Algorithms of direct simulation of chemical reaction under conditions of uncertainty of initial data

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Abstract. Accuracy of measurement of initial data is important in simulation of chemical processes. Distortion of the original parameters can have a significant impact on the result of calculations. In addition to this error, there is also the error of the chosen method of solving the problem. In this article discusses the methods of interval calculations, their using for measurement of initial data and determination of errors in solving problems. Algorithms were implemented in Pascal programming language in PascalABC.NET development environment, visualization of solution was obtained with using Mathcad system.

1. Introduction

Interval calculation methods are widely used in the field of mathematical modeling of chemical processes. This is determined by the fact that measurement error occurs already in the evaluation of the initial experimental data [1]. This error may have a significant impact on the results of future calculations. Therefore, the initial kinetic data should be recorded as intervals and then calculated using interval methods.

Direct modeling of the chemical reaction is a solution to the kinetic problem, such as calculating the concentrations of substances involved in the reaction process [2].

2. Description of algorithms

In the process of studying this topic, a mathematical model of the ethane pyrolysis reaction was built, and the use of interval analysis methods was considered on its example. Ethylene is one of the products of this reaction. It is a combustible gas without color and smell, which is widely used in the oil refining industry [3]. Ethylene can rarely be found in nature, so it is mostly produced artificially.

The ethane pyrolysis reaction scheme described and investigated in [4] is as follows:

\[
\begin{align*}
C_2H_6 & \rightarrow 2CH_3, \\
CH_3 + C_2H_6 & \rightarrow CH_4 + C_2H_5, \\
C_2H_5 & \rightarrow C_2H_4 + H, \\
H + C_2H_6 & \rightarrow H_2 + C_2H_5, \\
2C_2H_5 & \rightarrow C_4H_{10}.
\end{align*}
\]

(1)
Let's designate $A_1 - C_2H_6$ (ethane), $A_2 - CH_4$ (methyl), $A_3 - CH_4$ (methane), $A_4 - C_2H_5$ (ethanol), $A_5 - C_2H_4$ (ethylene), $A_6 - H$ (hydrogen atom), $A_7 - H_2$ (hydrogen molecule), $A_8 - C_4H_{10}$ (butane). The reaction scheme (1) can be represented as follows:

\[ A_1 \rightarrow 2A_2, \]
\[ A_2 + A_1 \rightarrow A_3 + A_4, \]
\[ A_4 \rightarrow A_5 + A_6, \]
\[ A_6 + A_1 \rightarrow A_7 + A_4, \]
\[ 2A_4 \rightarrow A_8. \]

Based on the law of acting masses [5] and taking into account the balance of stoichiometric coefficients [6], it is possible to write a mathematical reaction model in the form of the following system of differential equations:

\[
\frac{dx_i}{dt} = -k_1x_i - k_2x_ix_2 - k_4x_i x_6, \quad \frac{dx_5}{dt} = k_3x_4,
\]
\[
\frac{dx_3}{dt} = -k_2x_1x_2 + 2k_1x_1, \quad \frac{dx_6}{dt} = k_3x_4 - k_3x_8x_6,
\]
\[
\frac{dx_2}{dt} = k_3x_2x_2, \quad \frac{dx_4}{dt} = k_1x_3x_6,
\]
\[
\frac{dx_1}{dt} = k_2x_1x_2 - k_3x_3 + k_4x_1x_6 - 2k_3x_2^2, \quad \frac{dx_8}{dt} = k_5x_8^2,
\]

with starting conditions

\[ x_i(0) = x_i^0, i = 1,8. \]

Here $x_i$ is the concentration of the $i$-th component (mole fractions), $i = 1,8$, $k_j$ – rate constant $j$-th reaction ($s^{-1}$), $j = 1,5$. The reaction time $T$ is 0.26 c.

To solve the system of differential equations (3) with initial conditions (4), the following values of reagent concentrations and rate constants represented not by real numbers, but by intervals were used:

\[ k_1 = [1.273 \cdot 10^3; 1.407 \cdot 10^3], k_2 = [3.5435 \cdot 10^2; 3.9165 \cdot 10^2], k_3 = [3.5055 \cdot 10^1; 3.8745 \cdot 10^1], k_4 = [3.477 \cdot 10^3; 3.843 \cdot 10^3], k_5 = [1.539 \cdot 10^1; 1.701 \cdot 10^1], x_1 = [0.133; 0.147], x_2 = \ldots = x_8 = [0; 0]. \]

Thus rate constants are interval estimates with a spread within 5% of average values calculated according to literature data [7]:

\[ k_1 = 1.34 \cdot 10^3, k_2 = 3.73 \cdot 10^2, k_3 = 3.69 \cdot 10^1, k_4 = 3.66 \cdot 10^3, k_5 = 1.62 \cdot 10^2, x_1 = 0.14, x_2 = \ldots = x_8 = 0. \]

Any solution of the system of differential equations (3)-(4) was found in the form of an interval \([x_i^L, x_i^R]\), where $x_i^L, x_i^R$ is the left and right boundaries of the interval value of the concentration of the $i$-th component involved in the pyrolysis reaction of ethane.

To solve this system, the explicit Euler method was used [8], in which mathematical operations on real numbers were replaced by operations of interval arithmetic [9], such as (5)-(8).

\[ a + b = [a + b; a + b], \]  
\[ a - b = [a - b; a - b]. \]
\[
a^*b = \left[ \min\{ab, a\bar{b}, \bar{a}b, \bar{a}\bar{b}\}; \max\{ab, a\bar{b}, \bar{a}b, \bar{a}\bar{b}\} \right],
\]
(7)
\[
a/b = a^*\left[ 1/b; 1/b \right], 0 \notin b.
\]
(8)

To implement the algorithm of the modified Euler method, a program was compiled in the Pascal programming language in the PascalABC.NET development environment [10]. The resulting solution of the system of ordinary differential equations was written to a file and passed to Mathcad system. Further, the solutions were plotted in the form of reactant concentrations versus contact time and compared with the solution at specific points of initial intervals (figure 1).

![Figure 1](image)

**Figure 1.** Solving the direct problem for substances \(A_4\) and \(A_6\).

In figure 1, \(x4\_L, x4\_R, x6\_L, x6\_R\) – solutions found by program in Pascal programming language using interval operations. For comparison, graphs of the exact solution were also plotted at the initial average real values of the constants of the velocities of the reacting substances. In the graph \(x4, x6\) – solutions that Mathcad computes as a function value at specific points.

As can be seen from figure 1, the Moore effect is present when calculating reagent concentrations using the replacement of arithmetic operations with their interval analogues [11]. There is a significant divergence of the exact solution from the interval at the endpoint. As a consequence, we do not have an accurate result of calculations. In order to get rid of the said drawback, a two-side solution evaluation algorithm described in the work [12] was used. Using the definitions of isotonicity, antitonicity of the function by variable [13], we test the right parts of the system of differential equations for monotonicity by parameters. The results are shown in table 1.

**Table 1.** Compliance with monotony conditions by parameters

| Parameters by which the isotonicity condition is met | Parameters by which the antitonicity condition is met |
|----------------------------------------------------|------------------------------------------------------|
| \(x_1\) \(k_5, k_5\) \(k_1, k_2, k_4\) | \(k_3, k_4, k_5\) \(k_2\) |
| \(x_2\) \(k_1, k_3, k_4, k_5\) | \(k_1, k_2, k_4, k_5\) |
| \(x_3\) \(k_1, k_2, k_3, k_4, k_5\) | - |
| \(x_4\) \(k_1, k_2, k_4\) | \(k_3, k_2\) |
| \(x_5\) \(k_1, k_2, k_3, k_4, k_5\) | - |
| \(x_6\) \(k_1, k_2, k_3, k_5\) | \(k_4\) |
| \(x_7\) \(k_1, k_2, k_3, k_4, k_5\) | - |
| \(x_8\) \(k_1, k_2, k_3, k_4, k_5\) | - |
Then the lower and upper limits of the two-side solution can be obtained by solving the following independent systems [14]:

\[
\begin{align*}
    x'_1 &= -k_1 x_1 - k_2 x_2 - k_4 x_4 x_6, \\
    x'_2 &= -k_2 x_1 x_2 + 2k_1 x_1, \\
    x'_3 &= k_2 x_1 x_2, \\
    x'_{4} &= k_2 x_1 x_2 - k_4 x_4 x_6 + k_4 x_1 x_6 - 2k_3 x_2, \\
    x'_{5} &= k_3 x_1, \\
    x'_{6} &= k_3 x_1 - k_4 x_4 x_6, \\
    x'_{7} &= k_4 x_1 x_6, \\
    x'_{8} &= k_5 x_4, \\
    x(0) &= x_0.
\end{align*}
\]

As a result, the solution shown in figure 2.

\[
\begin{align*}
    x'_1 &= -k_1 x_1 - k_2 x_1 x_2 - k_4 x_4 x_6, \\
    x'_{2} &= -k_1 x_1 x_2 + 2k_1 x_1, \\
    x'_{3} &= k_2 x_1 x_2, \\
    x'_{4} &= k_2 x_1 x_2 - k_4 x_4 x_6 + k_4 x_1 x_6 - 2k_3 x_2, \\
    x'_{5} &= k_3 x_1, \\
    x'_{6} &= k_3 x_1 - k_4 x_4 x_6, \\
    x'_{7} &= k_4 x_1 x_6, \\
    x'_{8} &= k_5 x_4, \\
    x(0) &= x_0.
\end{align*}
\]

Figure 2. Solving the direct problem for substances \( A_4 \) and \( A_6 \), where \( x4, x6 \) – solutions calculated by Mathcad system as a value of function at a point, \( x4 \_L, x4 \_R, x6 \_L, x6 \_R \) – solutions found by the program in Pascal programming language using two-side method.

Figure 2 shows that the corridor of the results of calculations on concentrations of participating substances, obtained by the bilateral method, was halved.

The obtained concentration values for the substance were analyzed. The results are shown in table 2. The last two columns show the deviation of the left and right borders of the interval solution values obtained by the program in Pascal programming language from the point value [15]. As you can see, the maximum deviation reaches 12.01%. The average deviation is 6.351%.

3. Conclusion

Thus, the work built algorithms of direct simulation of chemical reaction under conditions of uncertainty of initial data, which are tested on reactions of pyrolysis of ethane. The first algorithm is based on replacing arithmetic operations with their interval analogues, the second algorithm uses two-sided estimates of the values of the function using the definition of its isotonicity or antitonicity.

Algorithm testing showed that the second method of solving proved to be more accurate and found intervals of values of sought functions under conditions of uncertainty of initial data with high accuracy compared to the first method.
Algorithms were implemented in Pascal programming language in PascalABC.NET development environment, visualization of solution was obtained with using Mathcad system.

Table 2. Comparison of interval solution with exact solution

| Response time, t | Left border of an interval, \( x_4^L \) | Right border of an interval, \( x_4^R \) | The decision in a point, \( x_4 \) | Deviation from left border | Deviation from right border |
|------------------|-----------------|-----------------|----------------|----------------|----------------|
| 0.026            | 1.003 \( \cdot 10^{-4} \) | 1.165 \( \cdot 10^{-4} \) | 1.140 \( \cdot 10^{-4} \) | 12.01% | 2.21% |
| 0.052            | 2.061 \( \cdot 10^{-4} \) | 2.392 \( \cdot 10^{-4} \) | 2.248 \( \cdot 10^{-4} \) | 8.32% | 6.38% |
| 0.078            | 3.051 \( \cdot 10^{-4} \) | 3.531 \( \cdot 10^{-4} \) | 3.292 \( \cdot 10^{-4} \) | 7.31% | 7.26% |
| 0.104            | 3.951 \( \cdot 10^{-4} \) | 4.553 \( \cdot 10^{-4} \) | 4.239 \( \cdot 10^{-4} \) | 6.79% | 7.42% |
| 0.130            | 4.741 \( \cdot 10^{-4} \) | 5.434 \( \cdot 10^{-4} \) | 5.063 \( \cdot 10^{-4} \) | 6.36% | 7.33% |
| 0.156            | 5.408 \( \cdot 10^{-4} \) | 6.156 \( \cdot 10^{-4} \) | 5.753 \( \cdot 10^{-4} \) | 6.00% | 6.99% |
| 0.182            | 5.942 \( \cdot 10^{-4} \) | 6.709 \( \cdot 10^{-4} \) | 6.300 \( \cdot 10^{-4} \) | 5.68% | 6.49% |
| 0.208            | 6.341 \( \cdot 10^{-4} \) | 7.904 \( \cdot 10^{-4} \) | 6.695 \( \cdot 10^{-4} \) | 5.28% | 5.95% |
| 0.234            | 6.607 \( \cdot 10^{-4} \) | 7.315 \( \cdot 10^{-4} \) | 6.938 \( \cdot 10^{-4} \) | 4.76% | 5.43% |
| 0.260            | 6.747 \( \cdot 10^{-4} \) | 7.385 \( \cdot 10^{-4} \) | 7.042 \( \cdot 10^{-4} \) | 4.19% | 4.86% |

4. Acknowledgments

The reported study was funded by Ministry of Science and Higher Education of the Russian Federation according to the research project № FZWU-2020-0027.

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