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ESTIMATION OF STEADY STATES NUMBER OF ONE-ROUTE CATALYTIC REACTIONS

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For one-route catalytic reactions the relationship between the number of reversible steps and the number of internal steady states (ISS) is investigated. For reactions having trimolecular steps, among which there is only one reversible stage, the number ISS increases to infinity together with the increase of the number of intermediate substances. The model of a reaction with 2n intermediate substances for which the ISS number is equal to n-1 is described. If there are no limitations in the number of reversible steps in a reaction mechanism, then the number of ISS grows exponentially together with the growth of number of intermediate substances. The model of a bimolecular homogeous reaction (a reaction whose steps have similar molecularity) with 3n intermediate substances is given. It can have 2^n ISS.

Keywords: catalytic reaction, internal steady states, intermediate substances, mechanism

Introduction

One of the important problems of catalytic reaction kinetics is to find out the reasons for the occurrence and the number of steady states (SS). If there are some SS under the same conditions of reaction, then the reaction rates in these SS are different. Therefore, the investigation of the possibility of existance of SS is a topical problem. Determining a SS which has the highest rate of reaction allows one to solve optimization probems. The classification of types of SS is given in [1]. According to this classification both internal (ISS) and boundary (BSS) steady states are determined. In these steady states the number of intermediate substances with zero concentrations is equal or not equal to zero, respectively. Some papers [2-4] were devoted to the investigation problems of multiplicity (MSS) of SS. The necessary conditions of MSS is the existence of interaction steps of different intermediate substances in a reaction mechanism [2]. The sufficient conditions of unique occurrence of ISS in catalytic reactions are presented in [3]. However, the results described in [2] and [3] do not have both necessary and sufficient conditions of multiplicity, that is they are not criteria for MSS. For the first time, the multiplicity criterion was described in [4]. Later on this criterion was presented in an algorithmic form and a computer program [5]. However, this criterion does not allow to determine the number of ISS. Some estimates of the number of ISS for several classes of catalytic reactions were obtained [6-8]. For one-route reactions of which the steps are irreversible and have arbitrary molecularity the ISS number does not exceed two [6]. Some reaction models with two intermediate substances of which ISS number can be infinite are presented in [7]. However, these reactions have a high molecularity of steps. For obvious reasons one may ask the question: are there any classes of reactions with low molecularity allowing an unlimited increase of the number of ISS? The answer is given in [8]. The reaction models with n intermediate substances of which the number of ISS is not less than n+1 are given in this paper. This means that with the help of these reaction models steady regimes can be obtained, which are characterized by a large number of ISS. The reactions investigated in [8] are multi-route, therefore, the possibility of the unlimited increase of the number of ISS for one-route reactions with a low molecularity of each of their steps has not yet been studied. This paper gives new results obtained by the authors on the investigation of ISS for different classes of catalytic reactions. For one-route reactions proceeding according to inhomogeneous schemes and having trimolecular steps we have proved the possibility of an unlimited increase of ISS accompanied by an increase of the number of steps. This means that the existence of one reversible step in reaction schemes having a great number of ISS is not only a necessary [6] but also a sufficient condition. Additionally, the exponential increase of the number of ISS under the condition of increasing the number of steps for one-route reactions proceeding via homogeneous bimolecular schemes is demonstrated.

Results and discussion

Let us describe the reaction A=>B proceeding via the scheme which contains 2n inhomogeneous (different molecularity) steps, one of which is reversible :

$$\begin{array}{ll}
1.\ A+X_1=X_2 & (n+1).\ X_1+X_2\rightarrow 2X_3; \\
2.\ 2X_1+X_3\rightarrow X_4+2X_2 & (n+2).\ X_3+X_4+X_2\rightarrow 2X_5+X_1 \\
3.\ X_4+X_5\rightarrow X_6+X_2 & (n+3).\ X_5+X_6+X_2\rightarrow 2X_7+X_4 \\
\cdots\cdots & \cdots\cdots \\
(n-2).\ X_{2n-6}+X_{2n-5}\rightarrow X_{2n-4}+X_2 & (2n-2).\ X_{2n-5}+X_{2n-4}+X_2\rightarrow 2X_{2n-3}+X_{2n-6} \\
(n-1).\ X_{2n-4}+X_{2n-3}\rightarrow 2X_{2n-2} & (2n-1).\ X_{2n-3}+X_{2n-2}+X_2\rightarrow 2X_{2n-1}+X_{2n-4} \\
n.\ X_{2n-2}+X_{2n-1}\rightarrow 2X_{2n} & 2n.\ X_{2n-1}+2X_{2n}\rightarrow 3X_1+B
\end{array} \qquad (1)$$

where A and B are reactants, X_1 are catalytic centers, X_i are intermediate substances $(i=2,...,2n)$. This reaction is one-route because it proceeds via 2n steps in which 2n-1 independent intermediate substances take part.

According to the theory of stationary reactions [9] under isothermal conditions of a gradientless differential reactor for scheme (1) the stationary equations have the following form:

$$\begin{array}{ll}
C_A k_1 x_1 - k_{-1} x_2 = r & k_{n+1} x_1 x_2 = r \\
k_2 x_1^2 x_3 = r & k_{n+2} x_2 x_3 x_4 = r \\
k_3 x_4 x_5 = r & k_{n+3} x_2 x_5 x_6 = r \\
\cdots\cdots & \\
k_{n-2} x_{2n-6} x_{2n-5} = r & k_{2n-2} x_2 x_{2n-5} x_{2n-4} = r \\
k_{n-1} x_{2n-4} x_{2n-3} = r & k_{2n-1} x_2 x_{2n-3} x_{2n-2} = r \\
k_n x_{2n-2} x_{2n-1} = r & k_{2n} x_{2n-1} x_{2n}^2 = r
\end{array} \qquad (2)$$

$$\sum_{i=1}^{n} x_i = 1$$

where $k_i = const$ are stage rate constants, C_A is the concentration of A, x_i are concentrations of intermediate substances X_i, r is the reaction rate.

Let us introduce new variables $x = c_1 x_2, y = c_2 x_2 / x_1$, where c_1, c_2 must be in such a form that the first two equations of scheme (2) after substituting r, lead to the equation $x + y = 1$. Further, let us mark all x_i by x and y.

$$\begin{array}{ll}
x_1 = p_1 x / y; & x_2 = p_2 x \\
x_3 = p_3 y; & x_4 = p_4 x / y^2 \\
x_5 = p_5 y \cdot x; & x_6 = p_6 / y^2 \\
\cdots\cdots & \\
x_{2n-3} = p_{2n-3} y \cdot x^{n-3}; & x_{2n-2} = p_{2n} x^{-n+4} / y^2 \\
x_{2n-1} = p_{2n-1} y \cdot x^{n-2}; & x_{2n} = p_{2n} x^{-n/2+2} / y
\end{array} \qquad (3)$$

where the p_i are determined by the equations

$$p_1 = \frac{k_{-1}}{k_{n+1}},\ p_2 = \frac{k_1}{k_{n+1}},$$

$$p_{2j-1} = \frac{k_{n+1}}{k_{-1}} \left(\frac{k_1}{k_{n+1}} \right)^{j-1} \prod_{m=1}^{j-1} \frac{k_{m+n}}{k_{m+1}},\ j = 2,...,n,$$

$$p_{2j} = \left(\frac{k_{-1}}{k_{n+1}} \right)^2 \left(\frac{k_{n+1}}{k_1} \right)^{j-1} \prod_{m=2}^{j} \frac{k_m}{k_{m+n}},\ j = 2,...,n-1,$$

$$p_{2n} = \sqrt{ \left(\frac{k_{-1}}{k_{n+1}} \right)^2 \left(\frac{k_{n+1}}{k_1} \right)^{n-2} \prod_{m=2}^{n} \frac{k_m}{k_{m+n}} }.$$

The numbers p_i can have any positive values by changing the rate constants k_i. Look at the relations

$$k_{-1} = p_1 k_{n+1},\ k_1 = p_2 k_{n+1},\ k_2 = \frac{p_2}{p_1 p_3} k_{n+1},$$

$$k_j = \frac{p_1 p_2}{p_{2j-2} p_{2j-1}} k_{n+1},\ k_{j+n-1} = \frac{p_1 p_2}{p_{2j-4} p_{2j-3}} k_{n+1},\ j = 3,...,n,$$

$$k_{2n} = \frac{p_1 p_2}{p_{2n-1} p_{2n}^2} k_{n+1}.$$

This note is necessary in order to work with such values of numbers p_i. Thus, let us mark all x_i by x and y, and reduce scheme (2) to one equation:

$$\begin{array}{l}
p_3 y + p_5 y \cdot x + ... + p_{2n-1} y \cdot x^{n-2} - 1 + \\
+ p_1 x / y + p_2 x + p_4 x / y^2 + p_6 / y^2 + ..., \\
+ p_{2n} x^{-n/2+2} / y = 0
\end{array} \qquad (4)$$

where $y = 1 - x$.

Let us consider the function $\varphi(x) = p_3 y + p_5 y \cdot x + ... + p_{2n-1} y \cdot x^{n-2} - 1$ and show that the number of different roots $\varphi(x)$ lying in the interval (0,1) is equal to n-1 for the corresponding selection of numbers $p_3, p_5, ..., p_{2n-1}$. The function $\varphi(x)$ can be represented in the form:

$$\begin{array}{l}
1 - p_3 + (p_3 - p_5) x + ... + (p_{2n-3} - p_{2n-1}) x^{n-2} + \\
+ p_{2n-1} x^{n-1} = p_{2n-1} \prod_{i=1}^{n-1} (x - x_i)
\end{array} \qquad (5)$$

Hence we obtain

$$p_{2n-1} \prod_{i=1}^{n-1} (x - x_i) = p_{2n-1} \left(x^{n-1} - s_1 x^{n-2} + ... + (-1)^{n-1} s_{n-1} \right) \qquad (6)$$

where the s_i are symmetrical root functions in x_i, whereby the parameters p_i, according to relations (5), can be written in the form $p_{2j-1} = 1 - \sum_{i=n-j+1}^{n-1} (-1)^i s_i$, $j = 2,\ldots,n$. By choosing different small positive roots x_i the symmetrical functions will be also small positive numbers and the p_{2j-1} values will be close to 1. Selecting the corresponding $p_1, p_2, p_4, \ldots, p_{2n}$ constants, the number of roots of equations (4) lying in the interval (0,1) is also equal to *n-1*. In fact, if we make the constants $p_1, p_2, p_4, \ldots, p_{2n}$ small, then this results from the theorem on the continuous dependence of the roots on coefficients [10]. Thus, scheme (1) has *n-1* ISS at some sets of rate constants.

In order to show the exponential increase of the number of ISS for an increasing number of steps, let us consider the reaction A=>B, proceeding via the following steps

$$
\begin{array}{lll}
1.\ A + x_2 + x_3 = 2x_1 & 1'.\ x_1 + x_2 \rightarrow 2x_5 & 1''.\ 2x_1 = 2x_3; \\
2.\ x_5 + x_6 = 2x_4 & 2'.\ x_4 + x_5 \rightarrow 2x_8 & 2''.\ 2x_4 = 2x_6; \\
\ldots & & \\
n.\ x_{3n-1} + x_{3n} = 2x_{3n-2} & n'.\ x_{3n-2} + x_{3n-1} \rightarrow 2x_2 & n''.\ 2x_{3n-2} = 2x_{3n} + B;
\end{array}
\qquad (7)
$$

The stationary equations are written in the following form:

$$
\begin{array}{lll}
k_1 c_A x_2 x_3 - k_{-1} x_1^2 = d_1 r & k_{1'} x_1 x_2 = d_{1'} r & k_{1''} x_1^2 - k_{-1''} x_3^2 = d_{1''} r \\
k_2 x_5 x_6 - k_{-2} x_4^2 = d_2 r & k_{2'} x_4 x_5 = d_{2'} r & k_{2''} x_4^2 - k_{-2''} x_6^2 = d_{2''} r \\
\ldots & & \\
k_n x_{3n-1} x_{3n} - k_{-n} x_{3n-2}^2 = d_n r & k_{n'} x_{3n-2} x_{3n-1} = d_{n'} r & k_{n''} x_{3n-2}^2 - k_{-n''} c_B x_{3n}^2 = d_{n''} r
\end{array}
\qquad (8)
$$

$$\sum_{i=1..3n} x_i = 1$$

Dividing the first three equations of system (8) in the first line by x_1^2 and substituting *r* we get two equations with two unknown values $y_2 = x_2 / x_1, y_3 = x_3 / x_1$. We continue the same procedure with three equations, then with four ones and so on. Further, let us select rate constants for these equations in such a way that the equations obtained could have two different solutions (for example, use the ISS multiplicity criterion for one-route reactions [5]). Then for these systems the solutions have the following form

$$x_{3j-1} = u_{i_j}^1 x_{3j-2}; x_{3j} = u_{i_j}^2 x_{3j-1} \quad i_j \in [1,2],\ j = 1..n \qquad (9)$$

Using these solutions we can exclude x_{3j-1}, x_{3j}, mark then x_{3j-2}, and reduce 3j-1 equations of systems (8) to the following form:

$$c_j x_{3j-2}^2 = d_{j'} r \quad i_j \in [1,2],\ j = 1..n \qquad (10)$$

Further, let us substitute *r* and mark x_{3j-2} by x_1. Using relations (9), let us denote all x_j by x_1. On the basis of the last equation of system (8) we calculate x_1 and then determine x_j. Knowing the data for $u_{i_j}^{;}, u_{i_j}^{-}$, the solutions of system (9) can be simply found. This means that the unique solution of system (9) corresponds to just one vector out of a set of 2^n vectors. We want to show that all the solutions are different. If it is not so, then all numbers coincide for two different u_i^j sets. This is impossible because these sets differ at least in one of the coordinates. Scheme (7) is constructed on the base of scheme (1) in *Table 1* of paper [11]. If we take any other scheme in *Tables 1* and 2 of paper [11] or their combination, we can construct schemes having the exponential increase of the number of ISS. The kinetic dependence in *Fig.1* illustrates the number of ISS for schemes (7). This dependence has the following interesting peculiarity: all the roots appear simultaneously (in a general case two solutions appear). This peculiarity is connected with system (8) by splitting the system into independent equation subsystems. This property of system (8) leads to this unusual type of kinetic dependence. Schemes (7) can be used as test for the efficiency of computer programs which determine the number of ISS. The absent of solutions at some C_A (*Fig.1*) is connected with the presence of boundary steady states [1] for scheme (7).

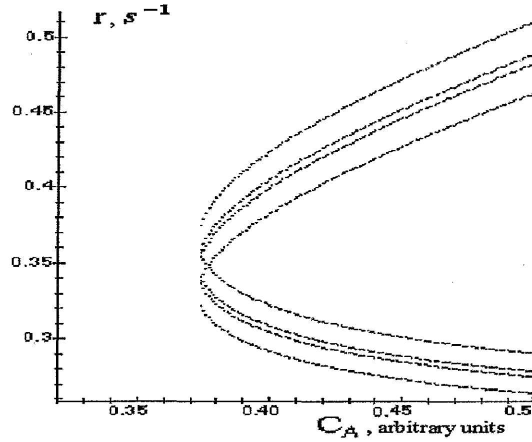

Fig.1 Dependence of rate on concentration o *A* for reaction proceeding via scheme (7) at $k_1 = 100$, $k_2 = 42$, $k_3 = 50$, $k_{-1} = k_{-2} = k_{-3} = 11.6$, $k_{1'} = k_{2'} = k_{3'} = 21$, $k_{1''} = k_{2''} = k_{3''} = 106$, $k_{-1''} = k_{-2''} = k_{-3''} = 169$ (s^{-1})

Conclusion

The presence of reversible steps in mechanisms of one-route catalytic reactions is a necessary and sufficient condition of an unlimited ISS number. If there are no limitations in the number of reversible steps, the number of ISS increases exponentially together with the number of intermediate substances.

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