

Analysis of Substances Concentration Sensitivity to the Variation of Kinetic Parameters

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Abstract: The paper shows a technique of researching of the direct kinetic problem sensitivity to the variation of the kinetic parameters within a given range. This technique is based on use of the computing device of the interval analysis. The direct problem solution in the conditions of kinetic parameters uncertainty was received by the interval method of the solution of a Cauchy problem for differential equations system. This interval method was adapted to the problems of chemical kinetics. The interval characteristics received during this method application were used for research of reagents and products concentration sensitivity in relation to kinetic parameters of mathematical model of industrially important reaction.

Keywords: chemical kinetics, direct kinetic problem, interval analysis, sensitivity of the decision, uncertainty range of kinetic parameters.

I. INTRODUCTION

The kinetic model is initial level in the mathematical modeling of chemical processes. The kinetic model determines the speed of reaction and generally turns on the reaction mechanism, equations of speed of separate stages, kinetic parameters of the model (rate constants and activation energies) and some additional simplifying regulations on a role of separate stages. Substances concentration change dynamics can be described by kinetic curves of an expenditure or formation of reaction reagents and products. For this purpose it is required to solve a direct kinetic problem. The direct problem of chemical kinetics is a calculation of multicomponent reacting mix composition and speed of reaction on the basis of the set mathematical model with known parameters.

Математическая модель реакции в формальной записи представляет собой систему обыкновенных дифференциальных уравнений первого порядка с заданными начальными условиями

$$\frac{dx_i}{dt} = f_i(t, \mathbf{x}, \mathbf{k}), t \in [0; T],$$
$$x_i(0) = x_i^0, i = \overline{1, n},$$
(1)

where x_i – concentration of the i -th component (molar shares), n – amount of substances, \mathbf{k} – vector of kinetic constants of reaction speeds of m dimension, T – reaction course time. The system of the equations with entry conditions (1) represents the definition of Cauchy problem for ordinary differential equations systems.

In some cases there is a need of the direct problem solution in the conditions of initial physical and chemical information uncertainty [1]. We will understand representation of speeds constants in an interval form as the partial uncertainty in kinetic data [2]. Thus we will present the speeds constants vector in the form

$$\mathbf{k} = (\mathbf{k}^{(1)}, \dots, \mathbf{k}^{(m)})^T,$$
(2)

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where $\mathbf{k}^{(j)} = [\underline{k}_j; \bar{k}_j]$ – interval estimates with dispersion within some percent of rather known average value, $j = \overline{1, m}$, \underline{k}_j – the lower, \bar{k}_j – the top interval borders. Let λ_j – value corresponding to the degree of variation of the kinetic rate constant with respect to a mean value k_j . Then the borders of the interval vector components $\mathbf{k}^{(j)}$ can be defined as $\underline{k}_j = k_j - \lambda_j k_j$, $\bar{k}_j = k_j + \lambda_j k_j$. The decision of system (1) in the conditions of (2) can be presented in the form

$$\mathbf{x} = (\mathbf{x}^{(1)}, \dots, \mathbf{x}^{(n)})^T, \quad (3)$$

where $\mathbf{x}^{(i)} = [\underline{x}_i; \bar{x}_i]$, $i = \overline{1, n}$.

The decision of system (1) in the conditions of (2) can be received by various numerical methods of the Cauchy problem interval solution [3]. In [4] the algorithm of the combined method of the sensitivity interval analysis adapted for the solution of chemical kinetics problems is described. Its main idea is reduced to the following actions.

To assess $\bar{x}^{(i)}$ – the upper bound of $\mathbf{x}(t)$ on i -th coordinate, $\bar{x}^{(i)} \geq x_i$ – we will consider system $\tilde{\mathbf{x}}' = f(t, \tilde{\mathbf{x}}, \tilde{\mathbf{k}})$, $\tilde{\mathbf{x}} \in \tilde{\mathbf{X}}$, $\tilde{\mathbf{k}} \in \tilde{\mathbf{K}}$, $\tilde{\mathbf{x}}(0) = \tilde{\mathbf{x}}_0 \in \tilde{\mathbf{X}}_0$, in which

$$\tilde{\mathbf{k}}_j = \begin{cases} \bar{k}_j, & \text{если } \mathbf{x}_{ij}^k(t) \leq 0, \\ \underline{k}_j, & \text{если } \mathbf{x}_{ij}^k(t) \geq 0, \\ \mathbf{k}_j, & \text{если } 0 \in \mathbf{x}_{ij}^k(t), \end{cases} \quad \tilde{\mathbf{x}}_0 = \begin{cases} \bar{x}_{0j}, & \text{если } \mathbf{x}_{ij}^0(t) \leq 0, \\ \underline{x}_{0j}, & \text{если } \mathbf{x}_{ij}^0(t) \geq 0, \\ \mathbf{x}_0, & \text{если } 0 \in \mathbf{x}_{ij}^0(t), \end{cases}$$

where $\mathbf{x}_{ij}^k(t)$ and $\mathbf{x}_{ij}^0(t)$ – interval expansions of $\partial x_i / \partial k_j$ and $\partial x_i / \partial x_{0j}$ respectively.

Interval functions $\mathbf{x}_{ij}^k(t)$, $\mathbf{x}_{ij}^0(t)$ can be defined, at the same time solving system (1) and systems

$$\mathbf{x}_{ij}^{k'} = \sum_{l=1}^n \frac{\partial f_i}{\partial x_l}(t, \mathbf{x}, \mathbf{k}) x_{lj}^k + \frac{\partial f_i}{\partial k_j}(t, \mathbf{x}, \mathbf{k}), \quad (4)$$

$$x_{ij}^k(0) = 0, \quad i = \overline{1, n}, \quad j = \overline{1, m},$$

$$\mathbf{x}_{ij}^{0'} = \sum_{l=1}^n \frac{\partial f_i}{\partial x_l}(t, \mathbf{x}, \mathbf{k}) x_{lj}^0, \quad (5)$$

$$x_{ij}^0(0) = \delta_{ij}, \quad i = \overline{1, n}, \quad j = \overline{1, n},$$

Where δ_{ij} – Kronecker's symbol

The research of the direct kinetic problem sensitivity to the variation of the kinetic parameters in some area of uncertainty (2) consists in an assessment of influence of kinetic model parameters on a reaction yield. This suggests what of speeds constants are defining at different stages of reaction. The result of solving the direct problem with interval kinetic parameters is the bilateral solution (3). It is characterized not by one dot value of concentration in each timepoint of reaction course, but by the interval of all possible values. The width of the received intervals of concentration can be used for an assessment of extent of rate constants influence to the corresponding concentration. The widest calculated interval testifies to the greatest influence of a constant on this concentration. The narrowest interval corresponds to the smallest constant influence. To adequately assess the sensitivity of the direct problem solution the condition $\lambda_1 = \lambda_2 = \dots = \lambda_m = \lambda = \text{const}$ has to be satisfied.

In [5] the next way of estimation of concentration sensitivity to the various constants changes in various timepoints is offered. Let as a result of the direct kinetic problem solving by the method of interval sensitivity analysis the solution of (1) under the conditions (2), the solution of (4)–(5) are obtained. Then for an sensitivity assessment it is possible to use the rated criterion, allowing to carry out an assessment of the constant k_j , $j = \overline{1, m}$ influence on the concentration x_i , $i = \overline{1, n}$ in the timepoint t :

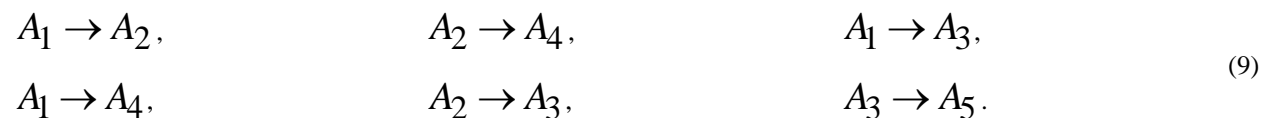
$$\hat{s}_i^j = \int_{t-h}^t \text{wid} \mathbf{I}(t) dt, \quad \mathbf{I}(t) = \frac{k_j \mathbf{x}_{ij}^k(t)}{\mathbf{x}_{\max}(t)}, \quad (7)$$

wher $\mathbf{x}_{ij}^k(t)$ decisionsofsystem(4), $\mathbf{x}_{\max}(t) = \mathbf{x}_{qj}^k(t)$,

$q : \text{wid} \mathbf{x}_{qj}^k(t) = \max\{\text{wid} \mathbf{x}_{1j}^k(t), \dots, \text{wid} \mathbf{x}_{nj}^k(t)\}$, h – the step of a numerical method of the interval solution of Cauchy problem for the differential equations system.

1.1. Discussion

We will carry out the sensitivity analysis on the example of the reaction of receiving phthalic anhydride proceeding without change of reactionary volume [4]. It should be noted that the technique given here is applicable to the reactions proceeding with change of reactionary environment moles number [5]. We will enter the following designations: A_1 - naphthalene (initial substance), A_2 - naphthoquinone, A_3 - target product - phthalic anhydride, A_4 - carbon dioxide, A_5 - maleic anhydride. A set of the chemical transformations describing reaction taking into account the entered designations is represented the following scheme of stages:



We will construct mathematical model of considered reaction course according to the general theory of creation of the mathematical description of chemical processes [6]. According to the law of the operating masses, the kinetic equations corresponding to the (9) can be expressed the equations:

$$\begin{array}{lll} \omega_1 = k_1 x_1, & \omega_2 = k_2 x_2, & \omega_3 = k_3 x_1, \\ \omega_4 = k_4 x_1, & \omega_5 = k_5 x_2, & \omega_6 = k_6 x_3. \end{array} \quad (10)$$

where ω_j – the j -th stage speed, $j = \overline{1,6}$, x_i – concentration of the i -th component, $i = \overline{1,5}$, k_j – the j -th reaction speed constant (s^{-1}), $j = \overline{1,6}$. The matrix of stoichiometric coefficients is represented in the table 1.

Table 1. The matrix of stoichiometric coefficients for the reaction of receiving phthalic anhydride

	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
x_1	-1	0	-1	-1	0	0
x_2	1	-1	0	0	-1	0
x_3	0	0	1	0	1	-1
x_4	0	1	0	1	0	0
x_5	0	0	0	0	0	1
sum	0	0	0	0	0	0

The reaction proceeds without a change in reaction volume, as evidenced by the last row of the matrix. Then the differential equations system describing the reaction kinetics is of the form:

$$\frac{dx_i}{dt} = f_i(t, x, k), \quad t \in [0; 0.6], \quad (11)$$

$$x_i(0) = x_i^0, \quad i = \overline{1,5}.$$

The right parts of the equations in system (11) taking into account (10) and the matrix of stoichiometric coefficients:

$$f_1(t, x, k) = -\omega_1 - \omega_3 - \omega_4 = -k_1x_1 - k_3x_1 - k_4x_1,$$

$$f_2(t, x, k) = \omega_1 - \omega_2 - \omega_5 = k_1x_1 - k_2x_2 - k_5x_2,$$

$$f_3(t, x, k) = \omega_3 + \omega_5 - \omega_6 = k_3x_1 + k_5x_2 - k_6x_3,$$

$$f_4(t, x, k) = \omega_2 + \omega_4 = k_2x_2 + k_4x_1,$$

$$f_5(t, x, k) = \omega_6 = k_6x_3.$$

We will understand representation of speeds constants in the form

$$\begin{aligned} k_1 &= [3.19324; 3.39076], & k_2 &= [0.61789; 0.65611], \\ k_3 &= [1.78577; 1.89623], & k_4 &= [0.48209; 0.51191], \\ k_5 &= [2.71309; 2.88091], & k_6 &= [0.03589; 0.03811], \end{aligned} \quad (12)$$

as uncertainty of kinetic data. They form an interval vector of parameters $\mathbf{k} = (k_1, \dots, k_m)$. As such, the rate constants are interval estimates with a range within 3% of the mean values calculated by the Arrhenius formula at a temperature $T = 620$ K, in accordance with the literature data [7]: $k_1 = 3.292$, $k_2 = 0.637$, $k_3 = 1.847$, $k_4 = 0.497$, $k_5 = 2.797$, $k_6 = 0.037$, forming a point parameter vector $\mathbf{k} = (k_1, \dots, k_6)$.

Before constructing a bilateral solution of (11) under the conditions (12) we take as the initial concentration of substances degenerate intervals: $x_1(0) = [1;1]$, $x_i(0) = [0;0]$, $i = \overline{2,5}$.

Graphic bilateral solution of the direct problem (on a target substance) for the reaction of receiving phthalic anhydride is shown in Fig. 1. In this case, the kinetic curves of changes in the concentration of substances which may be obtained by solving the direct problem with $x_1 = 1$, $x_i = 0$, $i = \overline{2,5}$ and $\forall k \in \mathbf{k}$, will belong to the set of solutions, indicate the boundaries of the two-state solution.

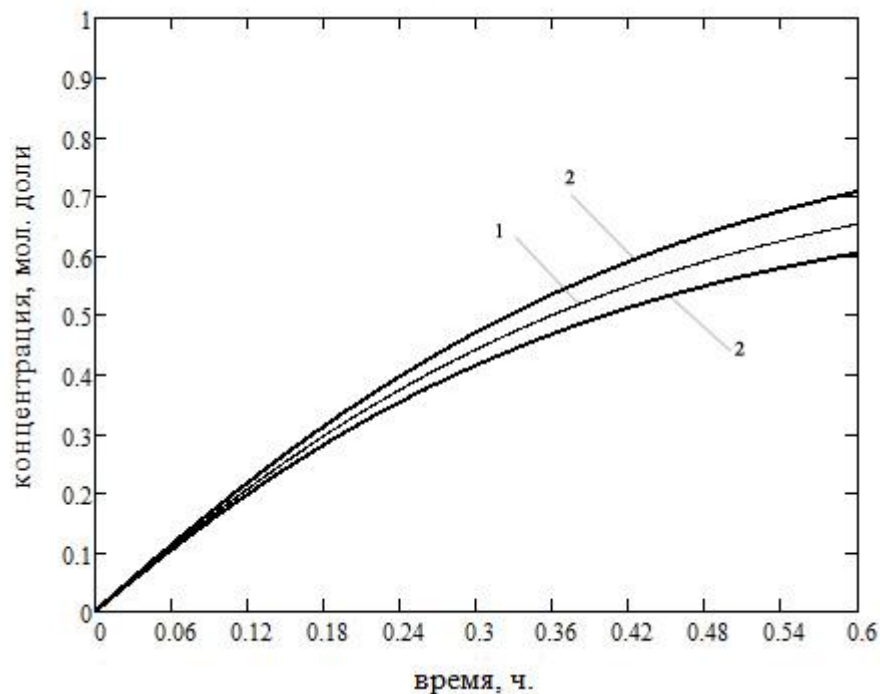


Fig1. Bilateral estimates of the solution of the direct problem (on a target substance) for the reaction of receiving phthalic anhydride: 1 - solution with average values of the parameters; 2-interval solution under the conditions (12)

II. CONCLUSION

Fig. 2-3 allows to analyze the substances concentration changes sensitivity in the variation of kinetic constants at certain time intervals (the number of columns in the chart, corresponding substance A_i , $i = \overline{1,5}$, equal to the number of segments of the partition slot in the numerical solution of the direct problem. The figures show that in all cases where the rate constant influence on the substance concentration occurs, there is a tendency to increase the width of the two-state solution of the direct problem in time. This once again confirms the Moore effect during the interval calculations.

Analysis shows that the concentration of the reaction products A_2 , A_5 are insensitive to changes in the parameter k_1 , thus influence of its change in limits of the considered uncertainty interval on concentration of substances A_1 , A_3 , A_4 occurs practically equally. The greatest influence of the rate constant k_2 is happening in relation to changes in the concentration of substance A_2 , and only one of the five substances A_1 is independent of its variation. The rate constant k_3 does not affect the concentration A_2 , but retains influence on the dynamics of the remaining reagents.

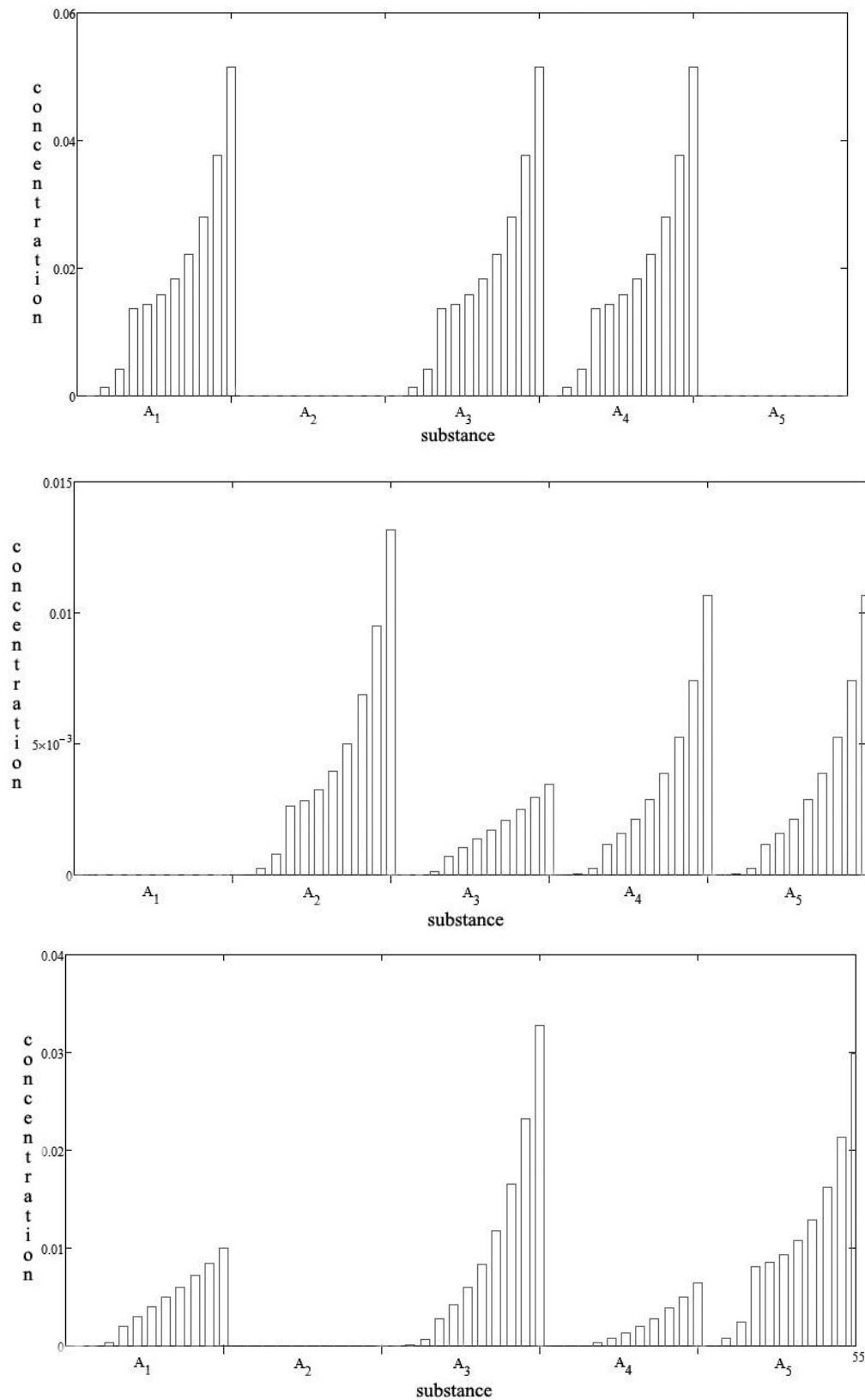


Fig2. Sensitivity of reactant concentrations and reaction product of phthalic anhydride with respect to the kinetic parameters a) k_1 b) k_2 c) k_3

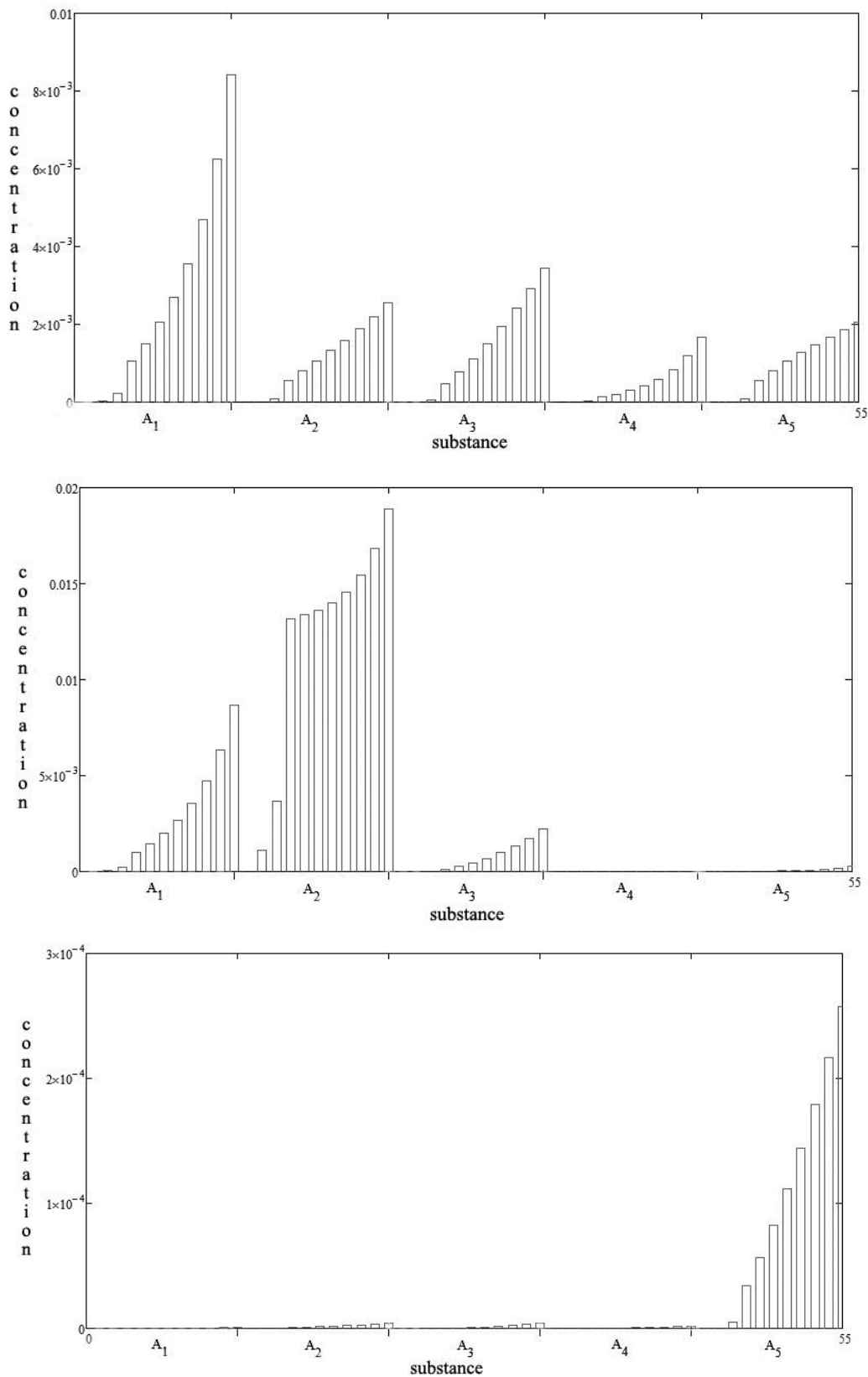


Fig3. Sensitivity of reactant concentrations and reaction product of phthalic anhydride with respect to the kinetic parameters a) k_4 b) k_5 c) k_6

The rate constant k_4 is the only parameter which change doesn't remain traceless at reaction course, though extent of its influence on concentration is rather small. The rate constant k_5 makes the maximum impact on substance A_2 , not affecting the output A_4 , A_5 . The rate constant k_6 has the least impact on the course of the reaction. Change of concentration of a target product depends on degree of a variation of all constants at the same time, thus, as expected, the rate constants k_1 , k_2 and k_4 have the greatest impact.

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