

The critical forms of the kinetic dependence in two- and three-stage catalytic reactions

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A description of self-crossing, isola and mushroom two- and three-stage schemes in the kinetics of catalytic reactions is given.

An investigation of critical phenomena such as the multiplicity of steady states (MSS) related to the particular structure of catalytic reaction mechanisms has been carried out in, for instance, refs. 1–3. In ref. 4, the MSS investigation criterion was derived, and a classification of the various MSS realization forms in the kinetics of catalytic reactions was given. S-form hysteresis was shown to be the most prevalent. The possibility of describing such hysteresis in the kinetics of two- and three-stage reactions was investigated in, for instance, refs. 5 and 6. Self-crossing, isolated and mushroom-shape kinetic dependences take place along with the S-form. The mushroom-like experimentally-obtained kinetic dependences of the catalytic oxidation of carbon monoxide were given in a few papers (for example, ref. 7). For the description of the mushroom and similar complex kinetic forms the authors offered in these papers the use of heterogeneous–homogeneous mechanisms with a view to describing the mushroom and similar complex forms of the kinetic dependences. The explanation of such kinetic dependences based on heterogeneous stage schemes seems to be of interest. In this report, we present the results of an investigation of the self-crossing, isolated and mushroom-form dependences for elementary two- and three-stage catalytic reactions proceeding in an isothermal gradientless differential reactor.

The analysis has shown that the critical forms of the kinetic dependence may appear for two reasons. The first relates to the existence of a singular point,⁸ and the second is the consequence of peculiarities of the kinetic curve projection on a plane as the rate vs. concentration dependence.⁹ The kinetic curve of the same reaction may take various forms depending on the reaction conditions. We have established the stoichiometric conditions of the existence of various forms of the complex kinetic dependence for two- and three-stage catalytic reactions. It was shown that changes in the reaction conditions lead to the evolution and mutual transition of these kinetic dependences.

We shall consider two-stage reaction of the type

$$\begin{cases} \sum_i b_{1i} B_i + a_{11} X_1 + a_{12} X_2 = \sum_i b_{-1i} B_i + a_{-11} X_1 + a_{-12} X_2 \\ \sum_i b_{2i} B_i + a_{21} X_1 + a_{22} X_2 = \sum_i b_{-2i} B_i + a_{-21} X_1 + a_{-22} X_2 \end{cases} \quad \begin{matrix} d_1 \\ d_2 \end{matrix} \quad (1)$$

where B_i are basic substances; X_1 and X_2 are intermediates; b_{ij} , b_{-ij} , a_{ij} , $a_{-ij} \geq 0$ are stoichiometric coefficients ($\sum a_{ij} = \sum a_{-ij}$) and $d_i > 0$ are the stoichiometric stage numbers ($i = 1, 2$). We shall

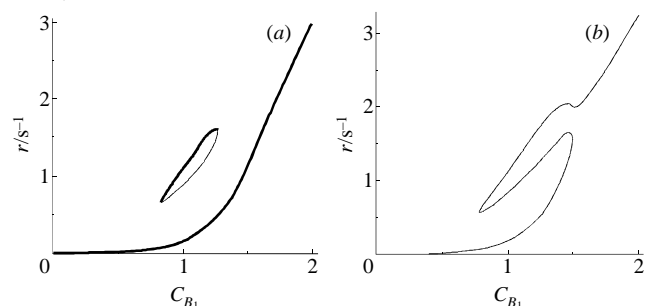


Figure 1 The isola (a) and S-form hysteresis (b) for scheme (6) at: (a) $k_{-1} = 0.510 \text{ s}^{-1}$; (b) $k_{-1} = 0.519 \text{ s}^{-1}$; (a) and (b) $k_1 = 4$, $k_2 = 77.5$, $k_{-2} = 54 \text{ s}^{-1}$.

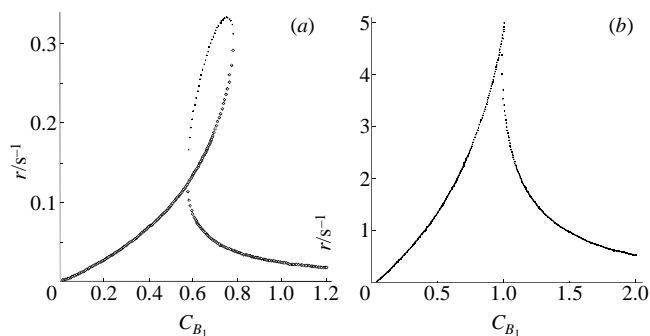


Figure 2 The self-crossing (a) and break (b) for scheme (8) at: (a) $k_1 = 2$, $k_2 = 2.344$, $k_{-1} = 0.143$, $k_{-2} = 0.175 \text{ s}^{-1}$; (b) $k_1 = 25$, $k_2 = 41.667$, $k_{-1} = 6.25$, $k_{-2} = 4.63 \text{ s}^{-1}$.

choose substance B_1 for the construction of the monoparametric rate (r) vs. concentration dependence. The scheme (1) satisfies the conservation law

$$F(r, C_{B_1}) = x_1 + x_2 - 1 = 0 \quad (2)$$

where $r_i - r_{-i} = d_i r$, $r_{\pm i} = k_{\pm i} \prod C_{B_i}^{b_{\pm i}} \prod x_j^{a_{\pm ij}}$, $k_{\pm i}$ are stage rate constants, and C_{B_i} and x_j , respectively, are the concentrations of B_i and X_j .

The singular point for reactions of type (1) exists under the following conditions:

$$F'_r = F'_{rC_{B_1}} = 0 \quad (3)$$

The conditions under which self-crossing and isola occur may therefore be written as

$$(F''_{rC_{B_1}})^2 - F''_{rr} F''_{C_{B_1}C_{B_1}} > 0 \quad (4)$$

$$(F''_{rC_{B_1}})^2 - F''_{rr} F''_{C_{B_1}C_{B_1}} < 0 \quad (5)$$

One of the schemes satisfying the conditions (2), (3) and (5) is

$$\begin{aligned} 2B_1 + X_1 &= X_2 + 3B_1 \\ B_1 + 3X_1 + X_2 &= 4X_1 + B_2 \end{aligned} \quad (6)$$

The isolated kinetic dependence for this scheme is illustrated in Figure 1(a). On this and subsequent figures, an $r (\text{s}^{-1})$ vs. C_{B_1} (c. u.) dependence is performed. When the kinetic parameters change, approaching and merging of the isola and the lower monotonous branch take place, and the S-form kinetic dependence arises [Figure 1(b)].

We have shown that self-crossing arises at equal reaction rates in two different stationary states. In two-stage reactions (1), the conditions of such self-crossing is

$$a_{11}a_{22} > a_{12}a_{21} \quad (7)$$

Inequality (7) can be satisfied by the following scheme:

$$\begin{aligned} B_1 + X_1 + X_2 &= 2X_1 \\ X_1 + 2X_2 &= 3X_2 + B_2 \end{aligned} \quad (8)$$

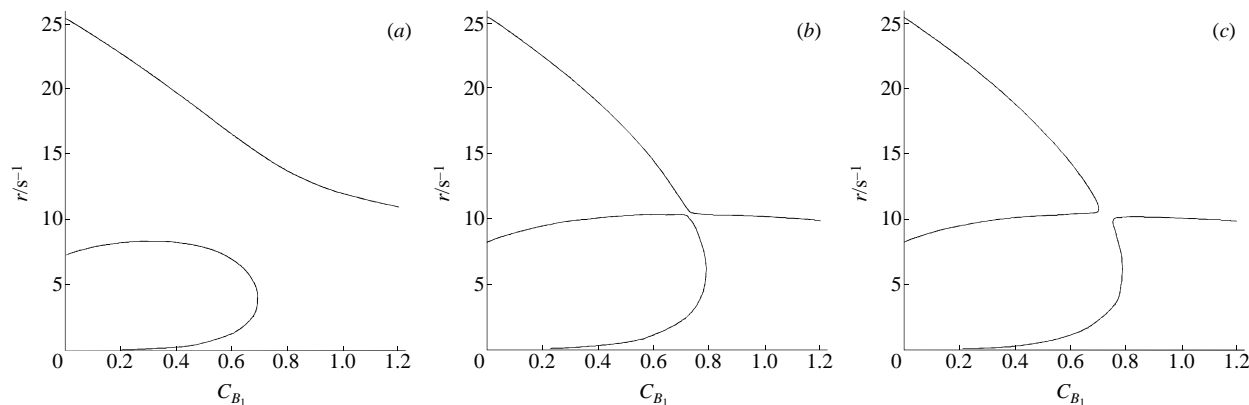


Figure 3 The isola (a), self-crossing (b) and mushroom (c) for scheme (9) at: (a) $k_1 = 48 \text{ s}^{-1}$; (b) $k_1 = 50.3 \text{ s}^{-1}$; (c) $k_1 = 50.33 \text{ s}^{-1}$; (a)–(c) $k_{-1} = 12$, $k_2 = 180$, $k_{-2} = 144$, $k_3 = 405$, $k_{-3} = 81 \text{ s}^{-1}$.

For this scheme, Figure 2(a) illustrates self-crossing. As the reaction conditions change, self-crossing will become a fracture ('break-line') [Figure 2(b)].

Similar results were obtained for three-stage reactions. In particular, the reaction $B_2 = 2B_1$ that proceeds via the scheme



satisfies the conditions of the isola (3), (5) formation from the singular point at certain values of rate constants of stages. Figure 3(a) illustrates the isola in this reaction. As the conditions change, approaching and merging of the isola and a monotonous branch takes place, and self-crossing arises [Figure 3(b)] with conversion into a mushroom [Figure 3(c)].

Plotting and calculation of the curves presented in Figures 1–3 were performed with the Maple V mathematical package as follows. Based on the system of stationary equations following from the reaction mechanism, we developed a polynomial depending on the reaction rate (r) by the intermediate concentration exclusion method. The coefficients of the polynomial are combinations of the stage rate constants ($k_{\pm i}$) and the basic substance concentrations (C_{B_i}). Substituting the numerical values of $k_{\pm i}$ and tabulated values of C_{B_1} we numerically solved the kinetic equation obtained with respect to r . The real and positive values of the reaction rate were plotted on a $r \text{ (s}^{-1}\text{) vs. } C_{B_1} \text{ (c. u.)}$.

Thus, the critical forms in the kinetics of catalytic reactions can be described simply enough with nonlinear two- and three-stage schemes. These forms change and pass from one to another as the reaction conditions change. The results obtained present new interrelations between the structure of the mechanisms and the particular course of the two- and three-stage reactions, characterized by different types of kinetic dependence.

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