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MULTIPLICITY OF STEADY STATES AND THE SHAPES OF ITS EXHIBITING IN CATALYTIC REACTIONS KINETICS

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The purpose of the presented review is the analysis of the existing approaches and mathematical methods for the investigation of the critical phenomena of a type of multiple steady states in kinetics of catalytic reactions

Keywords: multiplicity; steady state; hysteresis; self-crossing; breakdown; isola; mushroom; catalytic reaction; kinetics; step scheme.

Introduction

One of the current problems in kinetics is the investigation of the multiplicity of steady states (MSS) and the shapes of the phase portraits in catalytic reactions. Their existence was proved by extensive research, and the results were published in many papers and at conferences. The following sections review the development of mathematical methods and the research of MSS in catalytic processes. Well-known are Ya. Zeldovich's papers on the uniqueness of the equilibrium point [1] and the anomalous types of critical effects [2]; I. Prigozhin Brussel`s school publications [3,4]; monographs by G. Jablonskii, V. Bykov, V. Elokhin, A. Gorban [5-8]; and also the research work carried out at the G. Boreskov Institute of catalysis SD RAS, at the N. Zelinsky organic chemistry Institute, at the N. Semyonov chemical physics Institute, and at some other institutions are of great importance for the development of this branch of science.

At the beginning of the investigation of critical phenomena like MSS the experimental data on their existence in concrete heterogeneous catalytic reactions were collected: hydrogen oxidation [9-10], of carbon monooxide oxidation [11-13], ammonia synthesis [17] on platinum metals and others. Then researchers tried to describe these phenomena taking into account thermal and diffusional effects [18, 19]; phase transitions [20]; changes of the catalyst surface structure [21] under the influence of components which take part in a reaction, ramified-chain [22, 23] or homogeneous-heterogeneous [24] character of reactions. Discovering MSS in the kinetic region [25, 26] for some reactions led to the third step in which MSS is described by simple model mechanisms [5-8]. The modern fourth step is characterized by the development of the theoretical methods investigation of MSS and different forms of its catalytic reaction kinetics. Some important results in this field of research is reviewed in this paper.

Theory

To describe existing approaches of investigation of MSS and their various shapes let us regard a general one-route catalytic reaction

$$\sum_i d_i \sum_l b_{il}^{+} A_l \Leftrightarrow \sum_i d_i \sum_l b_{il}^{-} A_l \,, \qquad (1)$$

acting through steps

$$\sum_l b_{il}^{+} A_l + \sum_j a_{ij}^{+} X_j \overset{r_i^{+}}{\underset{r_i^{-}}{\Leftrightarrow}} \sum_l b_{il}^{-} A_l + \sum_j a_{ij}^{-} X_j \,,\ d_i \qquad (2)$$

$$i, j = 1,\dots,S; \quad l = 1,\dots,m \,,$$

where A_l and X_j are basic substances and intermediates; $a_{ij}^{\pm}$, $b_{ij}^{\pm} \geq 0$ are the stoichiometric coefficients ($\sum_j a_{ij}^{+} = \sum_j a_{ij}^{-}$); $d_i > 0$ are the stoichiometric numbers of steps, ($i = 1,...,S$); r_i^{+} and r_i^{-} are rates of *i-th* step in forward and reverse directions:

$$r_i^{\pm} = \omega_i^{\pm} \prod_{j=1}^{n} x_j^{a_{ij}^{\pm}}, \omega_i^{\pm} = k_i^{\pm} \prod_l C_l^{b_{il}^{\pm}}, \qquad (3)$$

ω_i^{+} and ω_i^{-} are the frequencies of steps in forward and reverse directions, x_j are the concentrations of intermediates X_j, C_l are the concentrations of basic substances A_l, $k_i^{\pm}$ are rate constants of the steps..

Under isothermal conditions in a gradientless differential reactor the scheme (2) describes the changes of concentrations of the reactants (A_l) and intermediate substances (X_j) by the following system of the stationary equations

$$\sum_i (a_{i,j}^{-} - a_{i,j}^{+})(r_i - r_{-i}) = 0, \qquad (4)$$

$$\sum_i (b_{i,k}^{-} - b_{i,k}^{+})(r_i - r_{-i}) + q^0 C_k^0 - q C_k = 0, \quad (5)$$

where q^0 and q are reactor inlet and outlet flows of a reaction mixture, C_k^0 and C_k are the concentrations of the $k-th$ reactants at inlet and outlet of the reactor.

The scheme (2) is characterized by the conservation law of the number of centers per unit of a catalyst surface

$$\sum_i x_i = 1, \qquad (6)$$

corresponding to the constant total quantity (or concentration) of active centers on the unit of the catalyst surface. Under stationary conditions, the rates of the reaction steps (1) are given by

$$r_i - r_{-i} = d_i r. \qquad (7)$$

We will first discuss the shapes of the kinetic curves which reveal multiplicity. MSS of reaction rates are investigated as a function of one parameter (concentration of one reactant, temperature, flow rate of one reactant etc.). These dependencies are characterized by the existence of some different stable regimes of reaction proceeding under the same conditions. The typical shapes of kinetic phase planes which are characterized by MSS [27] are given in Fig. 1.

Results and Discussion

S-shaped hysteresis

First the kinetic dependencies in the form of S-shaped hysteresis are considered which were often detected in experiments (Fig. 1a, 1b). The peculiarity of this hysteresis is, as a rule, the existence of two (solid lines) and one unstable (a broken line) branches. Only stable branches are observed experimentally. The hysteresis is

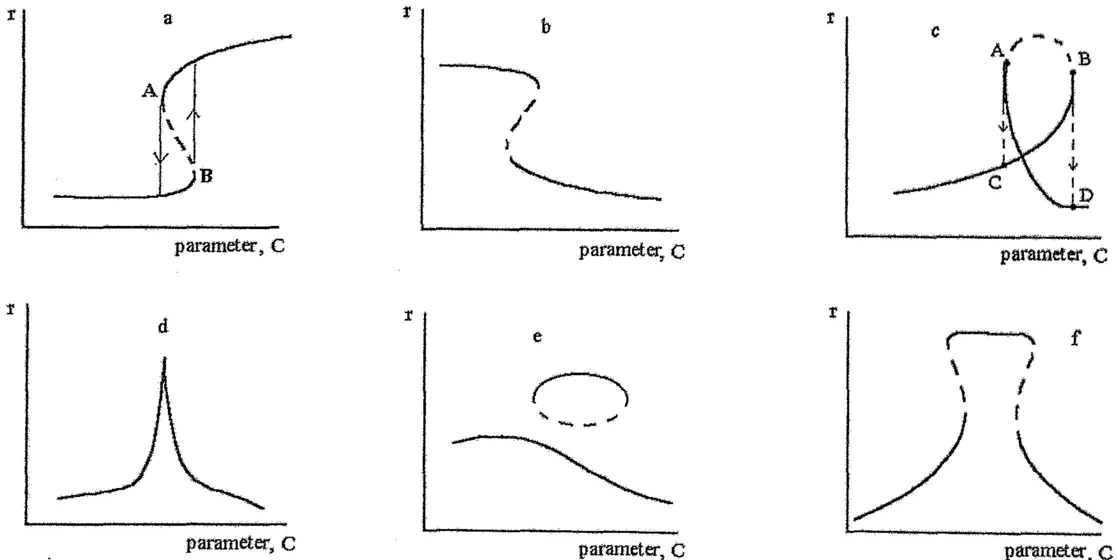

Fig. 1. Multiplicity shapes of steady states: a - "anticlockwise" hysteresis, b- "clockwise" hysteresis, c- self-crossing ("loop"), d- breakdown , e - isola, f - mushroom (solid lines-steady stationary states, broken lines-unsteady stationary states)

shown by the arrows in Fig 1a. For example, when the hysteresis is anticlockwise, the parameter C leads to an increase of the reaction rate along the low branch until the critical point B is reached (see Fig.1). A further change of reaction rate r takes place along the upper branch of the S-shaped curve. Decreasing the parameter C along the upper branch, a sudden jump to the lower branch takes place at the critical point A.

MSS of heterogeneous catalytic reactions in the form of S-shaped hysteresis were observed for the oxidation of hydrogen, carbon monoxide, ammonia, ethylene, benzene, propylene and ammonia synthesis processes. In most cases, for the description of hysteresis in the above-mentioned reactions, mechanisms characterized by interaction of adsorbed components on a catalyst surface were used. A reaction of carbon monoxide oxidation on the metals of the platinum group as a function of temperature "anticlockwise" hysteresis (Fig. 1a) (also concentration "clockwise" and "anticlockwise" hystereses) was described, for example, by the following reaction scheme [28]:

1. $O_2 + 2K = 2OK$,
3. $COK + OK \rightarrow 2K + CO_2$,
2. $CO + K = COK$,
4. $CO + OK \rightarrow K + CO_2$,

where K, OK, COK are free, occupied by oxygen or by carbon monoxide catalyst surface centers, respectively.

The most effective approach of detecting MSS is the mathematical criterion presented in the papers [29, 30]. The criterion allows, on the basis of the stoichiometric matrix of intermediate components of a step scheme of reaction, to detect definitely the existence of MSS, and also to define a set of steps ensuring MSS of catalytic reactions as a function of the concentration of intermediate components. This criterion will be formulated.

It is obvious that MSS can only occur in case that at least two stationary states are possible under the same reaction conditions. This statement is the basis for the MSS criterion formulation in paper [30]. The criterion includes the necessary conditions of existence of MSS like these:

$$\left(W - \sum_j a^+_{i,j} V_j - \sum_k b^+_{i,k} U_k\right) \cdot \left(\sum_j \left(a^+_{i,j} - a^-_{i,j}\right) V_j + \sum_k \left(b^+_{i,k} - b^-_{i,k}\right) U_k\right) > 0 \qquad (8)$$

for $\omega_{-i} \neq 0$

$$W = \sum_j a^+_{i,j} V_j + \sum_k b^+_{i,k} U_k \text{, for } \omega_{-i} = 0 \qquad (9)$$

The sufficient conditions of MSS are

$$\exists i, j : V_i < 0 < V_j \, . \qquad (10)$$

$$U_l \le 0 \le U_p \le W \text{ or } U_l \ge 0 \ge U_p \ge W \, . \qquad (11)$$

where $V_j = \ln \frac{x_j^{(2)}}{x_j^{(1)}}$, $U_k = \ln \frac{C_k^{(2)}}{C_k^{(1)}}$, $W = \ln\left(\frac{r^{(2)}}{r^{(1)}}\right)$,

$x_j^{(1)} \neq x_j^{(2)}$ $\qquad$ $r^{(1)} \neq r^{(2)}$

In general the criterion of MSS is formulated as follows: if for a reaction scheme of the corresponding relations (8) (or (9)), (10) and (11) are satisfied then the examined reaction is characterized by multiplicity. Otherwise there is only one stationary state. The values V_j, U_k and W at which MSS is realized can be applied for the determination of concentration of the reactants and intermediate substances [30].

Let us illustrate an application of the criterion of existence of multiplicity in a catalytic reaction of carbon monoxide oxidation $2CO + O_2 = 2CO_2$ on platinum [31] proceeding according to the scheme

1. $O_2 + 2K = 2KO$,
2. $CO + KO + K \rightarrow CO_2 + 2K$. $\qquad$ (12)

In the beginning we shall write down the criterion of MSS for this scheme in isothermal gradientless differential reactors at constant concentration of the reactants C_k, when all components of a vector U are equal to zero. With respect to relations (8) and (9) MSS will occur under the following conditions:

$$(2V_1 - W)(2V_2 - 2V_1) > 0 \text{, } W = V_1 + V_2 \, . \qquad (13)$$

where the parameters V_1 and V_2 correspond to substances K and KO. A simple analysis reveals that the inequalities (13) are only satisfied if all the vector components V have the same signs. In this case equation (10) is not satisfied. It specifies the impossibility of the description of MSS by the scheme (12) in the given reaction. If one takes into account changes of concentration the relations (8), (9) for reactants, the criteria take the form of

$$(2V_1 + U_1 - W)(2V_2 - 2V_1) > 0 \text{, } W = V_1 + V_2 + U_2 \, .$$

The relations obtained are carried out, for example, at $W = 2$, $V_1 = 6$, $V_2 = -2$, $U_1 = -13$, $U_2 = -2$ (the parameters U_1 and U_2 correspond to the concentrations of O_2 and CO). The given values satisfy a component of vectors V and U also the inequalities (10), (11). In Fig. 2 the dependence $r = f(C_{co})$ is given which demonstrate MSS as a S-shaped "counter-clockwise" hysteresis curve. Hence the scheme (12) can be used for the description of MSS in the catalytic reaction of carbon monoxide oxidation under isothermal conditions with respect to the change of concentration of the reactants.

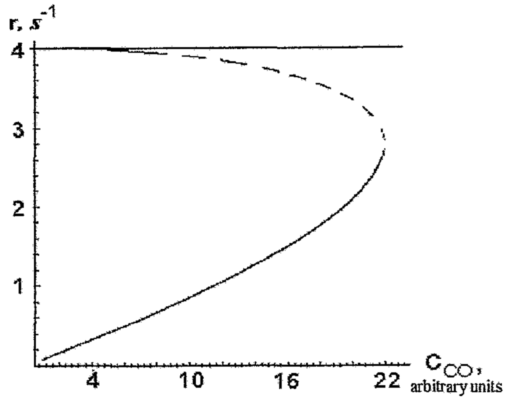

Fig.2. Dependence of rate on concentration of carbon monooxide for reaction of carbon monooxide oxidation proceeding on the scheme (12) at: , , (s-1)

The criterion developed was used for the investigation of both known and new mechanisms of catalytic hydrogen oxidation and carbon monoxide reactions. The most simple schemes of these reactions describing MSS in the form of S-shaped hysteresises are the following:

H_2 oxidation: 1. $O_2 + 2K = 2KO$,
2. $H_2 + KO + K \to 2K + H_2O$,

CO oxidation: 1. $O_2 + 2K = 2KO$,
2. $CO + KO \to K + CO_2$,
3. $CO + K = KCO$.

Self-crossing

Another shape of MSS is a kinetic curve with self-crossing (Fig. 1c). This critical phenomenon is characterized by the fact that the graph of reaction rate as a function of a parameter intersects at one point. This leads to a kinetic "loop". Fig. 1c shows that changing the parameter C from left to right and vice versa in the region of the loop self-crossing, kinetic dependence is realized in the form of a hysteresis - "eight" (see the direction of rate change along the CBDAC curve). It is worth noting that at the intersection point, which is characterized by various values of intermediate species concentrations on a catalyst surface, the reaction rate has the same value. This property was the basis for the mechanisms which describe self-crossing. As was shown in the papers [32, 33] in an isothermal gradientless differential reactor at constant concentration of the basic substances (when all components of a vector U are equal to zero) any one-route-reaction consisting of steps of a kind (2) in a point of self-crossing can be characterized by the following equations between rates

$$r^{(1)} = r^{(2)}, \; W = \ln\left(\frac{r^{(2)}}{r^{(1)}}\right) = 0 \qquad (14)$$

and for concentrations of intermediate substances one obtains:

$$\exists j: \; x_j^{(1)} \neq x_j^{(2)}, \; j = 1,\ldots,n \qquad (15)$$

in various steady states. The equations of MSS criteria (8), (9) in case of self-crossing will be written down for reversible and irreversible steps accordingly in the following way:

$$\sum_j a_{i,j}^+ V_j \Big(\sum_j (a_{i,j}^- - a_{i,j}^+) V_j\Big) > 0, \; (\omega_{-i} \neq 0) \qquad (16)$$

$$\sum_j a_{i,j}^+ V_j = 0, \; (\omega_{-i} = 0) \qquad (17)$$

In the case a two-step reaction consisting of steps of a type (2) it is possible if there stoichiometric coefficients satisfy relations:

$$\begin{vmatrix} a_{11}^+ & a_{12}^+ \\ a_{21}^+ & a_{22}^+ \end{vmatrix}, \begin{vmatrix} a_{11}^- & a_{12}^- \\ a_{21}^+ & a_{21}^+ \end{vmatrix}, \begin{vmatrix} a_{11}^- & a_{12}^- \\ a_{11}^+ & a_{12}^+ \end{vmatrix}, \begin{vmatrix} a_{11}^- & a_{12}^- \\ a_{21}^- & a_{22}^- \end{vmatrix} > 0. \qquad (18)$$

Hence the criterion of existence of a loop for two-step reactions is that all four inequalites (18) are fulfilled. The simplest mechanism satisfying this criterion for $A_1 \Leftrightarrow A_2$ reaction is

1. $A_1 + X_1 + X_2 = 2X_1 + A_2$,
2. $X_1 + 2X_2 = 3X_2$. (19)

Fig. 3a illustrates kinetic dependence self-crossing for this reaction.

Breakdown

The kinetic dependencies with self-crossing or breakdown are shown in Fig. 1c and 1d. As can be observed, under certain conditions points A and B in Fig.1c with self-crossing can exist very close to each other, which leads to a kinetic curve with breakdown.

The kinetic behavior of this form was obtained for reactions of carbon monoxide oxidation on palladium [34, 35] and also hydrogen oxidation on platinum [36]. Besides these examples the occurrence like breakdown were obtained at joint oxidation of carbon monoxide and nitrogen oxide [37].

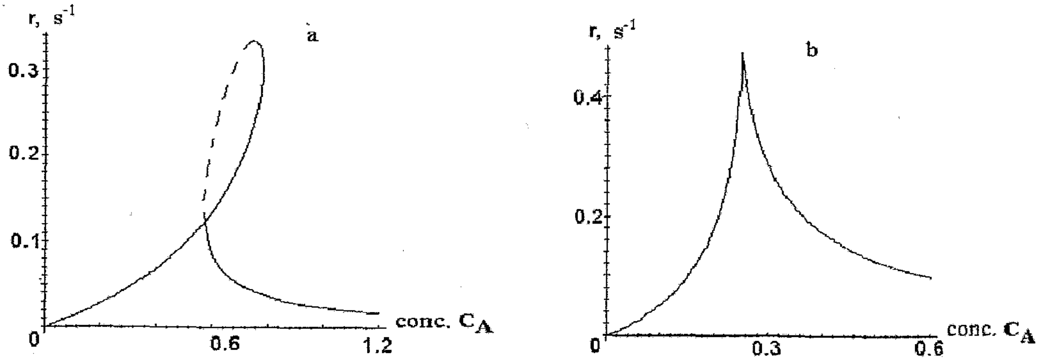

Fig. 3. Kinetic dependence r(C_{A1}) for reaction $A_1 \Leftrightarrow A_2$ proceeding via scheme (19): a) - $k_1 = 2$, $\omega_{-1} = 1/7$, $\omega_2 = 804/343$, $\omega_{-2} = 60/343$; b) - $k_1 = 10$, $\omega_{-1} = 2.495$, $\omega_2 = 0.668$, $\omega_{-2} = 0.131$ (s^{-1})

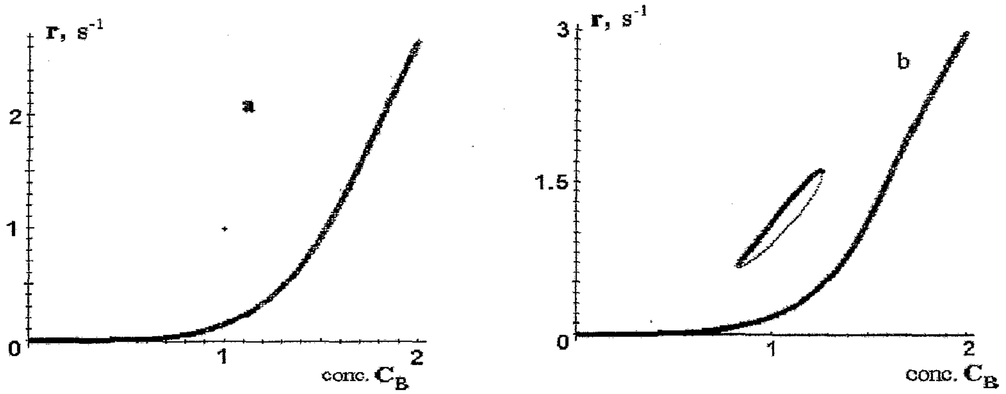

Fig. 4. Kinetic dependencies for scheme (20) at $k_1 = 4$, $k_2 = \frac{135}{2}$, $k_{-2} = 54$ (s^{-1}): a) - monotonous branch with an isolated "special point ($k_{-1} = \frac{1}{2}$)"; b) - isola ($k_{-1} = 0.51$)

The treatment of breakdowns as a function of kinetic parameters for reactions of oxidation of hydrogen, carbon monoxide, ammonia on platinum on the basis of multipathway mechanisms was presented in [37, 38] for the first time. It was supposed that for these reactions the rate constant of interaction between adsorbed particles on a catalyst surface is rather strong, also the occupation of the catalyst by oxidizing substances is small [38]. The same approach is presented in [39] for the reaction of carbon monoxide oxidation on platinum. The breakdown of kinetic dependence was interpreted within the framework of the scheme

$$A_2 + 2K = 2AK,$$
$$B + K = BK,$$
$$AK + BK \to 2K + AB$$

as a limiting case of the kinetic curve at $k_3 \to \infty$. The same explanation of the occurrence of breakdowns can be found in papers [40 - 42] for the reaction of oxidation of hydrogen on monocrystals of platinum.

In papers [43 - 46] the criterion of occurrence of a breakdown is offered at the finite values of rate constants. It is shown that the criteria relations of a breakdown are equivalent to the basic criteria of self-crossing of kinetic curves. This research shows that kinetic dependencies with self-crossing and with a breakdown are determined by an identical reaction stoichiometry, although they display different forms of the critical phenomena. Therefore, for describing breakdown it is quite enough to have reaction schemes giving self-crossing of kinetic curves. Fig. 3b illustrates breakdown for scheme (19). Breakdown and "loop" are two evolutional MSS forms.

The simplest schemes of catalytic hydrogen oxidation and carbon monoxide reactions describing MSS in the form of breakdown (or with self-crossing) of kinetic curves are the following:

H_2 oxidation: 1. $O_2 + 2K = 2KO$,
2. $H_2 + K = KH_2$,
3. $KO + KH_2 \to 2K + H_2O$,

CO oxidation: 1. $KO + KCO = 2K + CO_2$,
2. $CO + K + KCO = 2KCO$,
3. $O_2 + 2K = 2KO$.

Isola

Isola is a closed isolated branch of a stationary kinetic curve (Fig. 1d). The existence conditions of this shape for a non-isothermal reaction of the first order are formulated in paper [2].The basic cause of appearance of isola is a process of "rolling - unrolling" of a mushroom curve in Fig. 1f. It is described in papers [47, 48]. The isola in the graph of r(C) can be obtained from a kinetic curve having "a special point" (ref. [2, 49]). If one of the parameters changes slightly, this point becomes an isola.

The simplest model of a kinetic curve with isola realization is a A⇔D reaction proceeding via an intermediate, B, according to the following scheme

$$\begin{aligned}&1.\ A+2B+X_1=X_2+3B,\\&2.\ B+3X_1+X_2=4X_1+D\end{aligned}\qquad(20)$$

for which at some parameter values C_B, $r(C_B)$ shows "a special point" (Fig. 4a). If the k_{-1} parameter slightly increases the point turns into an isola (Fig. 4b).

Mushroom

Mushroom behavior (Fig. 1f) can be considered as a monoparameter kinetic curve which consists of two s-shaped hysteresis branches. This MSS shape rarely appears. There are a few papers in which this critical phenomenon is experimentally described. The kinetic behavior according to the mushroom type were experimentally reproduced in benzene [50] and carbon monoxide [51] oxidation on platinum catalysts.

The mushroom shape is a transitional one between isolated and self-crossing kinetic curves. The mushroom shape is connected with the existence of "a special point". The investigation of stoichiometric conditions of the existence of a "special point" showed some interesting results. For example, the B_2⇔$2B_1$ reaction proceeding via the following scheme

$$\begin{aligned}&1.\ B_2+X_1=X_2+B_1,\\&2.\ X_2=X_3+B_1,\\&3.\ 2X_1+X_3=3X_1\end{aligned}\qquad(21)$$

describes the kinetics with isola under certain conditions (Fig. 5a). If the conditions change, approaching and blending of the isola with a monotonous branch takes place. Thus, self-crossing appears (Fig. 5b), which finally turns into a mushroom form (Fig. 5c).

The above-mentioned examples show that kinetic dependencies with self-crossing, breakdown, isola and mushroom are variable forms of MSS curves, they can turn into one another if the conditions of reaction change.

Conclusion

For all kinetic dependencies except breakdown (Fig. 1) there is a general property, namely the existence of two different steady states, which are characterized by different values of concentrations of intermediate components and reactants and also rates under the same conditions. This statement is the basis for MSS criteria [30]. The criteria developed were used for the investigation of both known and unknown mechanisms of catalytic hydrogen oxidation and carbon monoxide reactions which reveal MSS in the form of S-shape, self-crossing, breakdown kinetic dependencies, respectively. These data are given in ref. [52 - 56]. The conditions of occurrence of kinetics with isola and mushroom are given in ref. [57, 58] in which the schemes of models and concrete catalytic reactions characterized by these kinetic dependencies are investigated in detail.

The conditions and criteria of MSS and its different shapes are mathematical relations which contain stoichiometry (molecularity of basic and intermediate components in each step of the investigated reaction mechanism), concentrations of components taking part

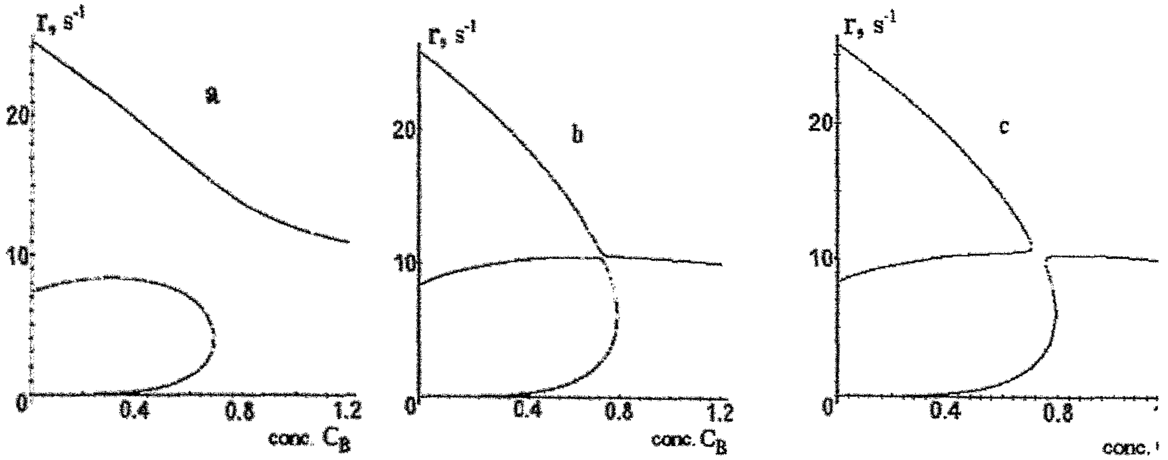

Fig. 5. Isola (a), self-crossing (b) and mushroom (c) for scheme (21) at: $k_{-1}=12$, $k_2=180$, $k_{-2}=144$, $k_3=405$, $k_{-3}=81$ (s^{-1}): a) - $k_1=48$; b) - $k_1=50.3$; c) - $k_1=50.33$ (s^{-1})

in a reaction and kinetic parameters (rate constants and step activation energies). The solution of these algebraic equations for catalytic reactions, which proceed via two or three steps, is not difficult; it can be done by hand. However, for multiple step reactions with a great number of intermediate compounds this analysis is practically impossible without applying computers. The algorithms and computer programs which can be used by chemists are described in ref. [56, 59 -62].

The above mentioned information connects MSS and their different shapes with the mechanisms of the catalytic reactions. This information can be used in the analysis and evalution of experimental results of catalytic reactions which are characterized by MSS.

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