Determining parametric functions kinetic constants using the decomposition method

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Abstract. The purpose of this work is to automation of the informativity content analysis of kinetic parameters based on one composing a chemical reaction independent route. The software for determining the basis of nonlinear parametric functions of kinetic measurements for the mechanisms of complex chemical reactions is developed and described.

1. Introduction

The parametric identifiability of the kinetic model, posed and developed, in the works of Slinko M G, Spivak S I, Gorsky V G [1, 2], attracting an increasing number of researchers and a variety of research methods [3, 4].

Parametric identification refers to the definition of independent combinations of kinetic constants. In the works of [5] detailed model mechanisms were studied, direct relationships (connections) between kinetic constants were found, and this implies non-uniqueness of the solution.

The determination of the number and type of parametric functions for the quasistationary case of reactions is studied in the works of Bykov V I, Yablonsky G S, Evstigneev V A, Eisenberg L A [6, 7] by the methods of elimination of intermediate substances. The problem of generalization to the case of an unsteady process is considered in the works of Asadullin R M [8].

Stationary theory reactions developed by Khorouti Dz and Temkin M I [9, 10] is the basis of the methodology for constructing kinetic models very different types of complex chemical reactions.

In the works of Spivak S I [11, 12] developed a decomposition method that allows one to divide the mechanism of a complex chemical reaction into systems of submechanisms, the number of which is equal to the number of basic routes. Decomposition of the mechanisms of complex chemical reactions allows us to move on to tasks of substantially lower dimension.

In the work [13] a graph and theoretic algorithm for determining the basis of nonlinear parametric functions of kinetic constants directly from the reaction graph was developed.

The use of the decomposition method for the studied systems of large dimension is advisable due to the fact that the geometric interpretation of the mechanism loses its visibility. The physical area of the computer screen has certain boundaries, therefore it is difficult to illustrate the functional relationships of kinetic parameters according to the Volpert’s graph [14].
2. An algorithm for determining the basis of nonlinear parametric functions of reactions of large dimension

In this paper, we propose an algorithm for determining the basis of nonlinear parametric functions using the decomposition method:

1. Build the Volpert’s graph of the mechanism of a complex chemical reaction.
2. Find the basis of routes \( \{M_i\} \ (1 \leq i \leq p) \) according to the Volpert’s graph.
3. Select for each subgraph of the Volpert’s graph (reaction route) by eliminating all Y-vertices and X-vertices that have only incoming edges (substances that are products in elementary stages and are not starting substances in any other elementary stage), and also W-vertices for which there are no previous X-vertices. Accordingly, exclude edges incident to these vertices.
4. Write for each subsystem the bond matrix \( A_{M_i} \). The rows of this matrix correspond to the rate constants of the elementary stages and the terms due to the measurement error of the starting substances and reaction products of the investigated subsystem. The number of columns in the matrix is equal to the number of X-vertices. The location of nonzero elements in the connection matrix is determined by W-vertices and X-vertices adjacent in the subgraph. The value of the element is determined by the edge connecting the X-vertex with the W-vertex (kinetic constant).
5. Combine the matrices \( A_{M_i} \) of the studied subsystems, write out the bond matrix \( A \) corresponding to the original system.
6. To solve the system of partial differential equations corresponding to the bond matrix \( A \) of the original circuit. Independent solutions form the basis of nonlinear parametric functions of kinetic parameters.

3. Software for determining the basis of nonlinear parametric functions of complex catalytic reactions

Software based on the algorithm for determining the basis of nonlinear parametric functions using the decomposition method was developed [15]. The program is implemented in the Microsoft Visual C ++ 2012 environment in the C ++ [16] programming language.

We describe the main stages of the construction of the program and illustrate the work of the program by the example of the mechanism of steam conversion of methane on a nickel catalyst [17]:

1) \( CH_4 + Z \rightarrow CH_2Z + H_2 \),
2) \( CH_2Z + H_2O \rightarrow COZ + 2H_2 \),
3) \( COZ \rightarrow CO + Z \),
4) \( H_2O + Z \rightarrow OZ + H_2 \),
5) \( CO + OZ \rightarrow CO_2 + Z \).

We introduce the following notation: \( \{X_1, X_2, X_3, X_4, X_5\} = \{CH_4, H_2, H_2O, CO, CO_2\} \) - starting substances and reaction products, \( \{Y_1, Y_2, Y_3\} = \{Z, C_2H_2Z, C_2H_4Z\} \) - intermediate substances.

The input data entered by the user is the name of the reaction mechanism, the number of stages in the reaction mechanism, the total number of participants in the mechanism, the number of intermediate substances. When the button “Next” is pressed, tables are formed for the user to enter the chemical reaction mechanism and chemical formulas of the reaction participants. The input of the reaction mechanism is carried out in the table character by character, with the exception of reversibility \( (\leftrightarrow) \) and irreversibility of the stage \( (\rightarrow) \), they should be entered in one cell of the table. In the “Menu” of the program in the paragraph “About the program” this rule is registered for the user. It is also possible to increase the columns of the table to enter the reaction mechanism.

Figure 1 shows the program interface for finding the basis of nonlinear parametric functions of decomposition methods.

Based on the input data, the program forms a stoichiometric matrix, the rate constants of elementary stages using algorithms similar to the previous program.
The decomposition of a multi-route catalytic reaction is carried out according to an index matrix. To put in the matrix of indices, it is necessary to index the vertices of the Volpert’s graph of the complex chemical reaction mechanism according to the following algorithm. A matrix of stoichiometric coefficients is used for indexing. In a cycle of rows of a stoichiometric matrix, columns with nonzero values are considered. At the first stage, index 0 is assigned to the substance vertices corresponding to columns with negative values in the first row, i.e. index 0 is assigned to all the starting materials of the first stage of the mechanism. Next, index 0 is assigned to the vertex corresponding to the first stage, since all the vertices preceding it received the index. Index 1 is assigned to substance vertices corresponding to columns with positive values in the current row, i.e. first stage products. Goes to the next row of the matrix. If all vertexes-substances corresponding to columns with negative coefficients in the row under consideration receive an index, then the corresponding vertex-reaction is assigned an index equal to the maximum index of all the initial vertices of substances at this stage. Otherwise, the initial substance vertices that do not have an index are assigned an index of 0 and the reaction vertex is assigned an index calculated similarly to the index for the first reaction vertex. As a result, all vertices are received an index (Figure 2):

![Figure 2. Table of vertex indices for the Volpert’s graph.](image)

Using the obtained indices and the stoichiometric matrix coefficients, a matrix of indices is constructed, the rows of which correspond to the vertices of the reaction, and the columns to the vertices of the intermediate substances.

The matrix elements are the vertex-substance indices taken with the sign of the corresponding coefficient in the stoichiometric matrix. Elements corresponding to zero values of stoichiometric coefficients are filled with the value 0. Therefore, elements of the matrix of indices equal to "0" and "-0" are put with the values "10" and "+10".

![Figure 3. The matrix of vertex indices of the Volpert’s graph.](image)
The next stage of the algorithm is a direct search for the sequence of row numbers of the matrix of indices forming a cycle. The search begins with each element whose value is not 0. In the column, a transition is made to the element opposite in sign, then there is a transition in the row to any element whose value is not equal to 0, etc., until we arrive at the element, from which started the “movement”. The sequences found form the basis of the routes of the chemical reaction mechanism:

![Volpert's graph](image1)

**Figure 4.** The basis of the routes of the chemical reaction mechanism.

The program implements a visual image of the Volpert’s graph according to a similar algorithm of the previous program. Figures 5, 6 show Volpert’s graphs on the corresponding routes, which are implemented in a separate software window. The bold subgraph is highlighted in bold lines.

![Volpert's graph](image2)

**Figure 5.** The Volpert’s graph corresponding to route $M_1$.

![Volpert's graph](image3)

**Figure 6.** The Volpert’s graph corresponding to route $M_2$.

Figures 7, 8 show matrixes of connections along routes $M_1$ and $M_2$, determined directly from the converted Volpert’s subgraphs.

Figure 9 shows the combined matrix of bonds for the methane vapor conversion mechanism on a nickel catalyst.

The main result of the program is to determine the basis of nonlinear parametric functions of kinetic parameters (Figure 10).
Thus, a graph and theoretic algorithm is proposed and implemented to determine the basis of nonlinear parametric functions by decomposing the mechanism of a complex chemical reaction along independent routes.

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5. References
[1] Slin'ko M G 1981 The problem kinetics of heterogeneous catalytic reactions for the simulation of chemical reactors Kinetics and catalysis XXII(1) 5-14.
[2] Spivak S I and Gorskij V G 1988 Identifiability research is one of most important stages of building mathematical models in chemistry Journal of structural chemistry 29(6) 119-125.
[3] Khursan S L, Ismagilova A S and Akhmetyanova A I 2018 Determining the basis of homodesmotic reactions of cyclic organic compounds by means of graph theory Russian Journal of Physical Chemistry A 92(7) 1312-1320.
[4] Shakurov I R and Asadullin R M 2014 Parameter identification for systems of nonlinear differential equations by the example of Lotka-Volterra model Biophysics 59(2) 339-340.
[5] Damian V, Sandua A, Damian M, Potra F and Carmichael G R 2002 The kinetic preprocessor KPP—a software environment for solving chemical kinetics Computers & Chemical Engineering 26 1567.

[6] Yablonskij G S, Evstigneev V A and Bykov V I 1988 Graphs in chemical kinetics. Application of graph theory in chemistry (Novosibirsk: Nauka) 70-143.

[7] Ajzenberg L A 1985 Multidimensional deductions and their applications Chapter 2 Multidimensional logarithmic deduction and its applications Complex analysis—many variables-2, Results of science and technology Series: Modern problems of fundamental mathematics 8 29-45.

[8] Asadullin R M and Bahtizin R N 1990 Analysis of solutions to inverse problems of chemical kinetics Kinetics and catalysis 31(3) 755-759.

[9] Khoruti Dz 1959 How to find the kinetic equation of the reverse reaction? Problems of physical chemistry (Moskva: Goskhimizdat) 39-49.

[10] Temkin M I 1975 Kinetics of heterogeneous catalytic reactions Journal ACS 20(1) 7-14.

[11] Spivak S I, Ismagilova A S and Gibaeva R A 2014 Graph-theoretic method for analyzing the informativity of kinetic experiments in determining parameters Bulletin of Bashkir University 19(4) 1126-1130.

[12] Spivak S I, Ismagilova A S and Hamitova I A 2010 Graph-theoretical method for determining routes of complex chemical reactions Doklady Physical Chemistry 434(4) 499-501.

[13] Ismagilova A S, Khamidullina Z A and Spivak S I 2017 Graph-theoretic method for finding basis of nonlinear parametric functions Materials of VII International scientific and practical conference “Mathematical modeling of processes and systems” (Sterlitamak: RIC SF BashG) 365-369.

[14] Vol’pert A I and Khudyaev S I 1975 Analysis in classes of discontinuous functions and equations of mathematical physics (Moscow: Nauka) 394.

[15] Khamidullina Z A and Ismagilova A S 2019 Analysis of information content of kinetic parameters using decomposition by independent routes FSIS (Rospatent) N 2019665171.

[16] Stroustrup B 2019 The C++programming language. Short course (Moscow: Dialektika) 322.

[17] Krylov O V 2004 Heterogeneous catalysis (Moscow: Akademkniga) 679.