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ON THE DEPENDENCE OF KINETIC PARAMETERS AND FUNCTIONS IN NON-ISOTHERMAL KINETICS

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ABSTRACT

The approaches to overcoming local ambiguity due to the dependence of the kinetic equation parameters are considered. The application of the mathematical apparatus of the Jacobi matrices enables one to determine the number of both independent kinetic parameters and kinetic functions used to describe a process. No more than five parameters in the Šestak–Berggren equation and only some kinetic functions are found to possess independence.

INTRODUCTION

Ambiguity of the inverse kinetic problem solution is the main hindrance in describing heterogeneous processes in terms of formal models. Following the classification adopted in ref. 1, local and global ambiguities are distinguished. Local ambiguity appears when the number of unknown kinetic parameters exceeds their ultimate quantity possible for particular experimental data. As a result, the kinetic parameters lose the property of independence while their numerical values lose physical sense. Global ambiguity implies that several equivalent sets of kinetic parameters may be determined for a single set of experimental data.

The problem of independent kinetic parameters and functions used to describe heterogeneous processes is considered in view of a practical application of the findings to overcome local ambiguity of the inverse kinetic problem.

MATHEMATICAL ASPECT

Assessment of the ultimate quantity of kinetic parameters that may be obtained by particular experimental data on a process is based on the mathematical apparatus of the Jacobi matrices [2]. Jacobi matrices were

applied with this aim for the first time in ref. 3. The essence of this approach was also dealt with in refs. 1 and 4 and is presented below in brief.

Thus, for some system of functions (1)

$$\begin{aligned}&\psi_1(x_1, x_2, \ldots, x_n)\\&\psi_2(x_1, x_2, \ldots, x_n)\\&\psi_n(x_1, x_2, \ldots, x_n)\end{aligned} \tag{1}$$

the Jacobi matrix is of the form of eqn. (2) [2]

$$\mathbf{J} = \left[\frac{\partial \psi_k}{\partial x_i}\right] \tag{2}$$

Here, if the system of eqn. (1) is other than independent, then the determinant of matrix (2) is zero, and the rank **J** equals the number of independent functions.

So, if ψ_i in eqn. (1) is some function of kinetic parameters, then the rank of the Jacobi matrix is, correspondingly, the number of independent parameters that may be determined using the experimental data [3]. To illustrate the effectiveness of this approach, we shall consider it in application to the well-known Šesták–Berggren equation [5] and compare the results with those reported in ref. 6.

ANALYSIS OF INDEPENDENCE OF KINETIC PARAMETERS IN THE ŠESTÁK–BERGGREN EQUATION

In the logarithmic form and allowing for the pre-exponent in the form $A = A_r T^r$ [6] the above equation acquires the form

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln A_r + r \ln T - \frac{E}{RT} + n \ln(1-\alpha) + m \ln \alpha + p \ln[-\ln(1-\alpha)] \tag{3}$$

In eqn. (3), the velocity logarithm is the function of six kinetic parameters

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_i = \psi_i\left(\ln A_r, r, -\frac{E}{R}, n, m, p\right) \tag{4}$$

where i is the ordinal number of the experimental velocity value. Substituting eqn. (4) into eqn. (2) gives the Jacobi matrix as

$$\mathbf{J} = \begin{bmatrix} \ln T_1 & 1/T_1 & \ln(1-\alpha_1) & \ln \alpha_1 & \ln[-\ln(1-\alpha_1)] \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \ln T_N & 1/T_N & \ln(1-\alpha_N) & \ln \alpha_N & \ln[-\ln(1-\alpha_N)] \end{bmatrix} \tag{5}$$

where $N \geqslant 6$. Then, the rank of matrix (5) determined in terms of experimental values of T and α yields the maximum number of independent parameters that may be specified from eqn. (3).

In order to determine the matrix rank, the forward running of the Gauss algorithm was used with partial choice of the governing element [7]. The number of non-zero elements on the main diagonal of the triangular matrix so obtained is equal to its rank [8].

In ref. 6, the determinant of the normalized matrix of type (5) was applied as a criterion of a possible quantity of parameters determined with the use of eqn. (3). For the experimental data on $CaCO_3$ decomposition [6], the absolute value of the determinant of the normalized matrix (5) calculated for three parameters ($\ln A, -E/R, n$) and four parameters ($\ln A, r, -E/R, n$) are equal to 0.476 and 0.102, respectively [6]. The latter value (0.102) is considered to characterize a poorly stipulated matrix. From this it was concluded impossible to make an estimation of more than three parameters, in principle. The main disadvantage of the method used in ref. 6 is that the value of the determinant is not a single-valued criterion of a poorly stipulated matrix [7,9]. On the contrary, the value of the matrix rank allows satisfactorily exact prediction of a possible number of parameters determined from eqn. (3). Thus, according to the data in ref. 6, the rank of matrix (5) equals three for both cases ($\ln A, -E/R, n$) and ($\ln A, r, -E/R, n$). This, in particular, indicates that the application of the relation $A = A_r T^r$ is useless since it results in the degeneration of the matrix and the parameter r becomes non-determinable. In fact, it was shown in ref. 6 that the application of $A = A_r T^r$ yields poor stipulation and the problem of the possibility of determining more than three parameters in the Šesták–Berggren equation remains debatable.

The estimation of the rank of matrix (5) using the experimental data for the decomposition of $Mg(OH)_2$ [10] and gypsum [11] with the aid of the above algorithm gives values of 4 or 5 for different segments of the experimental curve. So, disregarding $A = A_r T^r$ whose disadvantages were emphasized in ref. 12 allows estimation of 4 or 5 parameters of eqn. (3) against the three cited in ref. 6 as an ultimate value.

In practice, the following procedure may be recommended to overcome local ambiguity. First, build the Jacobi matrix based on the experimental data obtained. Second, specify its rank. Third, find independent parameters. To do so, C_N^R minors of the Jacobi matrix must be considered to find among them those whose rank is equal to the rank **R** of the reference matrix. The parameters included in the minors satisfying the previous condition will be independent.

ANALYSIS OF THE INDEPENDENCE OF KINETIC FUNCTIONS

The space formed by twenty most often used kinetic functions were considered in ref. 13. Not all kinetic functions entering this space are independent [13], i.e., the dimension of the space is less than twenty.

In accordance with the theorem of ref. 14, the rank of the system of vectors is equal to the rank of the matrix built by the co-ordinates of these vectors. Then, the dimension of the space of kinetic functions may be specified as a rank of the matrix

$$\left[f_j(\alpha_i)\right] \tag{6}$$

where i (the number of α values) is not less than j (the number of vectors, kinetic functions). Rank (6) was specified using the above algorithm. Twenty functions from ref. 13 were used in the calculation. The values of α were prescribed by the generator of equally distributed random numbers within the ranges 0–1 and 0–0.5. Within each of these intervals 100 combinations of 20 values were generated. It turned out that the rank of matrix (6) ranged, on average, from 9 to 12 for the former and from 8 to 11, for the latter interval, but did not exceed 14. So, the real dimension of the space of kinetic functions was twice as small as their total number.

This means that some of the kinetic functions may be represented through a linear combination of independent functions and cannot, therefore, give any extra information as compared to the latter ones. On the other hand, each of the linear independent functions that fairly describe the process characterize some individual feature of the process. So, the application of the entire set of kinetic functions provides a formally comprehensive description of the process. This is an argument for the non-traditional methodology [15] of solving the inverse problem of non-isothermal kinetics.

ANALYSIS OF THE INDEPENDENCE OF PARAMETERS IN THE MAIN NON-ISOTHERMAL KINETIC EQUATION

With regard for the results obtained in the previous part, any kinetic function may be represented through N linear independent ones

$$f(\alpha) = \sum_j^N c_j f_j(\alpha) \tag{7}$$

Then, the main equation of non-isothermal kinetics may be written as

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_i = \frac{A}{\beta}\exp\left(-\frac{E}{RT_i}\right)\sum_j^N c_j f_{ij} \tag{8}$$

where $f_{ij} = f_j(\alpha_i)$. In order to determine the number of independent parameters, we shall build the Jacobi matrix (2) for eqn. (8)

$$\begin{bmatrix} e_1\sum_j^N c_j f_{1j} & \frac{A}{\beta}\frac{1}{T_1}e_1\sum_j^N c_j f_{1j} & \frac{A}{\beta}e_1 f_{11} & \cdots \frac{A}{\beta}e_1 f_{1N} \\ \cdots & \cdots & \cdots & \cdots \\ e_{N+2}\sum_j^N c_j f_{N+2,j} & \frac{A}{\beta}\frac{1}{T_{N+2}}e_{N+2}\sum_j^N c_j f_{N+2,j} & \frac{A}{\beta}e_{N+2}f_{N+2,1} & \cdots \frac{A}{\beta}e_{N+2}f_{N+2,N} \end{bmatrix} \tag{9}$$

where $e_i = \exp(-E/RT_i)$. As the first column is a linear combination of N last ones, and the second one cannot be expressed with their use, the rank of matrix (9) equals $N + 1$. So, the number of the parameters in eqn. (8) to be determined is a unity less than the total number of parameters. Thus, when eqn. (8) is used, one of the parameters (either A or c_j) is superfluous. This fact generates a specific kinetic principle of uncertainty. It implies that the pre-exponent and all N coefficients of c_j in eqn. (8) cannot be determined simultaneously. The pre-exponential factor is, therefore, estimated due to the loss of one of the independent functions and, consequently, one of the individual process features is inevitably lost at the level of its formal description.

It should be noted that presentation of kinetic functions of a process through a linear combination of independent functions (eqn. (7)) provides a somewhat synthetic description. The application of similar process descriptions is a distinctive feature of the non-traditional methodology [15] used in solving the inverse kinetic problem. Therefore, the inverse problem formulated as the problem for determining the parameters in eqn. (8) makes it possible to relate its solution to the non-traditional methodology as well as to other methods cited in ref. 15.

CONCLUSION

In conclusion, the following aspects should be emphasized and allowed for in the practical calculation of the parameters of kinetic equations.

(i) The real experimental data may be used to determine 4–5 parameters in the Šesták–Berggren equation. The dependence of the number of parameters to be determined on the segment of the kinetic curve seems to indicate the extreme character of maximum value. It is evident that 4 parameters may be estimated with sufficient reliability.

(ii) The dependence $A = A_r T^r$ should be omitted in the Šesták–Berggren equation, since its use makes one of the parameters (E or r) undefinable.

(iii) Before determining the parameters of kinetic equations, a Jacobi matrix (2) should be built, and its rank and independent parameters estimated. The values of the parameters may have a physical sense only when they are independent.

(iv) The application of the mathematical approach under consideration makes it possible to completely avoid local ambiguity [1] of the inverse kinetic problem. This approach, however, disregards global ambiguity [1] whose complete elimination is impossible due to an inevitable incompleteness of describing real processes in terms of formal models.

In practice, global ambiguity may be decreased by applying the non-traditional methodology to the solution of the inverse kinetic problem [15]. One of its methods, implying a generalized description of a process as a linear

combination of independent kinetic functions, is pointed out in this work. Its more comprehensive discussion is a scope of another paper.

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