of the residual sum of squares ellipse which lenght of the big axe is less due to the bigger sensitivity of the linear form of the main equation of the non-isothermal kinetics to the type of the KF.

Practically, using the data of [4] , e.g., we could obtain the lessening of the value change interval n from $\Delta n=0.66$ for the linear form of the the Coats-Redfern equation up to $\Delta n=0.46$ for the non-linear form (2). The result of this is the more correct solving of the inverse kinetic problem, that is, the single-valued choise of n=1.5, corresponding to a certain mechanism of the process.

So, the second of the mentioned defects may be liquidated in the limits of the non-linear regression analysis.

CONCLUSIONS

Summing up, the authors of the given paper propose to use (1) and (5) when estimating the real bounds of the change of the KP; and increase the accuracy of the solving of the inverse kinetic problem they propose to use non-linearized forms of the main equation of the non-isothermal kinetics.

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