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Improvement of the Method for the Reduction of the Sets of Differential Equations in Chemical Kinetics

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Abstract—The method for reducing differential equations, which is applicable to any kinetic model, is improved. The improvement consists in taking into account only those steps of the process whose rates are higher than a certain value of a significance threshold at each moment of time. The error due to the approximation of the initial model by the reduced solution is estimated. It is shown that, at a sufficiently low value of the significance threshold, this error can be as small as desired. Examples are given to illustrate the effectiveness of using the refined reduction method.

A mathematical model for the kinetics of a chemical reaction that occurs via a nonlinear multistep mechanism is usually a set of first-order differential equations. The exact analytical solution to such equations is usually impossible to find. Even numerical integration often comes across difficulties that are due to the high dimensionality of the system and the stiffness of the set of differential equations. The latter can be due to a significant scatter of the rate constants of steps. Therefore, an important task is rearranging the model to exclude or reduce the effect of the model properties mentioned above. One of the methods to reduce the dimensionality of the model is to use the property of time separation [1–4]. This property consists in the fact that the whole time interval can be divided into subintervals, and only a part of the complex mechanism is operative at each of them. One of such methods is the method of pseudo-steady-state concentrations [1, 2]. The method proposed by Spivak and co-authors [3, 4] enables finding the number and lengths of characteristic intervals for any specific mechanism and the respective parts of the mechanism that determine the main properties of the system behavior at each interval. The goal of this work is to refine the method for reducing the set of differential equations and extend its applicability range.

The mathematical model of a chemical reaction that occurs via the steps

$$\sum_{i=1}^{n} a_{ji}^{+} X_i \longrightarrow \sum_{i=1}^{n} a_{ji}^{-} X_i, \quad j = 1, \dots, S \tag{I}$$

(reversible steps are written as two nonreversible ones) have the following form

$$\dot{x}_i = \sum_j w_j (a_{ji}^{-} - a_{ji}^{+}), \tag{1}$$

where the rates of steps w_j are determined according to the mass action law:

$$w_j = k_j \prod_{i=1}^{n} x_i^{a_{ji}^{+}} \tag{2}$$

with the rate parameters (the rate constants of steps) k_j, the concentrations x_i of species X_i, and the stoichiometric coefficients a_{ji}^{+}. Let us assume that the number of atoms of each type is conserved. Since each species is included in at least one conservation law for atoms, the concentrations of all species have some constant upper limit $|x_i| \le R$. The main idea for the improvement of the method for reducing set (1) is to preserve the conservation laws. This idea is based on the following reduction rule: the system changes only when the rate of any step (2) reaches the significance threshold value ε. If the rate increases and reaches this value, then the corresponding step is included in the mechanism. If the rate decreases to the threshold value, then the corresponding step is excluded. When this reduction method is used, set (1) of differential equations remains chemically sensible at each period of time, since it corresponds to the initial mechanism with several steps excluded. The solutions to the set are constrained because the conservation laws are determined by the list of species and their chemical formulas and do not change if steps are removed or added.

Note that the reduction method as it was initially formulated [3, 4] contained another reduction rule. It was based on the comparison of the monomials of the polynomial set of differential equations (1) rather than reaction rates with the significance threshold value. However, when monomials are excluded or returned to the system, the chemical properties of system (1) are lost. This may result in a substantial change in the properties of the reduced system compared to the initial model. For instance, reaction $X \longrightarrow 2Y$ is characterized by a monotonic decrease in the concentration of reactant X to zero and an increase in the concentration of product Y to a certain value. The mathematical model of this reaction takes the following form:

$$\dot{x} = -kx, \quad \dot{y} = 2kx, \quad x(t_0) = x_0, \quad y(t_0) = y_0. \quad (3)$$

For any positive value of the significance threshold ε and the initial concentration of X, which meets the condition $x_0 > \frac{\varepsilon}{2k}$, the reduction method in its initial formulation results in an initial decrease in the concentration of x to the value $x_1 = \varepsilon/k$. The monomial kx is excluded since it decreases and reaches the threshold value. The monomial $2kx$ remains significant at the point of switching to a reduced system. After switching, system (3) transforms to

$$\dot{x} = 0, \quad \dot{y} = 2kx, \quad x(t_1) = x_1, \quad y(t_1) = y_1. \quad (4)$$

Because the concentration of species X stops changing, monomials kx and $2kx$ do not change and there are no more switches. According to Eqs. (4), the concentration of Y infinitely increases in contrast to the real situation. The application of the improved reduction method to model (3) results in the simultaneous elimination of both monomials at the point of switching (because the corresponding step is removed), and both concentrations further remain constant. Therefore, the refined method preserves the chemical sense of the model. Note also that the deviation of the steady-state value $x_1 = \varepsilon/k$ of the concentration of species X from zero decreases with a decrease in the significance threshold value.

Let us estimate the accuracy of the improved reduction method or the error due to the replacement of the solution vector $x_i(t)$ of the initial system by the solution vector $y_i(t)$ of the reduced system depending on the significance threshold value ε. Suppose $t_0, t_1, t_2, \ldots$ are the moments when the list of active steps changes (call them switches). In the initial moment t_0 this list can also be changed (if one or several rates are lower than the threshold value).

The vectors of solutions to the initial and reduced systems satisfy the sets of polynomial equations $t = t_{m-1}$ and $t = t_m$ at each interval between consecutive switches $x_i' = \sum_j w_j(x)(a_{ji}^- - a_{ji}^+)$ and $y_i' = \sum_{J_+} w_j(y)(a_{ji}^- - a_{ji}^+)$; the sum over J_+ corresponds to significant steps (that is, steps with rates higher than the significance threshold values at the interval $t_{m-1} \le t < t_m$) and steps that acquire significance at $t = t_{m-1}$. Changes in the error $\Delta = \sqrt{\sum (x_i - y_i)^2}$ due to the replacement of the exact solution by the reduced solution is determined by the expression

$$\Delta' = \frac{1}{\Delta}\sum_i (x_i - y_i)\left(\sum_j (w_j(x) - w_j(y)) \times (a_{ji}^- - a_{ji}^+) + \sum_{J_-} w_j(y)(a_{ji}^- - a_{ji}^+)\right),$$

where the sum over J_- corresponds to steps that are insignificant at the interval $t_{m-1} \le t < t_m$ and steps that lose their significance at $t = t_{m-1}$. If M is the highest molecularity of steps in the mechanism and K is the maximal of all rate constants, then the derivative $\frac{\partial w_j}{\partial x_i}$ has an upper limit equal to $L = KMR^{M-1}$ at $|x_i| \le R$. Then, using the mean value theorem $w_j(x) - w_j(y) = \sum_j \frac{\partial w_j}{\partial x_i}(\xi)(x_i - y_i)$, where ξ is some point on the axis that connects points x and y, the values of $w_j(y)$ in the sum over J_- are not greater than the significance threshold value $w_j(y) \le \varepsilon$. Taking this into account, the error Δ can be estimated by the differential inequality $\Delta' \le nLMS\Delta + \sqrt{n}MS\varepsilon$. The solution to this inequality gives us the following estimate of Δ:

$$\ln\frac{\varepsilon + L\sqrt{n}\Delta(t_m)}{\varepsilon + L\sqrt{n}\Delta(t_{m-1})} \le nLMS(t_m - t_{m-1}). \quad (5)$$

Because $\Delta(t_0) = 0$, the use of expression (5) recurrently leads us to the estimate of Δ at any moment of time $t \ge t_0$:

$$\Delta(t) \le \frac{\varepsilon}{L\sqrt{n}}(e^{nLMS(t - t_0)} - 1). \quad (6)$$

Thus, the error that appears when one replaces the exact system by a reduced one is estimated by a value that is a linear function of the significance threshold ε. Therefore, it can be made as small as desired by choosing an appropriate value of ε although the factor in this linear function can be rather high in real examples. Obviously, further analysis would provide a more exact estimate of the factor.

Let us consider examples that illustrate the improved reduction method for specific reactions. The five-step irreversible mechanism

$$\begin{gathered} 1.\ X_5 \longrightarrow X_1, \quad 2.\ X_1 \longrightarrow X_2, \quad 3.\ X_2 \longrightarrow X_3, \\ 4.\ X_3 \longrightarrow X_4, \quad 5.\ X_4 \longrightarrow X_5 \end{gathered} \qquad \text{(II)}$$

is characterized by an almost monotonic function of the concentration on time for the following values of the rate constants $k_1 = 1$, $k_2 = 0.5$, $k_3 = 2$, $k_4 = 4$, and $k_5 = 3\ \text{s}^{-1}$ and the initial conditions $x_1(0) = x_2(0) = x_3(0) = x_4(0) = 0$, and $x_5(0) = 1$ (Fig. 1a). Figure 1b illustrates the dependence of the concentration $x_1(t)$ on time calculated for $\varepsilon = 0.01$. The same figure provides informa-

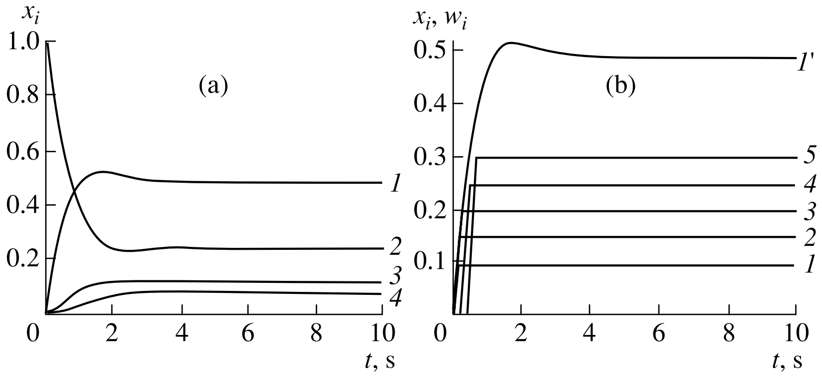

Fig. 1. Plots of $x_i(t)$ and $w_i(t)$ vs. time ($i = 1, \ldots, 5$) for scheme (II): (a) $x_i(t)$ is calculated using the exact model; (b) (*1'*) $x_i(t)$ and (*1–5*) $w_i(t)$ are calculated using the reduction method.

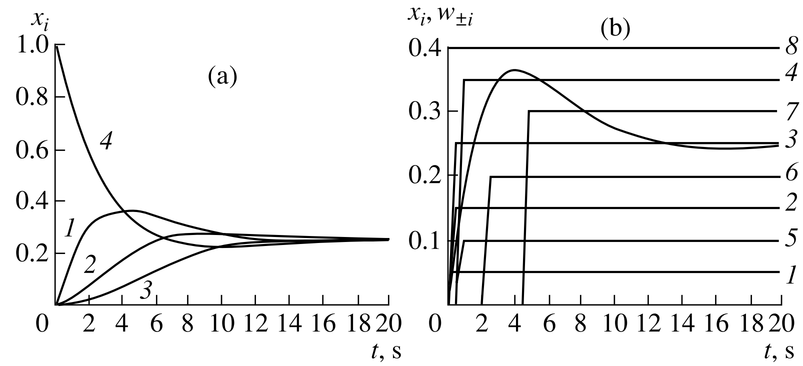

Fig. 2. Plots of $x_i(t)$ and $w_{\pm i}(t)$ vs. time ($i = 1, \ldots, 4$) for scheme (III): (a) $x_i(t)$ is calculated using the exact model; (b) (*1'*) $x_i(t)$, (*1–4*) $w_i(t)$, and (*5–8*) $w_{-i}(t)$ are calculated using the reduction method.

tion on the reduction process in the form of the functions of the rates of steps from scheme (II) on time. The intervals of insignificance are given zero values, whereas the significance intervals of steps 1–5 are marked by values 0.10, 0.15, 0.20, 0.25, and 0.30, respectively. As can be seen from Fig. 1b, these steps start to work with some delay one after another. This is explained by the fact that scheme (II) represent a chain mechanism. The difference between the exact and reduced values of $x_1(t)$ changes from –0.00004 to 0.00019 at the interval from 0 to 10 s; that is, it is rather small.

The four-step reversible mechanism

$$1.\ X_4 = X_1, \quad 2.\ X_1 = X_2, \quad 3.\ X_2 = X_3, \quad 4.\ X_3 = X_4 \qquad \text{(III)}$$

is characterized by the damping oscillation dependence of the concentrations on time at the values of rate constants $k_i = 0.25\ s^{-1}$ and $k_{-i} = 0.01\ s^{-1}$ and the initial conditions $x_1(0) = x_2(0) = x_3(0) = 0$ and $x_4(0) = 1$ (Fig. 2a). Figure 2b shows a plot of $x_1(t)$ vs. t for the reduced system with $\varepsilon = 0.001$, and the intervals of significance for the steps 1, –1, …, 4, and –4 characterized by the values 0.05, 0.10, …, 0.35, and 0.40, respectively. The reverse steps in mechanism (III) start to work with a significant delay. This is explained by the small values of rate constants. The difference of the exact and reduced solutions $x_1(t)$ in the interval from 0 to 20 s changes from –0.00015 to 0.00070.

The three-step scheme

$$1.\ X_3 = X_1, \quad 2.\ X_1 = X_2, \quad 3.\ 2X_3 + X_2 \longrightarrow 3X_3 \qquad \text{(IV)}$$

is characterized by the oscillatory regime when the rate constants take the values $k_1 = 2.89$, $k_{-1} = 0.01$, $k_2 = 0.034$, $k_{-2} = 0.1$, and $k_3 = 2000\ s^{-1}$ and when the initial conditions are $x_1(0) = 0.2$, $x_2(0) = 0.8$, $x_3(0) = 0$ (Fig. 3a). Figure 3b shows the curve $x_1(t)$ for the reduced system when the significance threshold is $\varepsilon = 0.001$. The significance intervals of steps 1, –1, 2, –2, and 3 are denoted by the values 0.1, 0.2, 0.3, 0.4, and 0.5. The second step in the reverse direction is characterized by the rate $k_{-2}x_2$ and has insignificance intervals not only during the initial period but during the whole course of the reaction. This is explained by the fact that a limit cycle, which

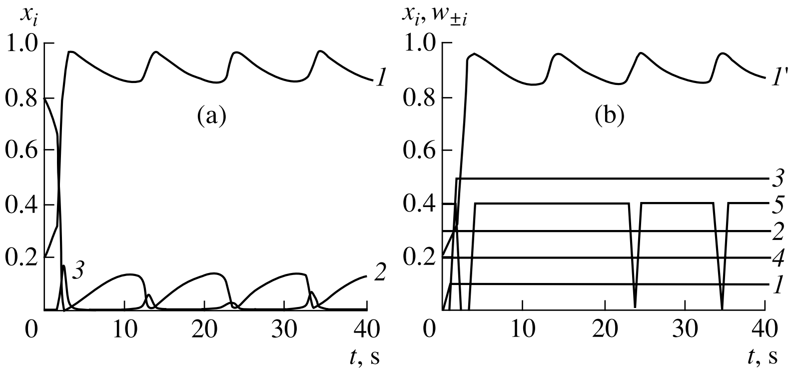

Fig. 3. Plots of $x_i(t)$ and $w_{\pm i}(t)$ vs. time (i = 1, 2, 3) for scheme (IV): (a) $x_i(t)$ is calculated using the exact model; (b) (*1'*) $x_i(t)$, (*1–3*) $w_i(t)$, and $w_{-i}(t)$ (*4, 5*) are calculated using the reduction method.

appears in this reaction, is characterized by the low values of x_2, and there is an insignificance interval of the second step in the reverse direction during each period of oscillations. The difference between the exact and reduced solutions $x_1(t)$ at the interval from 0 to 40 s is between –0.0078 and 0.0522 and is higher than the error calculated for mechanisms (II) and (III). This is explained by the fact that scheme (IV) is characterized by a more complex nonstationary behavior than the above schemes. However, analysis of inequality (6) shows that this error can be decreased to any desired level by changing the significance threshold.

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