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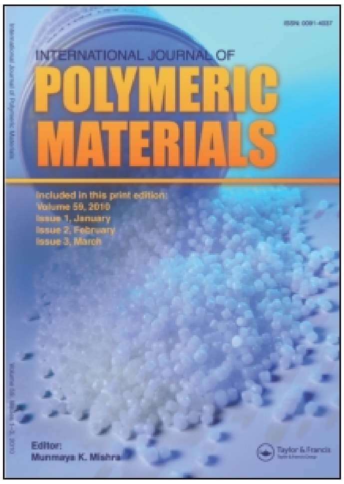

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Quasi-Stationary Approximation for Some Chemical Kinetics Models

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The accuracy of the quasi-stationary approximation for the set of chemical kinetics equations modelling some standard mechanisms of catalytic and biocatalytic reactions is evaluated.

KEY WORDS Kinetic modeling, sets of reactions, precision analysis, quasi-static approximation.

RESULTS AND DISCUSSION

The use of quasi-stationary approximation is one of the most widely used methods for kinetic modelling of complex chemical reactions. Many papers are devoted to mathematical substantiation of correct use of quasi-stationary concentrations (QSC) method for treating the set of chemical kinetics differential equations.[1-2] But even if the use of QSC method is sufficiently substantiated the accuracy of the QSC method is not always known. In this respect, interesting results were obtained by E. A. Gelman.[4,5] In her papers an algorithm was developed allowing us to compare the proximity of the estimates of initial differential equation set and its quasi-stationary approximation.

The aim of the paper is to obtain these estimates for the sets of chemical kinetics equations modelling some standard stream mechanisms of catalytic and bio-catalytic reactions.[8,9]

We consider the following reaction scheme describing the simplest catalytic circuit[8]:

$$\begin{gathered} A + K \xrightarrow{k_1} AK \\ AK \xrightarrow{k_2} BK \\ BK \xrightarrow{k_3} B + K, \end{gathered} \tag{I}$$

where A is a starting substance, B is a reaction product, K is a catalyst, AK and BK are catalyst complexes.

Scheme (I) corresponds to one-way isomerization reaction A = B on a metallic catalyst Z. Such reactions are thoroughly analyzed by Boudart.[10] The catalytic reactions with any sequence of reversible stages lead to such mechanisms if an intermediate compound participating in the last stage is mainly in the adsorption form. It follows from Reference 10, this scheme corresponds to one of the known mechanisms of ammonia synthesis reaction:

$$\begin{array}{c} Z + N_2 \rightarrow ZN_2 \\ ZN_2 \rightarrow (ZN_2)' \\ \underline{(ZN_2)' + 3H_2 \rightarrow 2NH_3 + Z,} \\ N_2 + 3H_2 = 2NH_3 \end{array} \qquad \text{(II)}$$

The following set of differential equations is true for Scheme (I)

$$\dot{x}_1 = -k_1x_1y_1 + k_3x_3, \quad \dot{x}_2 = k_1x_1y_1 - k_2x_2, \quad \dot{x}_3 = k_2x_2 - k_3x_3, \quad \dot{y}_1 = -k_1x_1y_1, \quad \dot{y}_2 = k_3x_3. \qquad (1)$$

The initial values of concentrations are preset:

$$x_1(0) = \varepsilon, \quad x_2(0) = x_3(0) = 0, \quad y_1(0) = 1, \quad y_2(0) = 0, \qquad (2)$$

where ε is a sufficiently small number. In other words ε is the small parameter for system (1)–(2). It was shown that the introduction of the small parameter as a ratio of catalyst concentration to the concentration starting substance is physically correct.[6]

Let's carry out variables substitution:

$$x_1^* = \frac{x_1}{\varepsilon}, \quad x_2^* = \frac{x_2}{\varepsilon}, \quad x_3^* = \frac{x_3}{\varepsilon}.$$

The balance of the initial scheme $x_1 + x_2 + x_3 = \varepsilon$ will be written as follows:

$$x_1^* + x_2^* + x_3^* = 1.$$

We rewrite set (1) in conformity with the new variables:

$$\varepsilon\dot{x}_1^* = -k_1x_1^*\varepsilon y_1 + k_3x_3^*\varepsilon, \quad \varepsilon\dot{x}_2^* = k_1x_1^*\varepsilon y_1 - k_2x_2^*\varepsilon, \quad \varepsilon\dot{x}_3^* = k_2x_2^*\varepsilon - k_3x_3^*\varepsilon, \quad \dot{y}_1 = -k_1x_1^*\varepsilon y_1, \quad \dot{y}_2 = k_3x_3^*\varepsilon,$$

and by means of necessary transformations we obtain:

$$\dot{x}_1^* = -k_1x_1^*y_1 + k_3x_3^*, \quad \dot{x}_2^* = k_1x_1^*y_1 - k_2x_2^*, \quad \dot{x}_3^* = k_2x_2^* - k_3x_3^*, \quad \frac{1}{\varepsilon}\dot{y}_1 = -k_1x_1^*y_1, \quad \frac{1}{\varepsilon}\dot{y}_2 = k_3x_3^*, \qquad (3)$$

$$x_1^*(0) = 1, \quad x_2^*(0) = x_3^*(0) = 0, \quad y_1(0) = 1, \quad y_2(0) = 0. \qquad (4)$$

System (3) makes it possible to select variables x_1, x_2, x_3 for the quasi-stationary concentrations.[6]

The main question of the paper is to obtain the upper estimates the accuracy of the quasi-stationary approximation. These estimates are derived according to the Gelman algorithm.[4,5]

The reduced system is written:

$$-k_1\bar{x}_1^*\bar{y}_1 + k_3\bar{x}_3^* = 0,\quad k_1\bar{x}_1^*\bar{y}_1 - k_2\bar{x}_2^* = 0,\quad k_2\bar{x}_2^* - k_3\bar{x}_3^* = 0,\quad \frac{1}{\varepsilon}\dot{\bar{y}} = -k_1\bar{x}_1^*\bar{y}_1,\quad \frac{1}{\varepsilon}\dot{\bar{y}} = k_3\bar{x}_3^*, \tag{5}$$

$$\bar{y}(0) = y(0), \tag{6}$$

where $\bar{x}^* = (\bar{x}_1^*, \bar{x}_2^*, \bar{x}_3^*)$ are the quasi-stationary concentrations.

According to the algorithm we introduce a new variable z:

$$x_i = \psi z_i,\quad i = 1, 2, 3, \tag{7}$$

where $\psi(k) \to 0(k \to \infty)$.

For the Scheme (I) we select $\psi = 1/k_2$.

And so we move from large vector parameter $\mathbf{k}$ to the restricted one $\bar{M}$:

$$\bar{M}_1 = k_1\psi,\quad \bar{M}_2 = k_2\psi = 1,\quad \bar{M}_3 = k_3\psi$$

are restricted when $k \to \infty$.

Quasi-stationary equations are of the following forms:

$$-\bar{M}_1 z_1 y_1 + \bar{M}_3 z_3 = 0,\quad \bar{M}_1 z_1 y_1 - \bar{M}_2 z_2 = 0,\quad \bar{M}_2 z_2 - \bar{M}_3 z_3 = 0. \tag{8}$$

Then

$$\bar{x}_i^* = \psi\varphi_i(y, \bar{M}),$$

where φ_i is the system (8) decision.

To derive the quasi-stationary approximation estimates the following values must be known:

$$c_i^-(y) < \varphi_i(y, \bar{M}) < c_i^+(y),\quad \left|\frac{\partial\varphi_i}{\partial y_j}\right| < c(y),\quad i = 1, 2, 3,\quad j = 1, 2. \tag{9}$$

For a concrete scheme these values can be obtained by means of rate constants and initial values of substances concentrations.

Let's write system on x^* in the following form:

$$\dot{x}^* = f(x^*, y, k) + q(y),$$

$$f(x^*, y, k) = \begin{pmatrix} -k_1 x_1^* y_1 + k_3 x_3^* \\ k_1 x_1^* y_1 - k_2 x_2^* \\ k_2 x_2^* - k_3 x_3^* \end{pmatrix}, \quad q(y) = \begin{pmatrix} 0 \\ 0 \end{pmatrix}.$$

Denote

$$\Delta f = f(x^*, y, k) - f(\bar{x}^*, y, k) = B(x^*, \bar{x}^*, y, k)(x^* - \bar{x}^*),$$

where

$$B(x^*, \bar{x}^*, y, k) = \begin{pmatrix} -k_1 y_1 & 0 & k_3 \\ k_1 y_1 & -k_2 & 0 \\ 0 & k_2 & -k_3 \end{pmatrix}.$$

Then for $\Delta = x^* - \bar{x}^*$ the equations set is of the form:

$$\dot{\Delta} = B(x^*, \bar{x}^*, y, k)\Delta - \dot{\bar{x}}^*, \tag{10}$$

where

$$\bar{x}^* = \psi\varphi(y, \bar{M}), \quad \dot{\bar{x}}_i^* = \psi \sum_{j=1}^{2} \frac{\partial \varphi_i}{\partial y_j} \dot{y}_j.$$

After the variable substitution $x^* = \psi z$ the system (6) assumes the form:

$$\dot{\Delta} = (I/\psi)D(z, \varphi(y, \bar{M}), y, \bar{M})\Delta$$

$$- \dot{\bar{x}}^*, \quad D(z, \varphi(y, \bar{M}), y, \bar{M}) = \begin{pmatrix} -\bar{M}_1 y_1 & 0 & \bar{M}_3 \\ \bar{M}_1 y_1 & -\bar{M}_2 & 0 \\ 0 & \bar{M}_2 & -\bar{M}_3 \end{pmatrix}.$$

It is required to estimate vector-function $\{|\Delta_i(t)|\}$.

By using Theorem I,[4] we consider the system for majorant function

$$\dot{v} = (I/\psi)D^*(z, y)v + \{|\dot{\bar{x}}_i^*|\}, \quad v(0) = \{|\Delta_i(t)|\} = \bar{x}^*(0), \quad \bar{x}^*(0) = \psi\varphi(y^0, \bar{M}). \tag{11}$$

$D^*(z, y)$ is a special majorant matrix for D one. (Special majorant of arbitrary matrix D is such a matrix whose diagonal elements coincide with those of matrix D, and elements outside the diagonal are equal to the respective matrix D elements modules.)

We present the following auxiliary estimates.

$z_i = x_i^*/\psi \leqslant l/\psi$ (since $x_i^* \leqslant l$ by force of balance $x_1^* + x_2^* + x_3^* = 1$).

Using this one and (9) we have

$$|\dot{x}_i^*| < \psi \left| \sum_{i=1}^{2} \frac{\partial \varphi_i}{\partial y_j} \dot{y}_j \right|,$$

where

$$\dot{y}_1 = -\bar{M}_1 z_1 y_1, \quad \dot{y}_2 = \bar{M}_3 z_3.$$

Hence

$$|\dot{x}_i^*| < \psi c \bar{M}_1 z_1 y_1 \leqslant \psi c k_1 \psi (l/\psi) y_1^0 = \psi c k_1, \quad i = 1, 2, 3.$$

Let's consider the system

$$\sum_{i=1}^{3} p_i d_{ij}^* = 0, \quad j = 1, 2, 3.$$

For matrix $D^*(z, y)$ it is of the form:

$$-\bar{M}_1 y_1 p_1 + \bar{M}_3 p_3 = 0, \quad \bar{M}_1 y_1 p_1 - \bar{M}_2 p_2 = 0, \quad \bar{M}_2 p_2 - \bar{M}_3 p_3 = 0.$$

Vector $\mathbf{p} = (1, 1, 1)$ may be taken as the decision of the system.
For linear combination $u = \Sigma_{i=1}^{3} p_i v_i$ from system (11) we obtain

$$\dot{u} = (l/\psi) \sum_{i=1}^{3} \sum_{j=1}^{3} d_{ij}^* p_i v_i + \{|\dot{x}_i^*|\} < \psi c k_1.$$

Then

$$|x^* - \bar{x}^*| < u < \psi c k_1 t + u(0), \quad u(0) = \sum_{i=1}^{3} p_i v_i(0) = 1.$$

By making reverse substitution $x^* = x/\varepsilon$ we get a summary estimate of the difference between precise and approximate decision as follows:

$$\sum_{i=1}^{3} |x_i - \bar{x}_i| < \varepsilon(\psi c k_1 t + 1). \tag{12}$$

Then it is necessary to receive approximate decision error estimate for starting substance and reaction product concentration.

For initial and reduced systems respectively

$$\dot{y}_1 = -k_1x_1y_1, \quad \dot{\bar{y}}_1 = -k_1\bar{x}_1\bar{y}, \quad \dot{y}_2 = k_3x_3, \quad \dot{\bar{y}}_2 = k_3\bar{x}_3.$$

Consider $\dot{y}_1 - \dot{\bar{y}}_1 = -k_1x_1y_1 + k_1\bar{x}_1\bar{y}_1$. Denote $|y_1 - \bar{y}_1| = \Delta_1$. Hence

$$\dot{\Delta}_1 = |-k_1x_1y_1 + k_1\bar{x}_1\bar{y}_1| \leqslant k_1x_1y_1 + k_1\bar{x}_1\bar{y}_1 - k_1\bar{x}_1y_1 + k_1\bar{x}_1y_1$$

$$= k_1y_1(x_1 - \bar{x}_1) + k_1\bar{x}_1\bar{y}_1 + k_1\bar{x}_1y_1 \leqslant k_1y_1|x_1 - \bar{x}_1| + k_1\bar{x}_1(\bar{y}_1 + y_1)$$

$$\leqslant k_1\varepsilon(\psi ck_1t + 1) + k_1\varepsilon^*2 = k_1\varepsilon(\psi ck_1t + 3), \quad \text{так как } x_i$$

$$\leqslant \varepsilon\ \forall i, \quad y_j \leqslant 1, \quad \bar{y}_j \leqslant 1, \quad j = 1, 2.$$

Integrating the inequality obtained under condition $\Delta_1(0) = 0$, we get

$$|y_1 - \bar{y}_1| \leqslant k_1\varepsilon(\psi ck_1t^2/2 + 3t) \tag{13}$$

Now we consider the difference $\dot{y}_2\dot{\bar{y}}_2 = k_3(x_3 - \bar{x}_3)$.

Denoting $|y_2 - \bar{y}_2| = \Delta_2$, we can write:

$$\dot{\Delta}_2 \leqslant k_3|x_3 - \bar{x}_3| = k_3\varepsilon(\psi ck_1t + 1).$$

Integrating last inequality under condition $\Delta_2(0) = 0$, we get

$$|y_2 - \bar{y}_2| \leqslant k_3\varepsilon(\psi ck_1t^2/2 + t) \tag{14}$$

To verify the obtained estimates a computer experiment is carried out. For Scheme (I) the problem is solved for two cases. The first case is for a full set of differential equations. The second one is for reduced set (there are three algebraic equations and two differential equations for starting substance and reaction product in this set). On the basis of the results obtained the theoretical estimates of quasi-stationary approximation are compared with the calculated values.

Rate constants equal:

$$k_1 = 0.02, \quad k_2 = 5.7, \quad k_3 = 0.00017,$$

Initial conditions for differential equation are:

$$x_1(0) = \varepsilon = 0.001, \quad x_2(0) = x_3(0) = 0, \quad y_1(0) = 1, \quad y_2(0) = 0.$$

The theoretical formulas of quasi-stationary approximation estimates (13) and (14) which take into account the concrete values are of the form:

$$\Delta_1 = |y_1 - \bar{y}_1| < 0.6 \cdot 10^{-4}t + 0.875 \cdot 10^{-6}t^2, \quad \Delta_2 = |y_2 - \bar{y}_2| < 0.17 \cdot 10^{-6}t + 0.75 \cdot 10^{-8}t^2.$$

Table I gives the quantities of Δ_1 and Δ_2 corresponding to different time calculated by theoretical formulas and experimental results.

From the Table I one can see that accuracy of the theoretical estimate is within the accuracy of experimental description.

Let us correlate the results obtained for the Scheme (I) with those for the Scheme (II). Since these mechanisms practically coincide, the derived estimates of quasi-stationary approximation are also applicable for the reaction mechanism of ammonia synthesis. Intermediate complexes of this mechanism Z, ZN_2, (ZN'_2) (as intermediate complexes of Scheme (I)) do not practically influence the accuracy of the quasi-stationary approximation. This validates the use of QSC method and the form of the estimating algorithm for Scheme (II).

We consider now the following scheme with reversible stages

$$\begin{gathered} A + K \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AK \\ AK \xrightarrow{k_2} BK \\ BK \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} B + K, \end{gathered} \tag{III}$$

TABLE I

Comparison of the theoretical and experimental values for Scheme (I)

t	Δ_1 theoretic.	Δ_1 experim.	Δ_2 theoretic.	Δ_2 experiment.
100.	$\Delta_1 < 0.015$	0.009	$\Delta_2 < 0.92\ 10^{-4}$	$0.733\ 10^{-4}$
150.	$\Delta_1 < 0.029$	0.01	$\Delta_2 < 1.95\ 10^{-4}$	$0.8\ 10^{-4}$
200.	$\Delta_1 < 0.048$	0.01	$\Delta_2 < 3.34\ 10^{-4}$	$0.83\ 10^{-4}$
250.	$\Delta_1 < 0.071$	0.01	$\Delta_2 < 5.13\ 10^{-4}$	$0.83\ 10^{-4}$
300.	$\Delta_1 < 0.099$	0.009	$\Delta_2 < 7.36\ 10^{-4}$	$0.84\ 10^{-4}$
600.	$\Delta_1 < 0.36$	0.01	$\Delta_2 < 0.0028$	$0.83\ 10^{-4}$
900.	$\Delta_1 < 0.77$	0.009	$\Delta_2 < 0.0062$	$0.9\ 10^{-4}$
1000.	$\Delta_1 < 0.96$	0.009	$\Delta_2 < 0.0077$	$0.9\ 10^{-4}$
1100.	$\Delta_1 < 1.155$	0.01	$\Delta_2 < 0.0092$	$0.8\ 10^{-4}$
1200.	$\Delta_1 < 1.368$	0.01	$\Delta_2 < 0.011$	$0.8\ 10^{-4}$

After taking into account the substitution

$$x_i^* = \frac{x_i}{\varepsilon}, \quad i = 1, 2, 3$$

we write for the Scheme III the set of differential equations with the small parameter:

$$\dot{x}_1^* = -k_1 x_1^* y_1 + k_{-1} x_2^* + k_3 x_3^* - k_{-3} x_1^* y_2, \quad \dot{x}_2^* = k_1 x_1^* y_1 - k_{-1} x_2^* - k_2 x_2^*, \quad \dot{x}_3^* = k_2 x_2^* - k_3 x_3^* + k_{-3} x_1^* y_2, \quad \frac{1}{\varepsilon} \dot{y}_1 = -k_1 x_1^* y_1 + k_{-1} x_2^*, \quad \frac{1}{\varepsilon} \dot{y}_2 = k_3 x_3^* - k_{-3} x_1^* y_2 \quad (15)$$

The reduced set for this scheme is of the form:

$$-k_1 \bar{x}_1^* \bar{y}_1 + k_{-1} \bar{x}_2^* + k_3 \bar{x}_3^* - k_{-3} \bar{x}_1^* \bar{y}_2 = 0, \quad k_1 \bar{x}_1^* \bar{y}_1 - k_{-1} \bar{x}_2^* - k_2 \bar{x}_2^* = 0, \quad k_2 \bar{x}_2^* - k_3 \bar{x}_3^* + k_{-3} \bar{x}_1^* \bar{y}_2 = 0, \quad \frac{1}{\varepsilon} \dot{\bar{y}}_1 = -k_1 \bar{x}_1^* \bar{y}_1 + k_{-1} \bar{x}_2^*, \quad \frac{1}{\varepsilon} \dot{\bar{y}}_2 = k_3 \bar{x}_3^* - k_{-3} \bar{x}_1^* \bar{y}_2, \quad (16)$$

where $\bar{x}_1^*, \bar{x}_2^*, \bar{x}_3^*$ are quasi-stationary concentrations.

Applying to this case the algorithm described above we obtain the following precision estimates of quasi-stationary approximation for the system (15) and (16):

$$\sum_{i=1}^{3} |x_i - \bar{x}_i| < \varepsilon(\psi c k^* t + 1), \quad (17)$$

where $k^* = k_1 + k_{-1} + k_3 + k_{-3}$;

$$|y_1 - \bar{y}_1| \leq 2k_1 \varepsilon t + k_{-1}\varepsilon(\psi c k^* t^2/2 + t), \quad (18)$$

$$|y_2 - \bar{y}_2| \leq 2k_3 \varepsilon t + k_3 \varepsilon(\psi c k^* t^2/2 + t). \quad (19)$$

The computer experiment was carried out for Scheme (III). The rate constants equal:

$$k_1 = 0.02, \quad k_{-1} = 0.00075, \quad k_2 = 5.7, \quad k_3 = 0.00017, \quad k_{-3} = 0.000071.$$

Initial conditions for differential equation are:

$$x_1(0) = \varepsilon = 0.001, \quad x_2(0) = x_3(0) = 0, \quad y_1(0) = 1, \quad y_2(0) = 0.$$

TABLE II

Comparison of the theoretical and experimental values for Scheme (III)

t	Δ_1 theoretic.	Δ_1 experim.	Δ_2 theoretic.	Δ_2 experiment.
50.	$\Delta_1 < 0.01069$	0.006	$\Delta_2 < 1.2\ 10^{-4}$	$0.534\ 10^{-4}$
100.	$\Delta_1 < 0.0223$	0.009	$\Delta_2 < 5.9\ 10^{-4}$	$0.733\ 10^{-4}$
150.	$\Delta_1 < 0.0346$	0.01	$\Delta_2 < 11.4\ 10^{-4}$	$0.8\ 10^{-4}$
200.	$\Delta_1 < 0.0477$	0.01	$\Delta_2 < 18.8\ 10^{-4}$	$0.83\ 10^{-4}$
250.	$\Delta_1 < 0.0616$	0.01	$\Delta_2 < 27.8\ 10^{-4}$	$0.83\ 10^{-4}$
300.	$\Delta_1 < 0.076$	0.009	$\Delta_2 < 37.2\ 10^{-4}$	$0.84\ 10^{-4}$
600.	$\Delta_1 < 0.18$	0.01	$\Delta_2 < 0.014$	$0.83\ 10^{-4}$
900.	$\Delta_1 < 0.313$	0.01	$\Delta_2 < 0.03$	$0.9\ 10^{-4}$
1000.	$\Delta_1 < 0.362$	0.01	$\Delta_2 < 0.0374$	$0.9\ 10^{-4}$
1100.	$\Delta_1 < 0.415$	0.01	$\Delta_2 < 0.045$	$0.6\ 10^{-4}$
1200.	$\Delta_1 < 0.472$	0.01	$\Delta_2 < 0.0533$	$0.8\ 10^{-4}$

The theoretical formulas of quasi-stationary approximation estimates (18) and (19) with concrete values are of the form:

$$\Delta_1 = |y_1 - \bar{y}_1| < 0.482 \cdot 10^{-5}t + 0.35 \cdot 10^{-7}t^2, \quad \Delta_2 = |y_2 - \bar{y}_2|$$
$$< 0.415 \cdot 10^{-3}t + 0.155 \cdot 10^{-6}t^2.$$

Table II gives quantities of Δ_1 and Δ_2 corresponding to different times calculated by theoretical formulas and experimental results.

From the Table II we see that the theoretical estimates are within the range of experimental values Δ_1 and Δ_2 at the respective times.

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