



Study of Accuracy in Chemical Kinetics Problems

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ABSTRACT

This paper was devoted to taking into account the influence of uncertainty in the kinetic parameters on the solution of direct problems. A computational algorithm for obtaining interval estimates of direct modeling, based on a two-sided uncertainty method, was constructed. A computational experiment was performed using the example of a reaction for obtaining phthalic anhydride by constructing two-sided estimates of solutions in differential equations including interval parameters.

Keywords: Interval analysis; two-sided method; Kinetic model; Constants of speed; Direct kinetic problem; Intervals of uncertainty of kinetic parameters

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INTRODUCTION

A direct problem of chemical kinetics is the calculation of the composition of a multicomponent reacting mixture and the reaction rate on the basis of a mathematical model with known parameters, such as the rate constants and the activation energy of the reaction. As a rule, the kinetic parameters are in a range of possible values, since they are determined on the basis of the obtained set of experimental data, which is inherent in a certain inaccuracy. However, when modeling chemical reactions, it is customary to use average values of kinetic constants, which does not guarantee the mode of functioning that occurs during operation. Thus, when solving the direct problem of chemical kinetics, there is a need to apply methods of interval analysis [1].

By now, techniques for interval computations, packages of applied programs and algorithmic macro languages have been developed that implement elements of interval analysis. At the heart of such approaches and programs is the replacement of arithmetic operations and real functions over real numbers by intervening operations and functions over interval numbers. In packages of applied programs in which interval calculations are realized, it is possible to carry Matlab, Maple, Scilab, etc. [2]. The main

lack of these packages is that there is no possibility of changing the program code, the need for which can arise during the simulation of real chemical processes.

MATERIALS AND METHODS

The mathematical model of a chemical process is a system of ordinary nonlinear differential equations:

$$x'_i = f_i(t, x, k), t \in [0; T] \quad (1)$$

with initial conditions at $t = 0$:

$$x_i(0) = x_i^0, i = 1 \dots n, \quad (2)$$

where $t \in [0; T]$ – the reaction time, x – the concentration vector of the components, n – the number of reagents, k – the vector of kinetic constants of the reaction rates of dimension.

The system (1)-(2) represents Cauchy problem for the systems of the ordinary differential equations which can be solved, for example, by an explicit or implicit method of Runge-Kutta of the 4th order of accuracy [3]. Time kinetic constants in the researched processes can be presented in the form of intervals:

$$k = (k_1, \dots, k_m)^T \in \mathbf{k}, \quad (3)$$

where

$$k_j = [\underline{k}_j, \bar{k}_j] = \{k_j \in R | \underline{k}_j \leq k_j \leq \bar{k}_j\},$$

$j = 1, \dots, m$, - interval is estimated with a dispersion in limits of some percentages of rather known mean value, \underline{k}_j - lower bound of

an interval, \bar{k}_j - upper interval boundaries.

Then Runge-Kutta's method as a method for the decision of tasks in direct simulations is not suitable, so the method was not adapted to operation with intervals.

In the conditions of (3), we would look for the solution of system (1)-(2) in a look

$$x = (x_1, \dots, x_n)^T \in \mathbf{X},$$

where

$$x_i = [\underline{x}_i, \bar{x}_i] = \{x_i \in R | \underline{x}_i \leq x_i \leq \bar{x}_i\},$$

$i = 1, \dots, n$, \underline{x}_i - lower and \bar{x}_i - upper boundaries of the appropriate interval.

For the solution of an objective (1)-(3), a two-sided method will be used [4], and an objective algorithm in an interval look will be constructed.

The main idea of a two-sided method consisted in the analysis of private derivative right parts of differential equations on a monotonicity in parameters k_j and x_i .

For this purpose in operation [5] support material functions

$Q^l(t, u_1, \dots, u_n, v_1, \dots, v_n)$, $l = 1, 2$, are entered into reviewing $\underline{u} \leq \bar{u}$, $\underline{v} \leq \bar{v}$ that are satisfied in case of conditions:

$$Q_i^l(t, \underline{u}, \bar{v}) \leq Q_i^l(t, \bar{u}^{[u_i]}, \underline{v}),$$

$$l = 1, 2, i = 1 \dots n,$$

where $u^{[v_i]} = (u_1, \dots, u_{i-1}, v_i, u_{i+1}, \dots, u_n)$.

At the same time for functions of the right parts of system (1), inequalities were executed:

$$Q_i^1(t, x, x) < f_i(t, x, k) < Q_i^2(t, x, x).$$

We supposed that the vector function $\underline{x}, \bar{x} \in R^n$ satisfied to the following ratios:

$$\underline{x}' \leq Q^1(t, \underline{x}, \bar{x}),$$

$$\bar{x}' \geq Q^2(t, \bar{x}, \underline{x}),$$

$$\underline{x}(0) \leq \underline{x}_0,$$

$$\bar{x}(0) \geq \bar{x}_0.$$

Then any decision x of the problem (1)-(2) with an initial condition $\underline{x}_0 \leq x(0) \leq \bar{x}_0$ satisfied the estimates:

$$\underline{x}_t \leq x(t) \leq \bar{x}_t.$$

It was marked that at the same time the following conditions were satisfied:

$$Q^1(t, \underline{x}, \bar{x}) \leq \inf f(t, x, k),$$

$$Q^2(t, \underline{x}, \bar{x}) \geq \sup f(t, x, k).$$

In quality Q , it was possible to take boundaries of the monotonic on switching the interval extension of function f in the right differential equations of system (1). Then the system (1) could be rewritten as follows:

$$\underline{x}' \leq f(t, x^{[x_i]}, k),$$

$$\bar{x}' \geq f(t, x^{[\bar{x}_i]}, k),$$

$$\underline{x}(0) \leq \underline{x}_0,$$

$$\bar{x}(0) \geq \bar{x}_0.$$

The solution of the constructed system generally gave wider two-sided decision, than optimum. In case of execution, the following conditions were described in operation [6]:

$$\frac{\partial f_i}{\partial x_j} \geq 0, i \neq j, i, j = 1, 2, \dots, n, \quad (4)$$

$$\text{sign} \frac{\partial f_i}{\partial k_j} = \text{const}, j: \text{wid}(\mathbf{k}_j) \neq 0, \forall k \in \mathbf{k}, \forall x \in \mathbf{x} \quad (5)$$

the system (1)-(2) can be presented in the following form

$$\underline{x}' = f(t, \underline{x}, k^1),$$

$$\bar{x}' = f(t, \bar{x}, k^2),$$

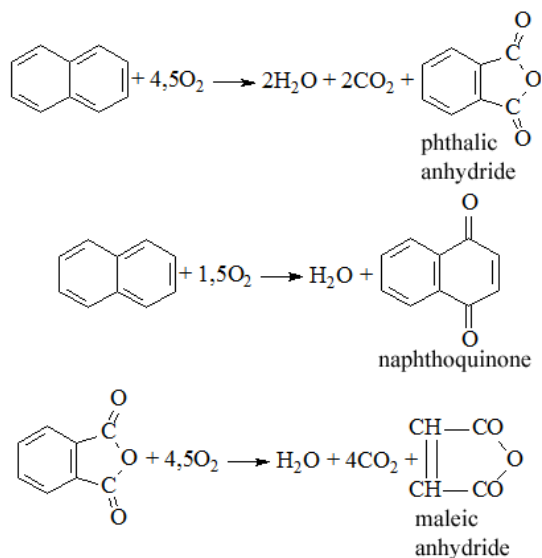
$$\underline{x}(0) = \underline{x}_0,$$

$$\bar{x}(0) = \bar{x}_0. \quad (6)$$

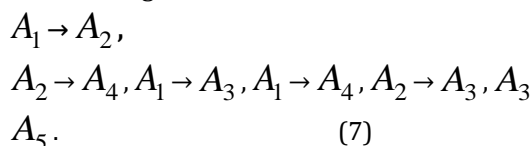
where $k^1, k^2 \in \mathbf{k}$, $\text{wid}(\mathbf{k}_j)$ - width of interval value. In this case \underline{x}, \bar{x} were some private solutions of the initial system and, therefore, they were optimum.

RESULTS

The constructed algorithm was applied to carry out a computing experiment of response in receiving phthalic anhydride:



The diagram of response could be presented in the following form:



where A_i - substances, $i = \overline{1,5}$ (1 - naphthalene, 2 - naphthoquinone, 3 - phthalic anhydride, 4 - carbon dioxide, 5 - maleic anhydride) [7].

According to the diagram (7), the system of the differential equations describing kinetics of this response was written as follows:

$$\begin{aligned} x_1' &= -k_1 x_1 - k_3 x_1 - k_4 x_1, \\ x_2' &= k_1 x_1 - k_2 x_1 - k_5 x_2, \\ x_3' &= k_3 x_1 + k_5 x_2 - k_6 x_3, \\ x_4' &= k_2 x_2 + k_4 x_1, \\ x_5' &= k_6 x_3, \end{aligned} \quad (8)$$

where x_i - concentration of the i -th substance ($i = \overline{1,5}$) (molar shares), k_j - rate constant of the j -th reaction ($j = \overline{1,6}$) was calculated according to Arrhenius's equation. As initial concentration of substances, degenerate intervals were accepted, i.e. the discrete values of initial concentration were provided through intervals which width was equal to zero:

$$x_1(0) = [1; 1], \quad x_i(0) = [0; 0], \quad i = \overline{2,5}. \quad (9)$$

The response course time in the interval form was also presented:

$$t \in [0; 0.5]. \quad (10)$$

In article [8], kinetic constants of response of receiving phthalic anhydride were found by solving the reverse problem. The constants at a temperature of $T=620\text{K}$ took the following form: $k_1 = 3.292, k_2 = 0.637, k_3 = 1.847, k_4 = 0.497, k_5 = 2.797, k_6 = 0.037$.

For the decision of the direct kinetic problem, the constants were provided as interval estimates with a dispersion within 3% of the mean values calculated by Arrhenius's formula to within 10^{-5} :

$$\begin{aligned} k_1 &= [3.19324; 3.39076], \\ k_2 &= [0.61789; 0.65611], \\ k_3 &= [1.78577; 1.89523], \\ k_4 &= [0.48209; 0.51191], \\ k_5 &= [2.71309; 2.88091], \\ k_6 &= [0.03589; 0.03811]. \end{aligned}$$

In case of creation of the decision, it was possible to be convinced by a two-sided method that private derivatives of functions of system (7) meet conditions (4) and do not meet conditions (5). Therefore, the decision of the problem can be received by the serial solution of independent subproblems:

$$\begin{cases} \underline{x}_1' = -\underline{k}_1 \underline{x}_1 - \underline{k}_3 \underline{x}_1 - \underline{k}_4 \underline{x}_1, \\ \underline{x}_2' = \underline{k}_1 \underline{x}_1 - \underline{k}_2 \underline{x}_2 - \underline{k}_5 \underline{x}_2, \\ \underline{x}_3' = \underline{k}_3 \underline{x}_1 + \underline{k}_5 \underline{x}_2 - \underline{k}_6 \underline{x}_3, \\ \underline{x}_4' = \underline{k}_2 \underline{x}_2 + \underline{k}_4 \underline{x}_1, \\ \underline{x}_5' = \underline{k}_6 \underline{x}_3, \end{cases} \quad (11a)$$

$$\begin{cases} \overline{x}_1' = -\overline{k}_1 \overline{x}_1 - \overline{k}_3 \overline{x}_1 - \overline{k}_4 \overline{x}_1, \\ \overline{x}_2' = \overline{k}_1 \overline{x}_1 - \overline{k}_2 \overline{x}_2 - \overline{k}_5 \overline{x}_2, \\ \overline{x}_3' = \overline{k}_3 \overline{x}_1 + \overline{k}_5 \overline{x}_2 - \overline{k}_6 \overline{x}_3, \\ \overline{x}_4' = \overline{k}_2 \overline{x}_2 + \overline{k}_4 \overline{x}_1, \\ \overline{x}_5' = \overline{k}_6 \overline{x}_3, \end{cases} \quad (11b)$$

With initial data corresponded to the boundaries of initial interval concentration. The creation of subsystems was carried out on the basis of the analysis of characters of a monotonicity (an isotone property and an

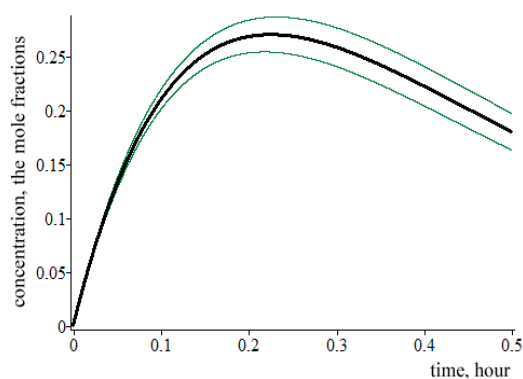
antitone property) of [5] right parts of differential equations of the system in the kinetic parameters entering their record (table 1).

Table 1. Execution of conditions of a monotonicity in parameters in case of the decision for the direct problem by a two-sided method for response of receiving phthalic anhydride

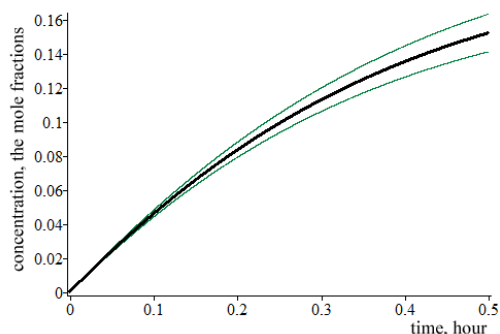
f	Parameters in which the condition isotone property is satisfied	Parameters in which the condition antitone property is satisfied
f_1	k_2, k_5, k_6	k_1, k_3, k_4
f_2	k_1, k_3, k_4, k_6	k_2, k_5
f_3	k_1, k_2, k_3, k_4, k_5	k_6
f_4	$k_1, k_2, k_3, k_4, k_5, k_6$	-
f_5	$k_1, k_2, k_3, k_4, k_5, k_6$	-

To solve the subsystems obtained, we could use the fourth-order Runge-Kutta algorithm, since the subsystems (11) are a system with real values of the kinetic constants.

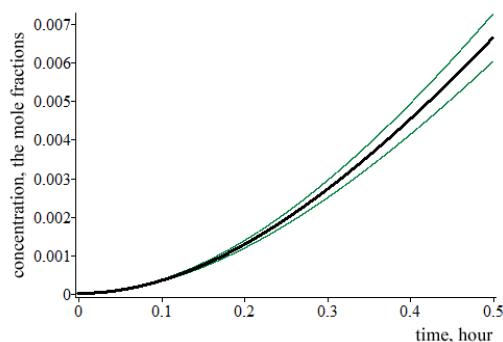
A graphical two-sided solution of the direct problem for the reaction for the production of phthalic anhydride is presented in Fig. 1 (solid bold line - solution with mean values of parameters, solid lines - solution obtained by two-sided method).



a) naphthoquinone



c) carbon dioxide



d) maleic anhydride

Figure 1. Two-sided constraints of the solutions of the direct problem for the reaction for the production of phthalic anhydride

In finite time point in case $t = 0.5$ hours, a variation of kinetic constants of speeds within 3% of mean values resulted in values of concentration of the substances lying within mean relative error from the decision corresponding to mean values of constants of speeds: $\delta(A_1) = 11.01\%$, $\delta(A_2) = 11.4\%$, $\delta(A_3) = 8.16\%$, $\delta(A_4) = 8.07\%$, $\delta(A_5) = 9.93\%$. The received kinetic curve changed the concentration of substances as a result of the decision for the direct kinetic problem belonging to a set of the decisions which were boundaries of this two-sided decision.

CONCLUSION

Thus, in operation, the search algorithm of the interval solution for a straight line of the kinetic problem which allows defining a confidential interval of change in the concentrations participating in response of the substances in the conditions of the given error of starting values of kinetic parameters was constructed.

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