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Solution of some inverse kinetics problems of complex chemical reactions

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Abstract. *In this paper, some special cases of solving inverse problems depending on the complex chemical reaction equation are presented. It is proposed to use a fundamentally different approach related to the method of modulating functions. This approach allows to avoid the need to solve a direct problem, the defined complexes can be singled out and the estimates of their errors and stability can be obtained.*

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1 Introduction

The kinetic model of a complex chemical reaction can be described by a system of differential equations:

$$\frac{d\overline{x}}{dt}=\mathit{\Gamma}^{T^-}\omega;\ \overline{x}\ (0)=\overline{x}_0 \tag{1.1}$$

where $\overline{x}=(x_1,\dots,\omega_s)$ is a column vector of component concentrations; $\overline{x}=(x_1,\dots,\omega_s)$ is a column vector of velocities of elementary stages; $\mathit{\Gamma}$ is a stoichiometric matrix, each element of which γ_{ij} represents the number of moles (molecules) of substance j participating in the i-th elementary stage of the process; $\omega_i=\omega_i\left(\overline{k},\overline{x}\right)$ is a polynomial not higher than the third degree in concentrations and linear in constants.

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With a given reaction mechanism, the inverse problem is understood as the determination of the vector of the velocity constants $\overline{k}$ from system (1.1), when experimental kinetic curves for substances are known.

One of the main difficulties in solving inverse problems is the ambiguity of the definition of constants, since in a real experiment the concentrations of only a part of the substances participating in the reaction are measured. Therefore, depending on the experimental information, it is possible to determine some complexes of velocity constants. The identification of such complexes is a very difficult task [9, 10].

The methods proposed in [1, 2, 8] for solving inverse problems of chemical kinetics are usually reduced to minimizing a certain function-criterion that characterizes the degree of agreement between experimental and model-calculated quantities. The minimization procedure requires multiple solutions to a direct problem, which is associated with a large amount of machine time. In addition, in a number of cases, there are algorithmic difficulties in identifying an explicit type of defined complexes of velocity constants and assessing the reliability of the results obtained [6].

In this paper, some special cases of solving inverse problems depending on the right parts of the system are considered (1.1). In these cases, it is proposed to use a fundamentally different approach related to the method of modulating functions [4]. A modification of this approach is considered in [3, 5]. At the same time, the need to solve a direct problem is avoided, the defined complexes are singled out and estimates of their errors can be obtained.

2 Inverse problem approach

Let us consider a complex chemical reaction in the case when all reactions are no more than 1st order. The model is written as a system of linear differential equations of the 1st order with respect to the measured concentrations of the substance $x_1, \ldots, x_n$ and non-measurable $y_1, \ldots, y_n$. This system of $m + n$ equations can be reduced to a system of n linear equations of no more than $m + 1$ order with respect to only the measured concentrations.

The coefficients of this system, which are some combinations of the velocity constants of the original system, can be estimated from measurements of concentrations $\widetilde{x_1}, \ldots, \widetilde{x_n}$ on the time interval $t \in [t_1,\ t_2]$. The converted system will be written as

$$L_i\left(\overline{x}\right) \equiv x_i^{(p_i)} - \sum_{j=1}^{n} \sum_{l=0}^{q_{ij}} \alpha_{ijl} x_j^{(l)} = 0, \tag{2.1}$$

where $q_{ij}, p_i \in N$, $0 \leq q_{ij} < p_i \leq m + 1$.

Thus, the problem is to estimate the parameters of the α_{ijl} by the approximate solution $\tilde{x}_i = x_i + d_i$ of the system (2.1).

Let us consider class B vector functions $\overline{x}\left(t\right) = \left\{x_1\left(t\right), \ldots, x_n\left(t\right)\right\}$ continuous on $I = [t_1,\ t_2]$.

The solution of system (2.1) presupposes the fulfillment of integral equations $\left(L_i\left(\overline{x}\right), \varphi\right) = 0$, where $\overline{x} \in B$ and $\varphi\left(t\right)$ are a finite function with a carrier in I, and

$$(f, f) = \int_I \varphi \cdot f \cdot dt.$$

Let us denote by E the class of solutions of the system (2.1) in the above sense, satisfying (2.1) only with one set of parameters. It is easy to prove that only those solutions whose coordinates are constant on I can not be included in E.

Since the equations of system (2.1) serve to determine the parameters of a_{ijl}, we will consider the *i*-th equation and omit the index *i* in the future.

Let's denote with $\beta = \{\alpha_{ijl}\} = \{a_{10}, a_{11}, \ldots, \alpha_{1q_1}, \ldots \alpha_{n0}, \ldots, \alpha_{nq_n}\} = \{\beta_1, \ldots, \beta_r\}$,

$$r = n + \sum_{j=1}^{n} q_j.$$

Let us introduce the function $\varPsi\left(t, t\right)$ such that it is nonnegative by $I_t = [t_1, \tau]$– since it is continuously $(m+1)$ times differentiable and

$$\varPsi^{(k)}\left(t_1, t\right) = \varPsi^{(k)}\left(\tau, \tau\right) = 0, \quad \begin{array}{c} \tau \in I, \\ k \leq m+1. \end{array}$$

For example, a function $\varPsi\left(t, t\right)$ we can present in the following form;

$$\varPsi^{(k)}\left(t_1, \tau\right) = \varPsi^{(k)}\left(\tau, \tau\right) = 0, \quad \begin{array}{c} \tau \in I, \\ k \leq m+1. \end{array}$$

For $\overline{x} \in B$, the following functions can be defined using $\varPsi$:

$$g_0\left(\tau\right) = (-1)^p \left(x_i, \varPsi^{(p)}\right),$$

$$g_k\left(\tau\right) = (-1)^k \left(x_j, \varPsi^{(k)}\right), \; k = 1, \ldots, r.$$

It follows from the definition of $\overline{x} \in B$ that there is a ratio of

$$g_0 - \sum_{k=1}^{r} \beta_k g_k = 0. \tag{2.2}$$

Now let $\tilde{x} = \{\tilde{x}_1, \ldots, \tilde{x}_n\}$ and $|\tilde{x}_j - x_j| \leq d_j$ for some $x \in B$, i.e.:

$$\tilde{x} = \overline{x} + \delta, \;\; \delta = \{\delta_1, \ldots, \delta_n\}, \quad |\delta_i| \leq \delta_0$$

The functions $\tilde{x}$ with the help of $\varPsi\left(t, t\right)$ will correspond to the function

$$\widetilde{g_0}\left(t\right) = (-1)^p \left(\widetilde{x_i}, \varPsi^{(p)}\right),$$

$$\widetilde{g_k}\left(t\right) = (-1)^k \left(\widetilde{x_j}, \varPsi^{(k)}\right).$$

But for these functions, the exact expression (2.2) may no longer be met.

As approximate parameter values, let's take a vector minimizing the quadratic shape

$$T\left(\beta'\right) = \left\| \tilde{g}_0 - \sum_{k=1}^{r} \beta'_k \tilde{g}_k \right\|^2 = \sum_{k,j=1}^{n} a_{kj} \beta'_k \beta'_j + \sum_{k=1}^{n} b_k \beta'_k + c, \tag{2.3}$$

where $a_{ki} = (\tilde{g}_k, \tilde{g}_j)$, $b_k = (\tilde{g}_k, \tilde{g}_0)$, $c = (\tilde{g}_0, \tilde{g}_0)$.

Thus, the determination of β_{i0} parameters is reduced to the solution of a system of linear algebraic equations

$$2A\beta' = -B, \tag{2.4}$$

where:

$$A = \{a_{kj}\}_{k,j=1}^{n};; \; B = \{b_1, \ldots, b_n\}, \;\; \beta' = \left\{\beta'_1, \ldots, \beta'_n\right\}.$$

It can be shown that if there are no constants on I functions among the $\tilde{x}$ coordinates, then the determinant of the matrix A, which is the determinant of the Gram functions g_k, $k = 1, \ldots, r$, is non-zero. Thus, system (2.2) has a single solution.

Let's evaluate the accuracy of the obtained parameter estimates. Denote

$$\gamma_l = \int_l \left|\Psi^{(l)}\right| dt, \quad \gamma = \max_t \gamma_l \ , \quad \mu = 1 + \sum_{k=1}^{r} |\beta_{k,0}|, \ \|\overline{\beta} - \overline{\beta}_0\| \leq \frac{\gamma \cdot \mu}{\sqrt{\lambda}} \delta_0 \qquad (2.5)$$

where λ is the smallest eigennumber of the matrix A of (2.4).

Formula (2.5), a kind of analogue of the relative error estimate, shows that when the error level δ_0 tends to zero, the parameters $\overline{\beta}_k$ tend to exact values $\overline{\beta}_{k,0}$.

3 Conclusions

Some special cases of solving inverse problems depending on the complex chemical reaction equation are presented. It is proposed to use a fundamentally different approach related to the method of modulating functions. This approach allows to avoid the need to solve a direct problem, the defined complexes can be singled out and the estimates of their errors and stability can be obtained. The explicit dependence of complexes on constants is obtained for a particular system of equations. Based on the available experimental information, it is possible to determine some complexes of the coefficients of system (2.1), but not the initial coefficients themselves.

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