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Quasi-Invariants of Chemical Reactions with Nonideal Kinetics

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Abstract—A method is developed to determine approximate dynamic kinetic invariants (quasi-invariants) of complex chemical reactions with nonideal general-form kinetic laws. The quasi-invariants are expressions relating nonequilibrium reactant concentrations and temperatures, measured in two or more experiments under different initial conditions (multiexperiments) that remain almost constant throughout the reaction. The number of quasi-invariants is determined by the number of independent reactants. The application of the method was illustrated by the example of a two-step reaction in an open system with the Marcelin–de Donder kinetics. The quasi-invariant curves obtained for this reaction were compared with the concentration curves for the entire reaction time. It was shown that the quasi-invariants vary over a narrower range than their corresponding concentrations and temperature in various temperatures; i.e., the quasi-invariants remain nearly constant over time. The method expands the range of tools for the solution of inverse problems of unsteady-state kinetics of chemical reactions in nonideal systems.

Keywords: nonideal chemical systems, Marcelin–de Donder kinetics, method of multiexperiments, quasi-invariants

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One of the main postulates of chemical kinetics is the kinetic law, which underlies the theoretical analysis of models of chemical reactions. The classical law of mass action is the simplest kinetic law; it expresses a power-law dependence of the rate of an elementary reaction on concentrations A_j of reactants: $r_j \sim A_j^{aij}$, where a_{ij} are stoichiometric coefficients. However, the law of mass action is closely followed only by ideal isothermal systems. A theory of more common kinetic laws was developed by Marcelin, de Donder, van Rysselberghe, Prigogine, Feinberg, and others (see, e.g., [1–5]). In their works, the rate of an elementary reaction was defined in terms of a new thermodynamic state function, affinity. The development of the theory of general kinetic laws was continued by Yablonskii, Gorban', Bykov, et al. [6–11], who systematized kinetic and thermodynamic aspects of applying nonideal kinetics to studying chemical reactions. Nonideal general-form kinetic laws were also used in the investigation of catalytic reactions on heterogeneous surfaces [12–15]. Affinity is used in a more complex hypothesis for the rate of an elementary reaction; it can be represented as $r_i \sim A_j^{aij}[1 + f_j(A_j)]$, where f_j is the degree of (kinetic) nonideality. This dependence is valid for a wide range of nonideal systems, and at $f_j = 0$, coincides with the ideal law of mass action. If one relates affinity to the chemical potentials of reactants, $m_j = g_j(A_j)$, then the reaction rate function for nonideal systems can be written as a general-form kinetic law: $r_j \sim A_j^{aij}[1 + F_j(m_j(A_j))]$, where F_j is the degree of (thermodynamic) nonideality. Note that, the thermodynamic approach to defining a general-form kinetic law imposes significant constraints on the form of potential functions, which should be taken into account in modeling nonideal systems (see, e.g., [10, 11, 16–18]). For example, it has been shown [16–18] that thermodynamically unconstrained chemical nonideality can lead to false critical phenomena (multiplicity of equilibria, self-oscillations) even in closed systems. At the same time, in open systems, chemical nonideality can cause critical effects even under thermodynamic constraints. New fields of nonequilibrium chemical kinetics are methods of dual experiments [19, 20] and multiexperiments [21]. By these methods, from the results of several nonequilibrium experiments performed under different initial conditions, one can determine exact thermodynamic time invariants of chemical reactions for systems having exact solutions [19, 20] or approximate kinetic invariants (quasi-invariants) for systems whose exact solutions are unknown [21]. Quasi-invariants are combinations of nonequilibrium concentrations of reactants that remain almost constant throughout a reaction. This property allows one to use them as an additional tool for solving inverse problems of nonstationary chemical kinetics. Let us generalize these results and find kinetic quasi-invariants of reactions occurring in nonideal systems with general-form kinetics.

Consider a multistep chemical reaction involving substances A_j:

$$\begin{aligned} &a_{i1}A_1 + a_{i2}A_2 + \ldots + a_{in}A_n \\ &= b_{i1}A_1 + b_{i2}A_2 + \ldots + b_{in}A_n, \end{aligned} \quad (1)$$

where $a_{ij} \geq 0$, $b_{ij} \geq 0$ are stoichiometric coefficients; $i = 1, \ldots, s$ is the number of a step; and $j = 1, \ldots, n$ is the number of a reactant. The dynamics of reaction (1) in a well-stirred nonisothermal reactor is described by a system of ordinary differential equations of order $(n + 1)$ [22]:

$$A_j' = \sum_i (b_{ij} - a_{ij})r_i + q_0A_{j0} - qA_j, \quad (2)$$

$$T' = \sum_i r_iQ_i + q_0T_0 - qT + \alpha(T_x - T), \quad (3)$$

where $r_i(k_{\pm i}, A_j, T)$ are the step rates determined by a certain nonideal kinetic law, 1/s; $k_{\pm i} = k_{\pm i0}\exp(-E_{\pm i}/RT)$ are step rate constants, 1/s; $k_{\pm i0}$ and $E_{\pm i}$ are the pre-exponential factors and activation energies of steps, respectively; A_j are the concentrations (mole fractions) of reactants; T is temperature, K; A_{j0} and T_0 are the initial conditions; q_0 and q are the initial and current flow rates, respectively, 1/s; T_x is the reactor wall temperature, K; α is the heat-transfer coefficient through the reactor wall, 1/s; and Q_i are the relative heats of steps, K.

Choose a nonideal kinetic law in the Marcelin–de Donder form [10–18]:

$$r_i(k_{\pm i}, A_j, T) = \varphi_i(A_j)\left(\exp\sum a_{ij}\mu_j - \exp\sum b_{ij}\mu_j\right), \quad (4)$$

where $\varphi_i > 0$ is the kinetic factors of steps, $\mu_j = \mu_{j0} + \ln A_{j0} + f_j(A_j) = m_j/RT$ are pseudochemical potentials (Feinberg's term [5]), the subscript 0 refers to ideal kinetics, the degree of nonideality is given by the linear function $f_j = \sum \alpha_j A_j$, α_j are real-valued parameters (nonideality vector), and R is the universal gas constant. For an ideal kinetics, from expression (4), the classical law of mass action follows: $r_i = k_i\prod A_j^{aij} - k_{-i}\prod A_j^{bij}$.

System (2)–(4) cannot be solved analytically; i.e., its exact variants are unknown and cannot be found. Let us find quasi-invariants. We expand the solutions of system (2)–(4) into a series and substitute the values of the derivatives into them:

$$A_j(t) \approx A_{j0} + \sum_i (b_{ij} - a_{ij})r_{i0}t + (q_0A_{j0} - qA_j)t, \quad (5)$$

$$T(t) \approx T_0 + \sum_i r_{i0}Q_it + (q_0T_0 + \alpha T_x)t - (q + \alpha)Tt, \quad (6)$$

where r_{i0} are the initial step rates. We calculate the values of expressions (5), (6) under two initial conditions, A_{j01}, T_{01} and A_{j02}, T_{02}, which differ from the equilibrium values. We obtain

$$\begin{aligned} A_{j1} - A_{j01} &\approx \Delta qA_{j01}t + \sum_i (b_{ij} - a_{ij})r_{i01}t, \\ A_{j2} - A_{j02} &\approx \Delta qA_{j02}t + \sum_i (b_{ij} - a_{ij})r_{i02}t, \end{aligned} \quad (7)$$

$$\begin{aligned} T_1 - T_{01} &\approx \Delta T_{01}t + \sum_i Q_ir_{i01}t, \\ T_2 - T_{02} &\approx \Delta T_{02}t + \sum_i Q_ir_{i02}t, \end{aligned} \quad (8)$$

where

$$\begin{aligned} r_{i01} &= k_i\prod A_{j1}^{aij}\exp\sum a_{ij}\mu_{j1} \\ &- k_{-i}\prod A_{j1}^{bij}\exp\sum b_{ij}\mu_{j1}, \\ \mu_{j1} &= \mu_{j01} + \ln A_{j01} + \sum \alpha_jA_{j1}, \\ r_{i02} &= k_i\prod A_{j2}^{aij}\exp\sum a_{ij}\mu_{j2} \\ &- k_{-i}\prod A_{j2}^{bij}\exp\sum b_{ij}\mu_{j2}, \\ \mu_{j2} &= \mu_{j02} + \ln A_{j02} + \sum \alpha_jA_{j2}, \end{aligned}$$

$$\Delta q \equiv q_0 - q, \quad \Delta T_{01} \equiv (q_0 - q - \alpha)T_{01} + \alpha T_x,$$
$$\Delta T_{02} \equiv (q_0 - q - \alpha)T_{02} + \alpha T_x.$$

Eliminate time from each of pairs (7), (8) and obtain $n + 1$ main potential quasi-invariants:

$$I_j \equiv A_{j1} - A_{j2}R_{j0} \approx A_{j01} - A_{j02}R_{j0} \equiv K_{j0}, \quad (9)$$

$$T \equiv T_1 - T_2R_{T0} \approx T_{01} - T_{02}R_{T0} \equiv K_{T0}, \quad (10)$$

where

$$R_{j0} \equiv \left[\sum_i (b_{ij} - a_{ij})r_{i01} + \Delta qA_{j01}\right] \Big/ \left[\sum_i (b_{ij} - a_{ij})r_{i02} + \Delta qA_{j02}\right],$$
$$R_{T0} \equiv \left(\sum_i Q_ir_{i01} + \Delta T_{01}\right) \Big/ \left(\sum_i Q_ir_{i02} + \Delta T_{02}\right).$$

Obviously, any linear combinations of these expressions are also quasi-invariants. Quasi-invariants (9) and (10) can be improved using the snail criterion [21], which takes the following form:

$$K_{j\infty} \equiv A_{j\infty}(1 - R_{j0}) \approx K_{j0}, \quad (11)$$

$$K_{T\infty} \equiv T_\infty(1 - R_{T0}) \approx K_{T0}, \quad (12)$$

where $A_{j\infty} = A_{j1\infty} = A_{j2\infty}$ and $T_\infty = T_{1\infty} = T_{2\infty}$ are the equilibrium concentrations and temperature, respectively. which are found by solving the system of equations $A_j' = T' = 0$. Relations (11) and (12) determine the best conditions for performing pairs of experiments and observing quasi-invariants. For ideal systems, from expressions (9)–(12), the results of our previous work [21] follow.

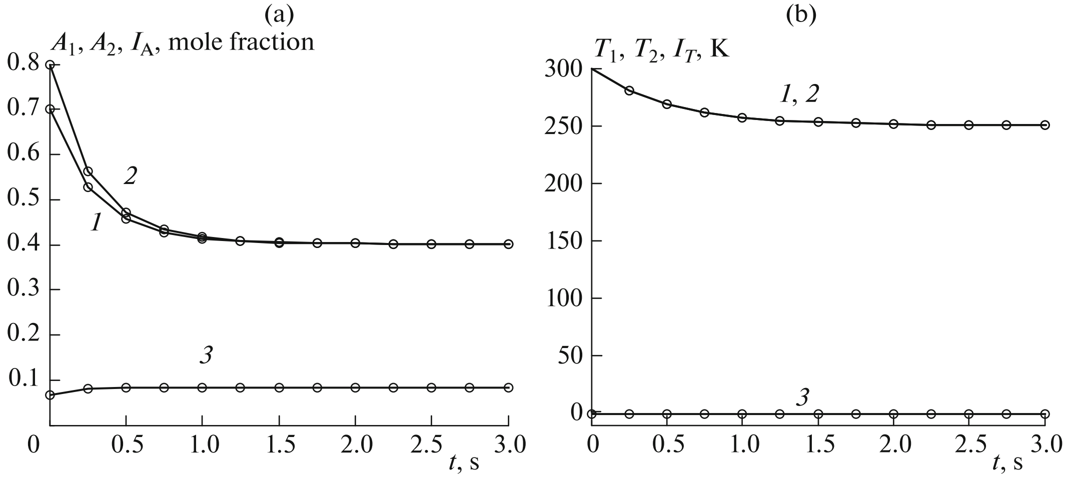

Fig. 1. Kinetic curves: (a) (*1*) $A_1(t)$, (*2*) $A_2(t)$, and (*3*) $I_A(t)$ and (b) (*1*) $T_1(t)$, (*2*) $T_2(t)$, and (*3*) $I_T(t)$ for the nonideality vector $a = b = c = 1$ under the initial conditions $A_{01} = 0.7$, $B_{01} = 0.2$, $C_{01} = 0.1$, $A_{02} = 0.8$, $B_{02} = 0.1$, $C_{02} = 0.1$, $T_{01} = 300.4$, and $T_{02} = 300.3$.

Let us apply the obtained relations to two-step reaction

$$\mathrm{A = B,\ \ B = C.} \tag{1.1}$$

For this reaction, system (2)–(4) takes the form

$$\begin{gathered} A' = -r_1 + q_0A_0 - qA, \quad B' = r_1 - r_2 + q_0B_0 - qB, \\ C' = r_2 + q_0C_0 - qC, \end{gathered} \tag{1.2}$$

$$T' = r_1Q_1 + r_2Q_2 + q_0T_0 - qT + a\left(T_x - T\right), \tag{1.3}$$

$$r_1 = k_1Ae^{aA} - k_{-1}Be^{bB}, \quad r_2 = k_2Be^{bB} - k_{-2}Ce^{cC}, \tag{1.4}$$

where $k_{\pm1} = k_{\pm10}\exp(-E_{\pm1}/RT)$, $k_{\pm2} = k_{\pm20}\exp(-E_{\pm2}/RT)$; $a = \alpha_1$, $b = \alpha_2$, $c = \alpha_3$ are the nonideality vector. For system (1.2)–(1.4), relations (9)–(12) give $n + 1 = 4$ main quasi-invariants:

$$I_\mathrm{A} \equiv A_1 - A_2R_\mathrm{A0} \approx A_{01} - A_{02}R_\mathrm{A0} \equiv K_\mathrm{A0}, \tag{1.5}$$

$$I_\mathrm{B} \equiv B_1 - B_2R_\mathrm{B0} \approx B_{01} - B_{02}R_\mathrm{B0} \equiv K_\mathrm{B0}, \tag{1.6}$$

$$I_\mathrm{C} \equiv C_1 - C_2R_\mathrm{C0} \approx C_{01} - C_{02}R_\mathrm{C0} \equiv K_\mathrm{C0}, \tag{1.7}$$

$$I_T \equiv T_1 - T_2R_\mathrm{T0} \approx T_{01} - T_{02}R_\mathrm{T0} \equiv K_\mathrm{T0}, \tag{1.8}$$

where

$$\begin{gathered} R_\mathrm{A0} = (-r_{101} + \Delta qA_{01})/(-r_{102} + \Delta qA_{02}), \\ R_\mathrm{B0} = (r_{101} - r_{201} + \Delta qB_{01})/(r_{102} - r_{202} + \Delta qB_{02}), \end{gathered}$$

$$\begin{gathered} R_\mathrm{C0} = (r_{201} + \Delta qC_{01})/(r_{202} + \Delta qC_{02}), \\ R_\mathrm{T0} = (Q_1r_{101} + Q_2r_{201} + \Delta T_{01})/(Q_1r_{102} + Q_2r_{202} + \Delta T_{02}), \end{gathered}$$

$$\begin{gathered} r_{101} = k_{101}A_{01}\exp(aA_{01}) - k_{-101}B_{01}\exp(bB_{01}), \\ r_{102} = k_{101}A_{02}\exp(aA_{02}) - k_{-101}B_{02}\exp(bB_{02}), \end{gathered}$$

$$\begin{gathered} r_{201} = k_{201}B_{01}\exp(bB_{01}) - k_{-201}C_{01}\exp(cC_{01}), \\ r_{202} = k_{202}B_{02}\exp(bB_{02}) - k_{-202}C_{02}\exp(cC_{02}), \end{gathered}$$

$$\begin{gathered} k_{\pm101} = k_{\pm10}\exp(-E_1/RT_{01}), \\ k_{\pm102} = k_{\pm10}\exp(-E_1/RT_{02}), \\ k_{\pm201} = k_{\pm20}\exp(-E_2/RT_{01}), \\ k_{\pm202} = k_{\pm202}\exp(-E_2/RT_{02}). \end{gathered}$$

Conditions (11) and (12) are rewritten as follows:

$$K_{\mathrm{A}\infty} \equiv A_\infty(1 - R_\mathrm{A0}) \approx A_{01} - A_{02}R_\mathrm{A0}, \tag{1.9}$$

$$K_{\mathrm{B}\infty} \equiv B_{j\infty}(1 - R_\mathrm{B0}) \approx B_{01} - B_{02}R_\mathrm{B0}, \tag{1.10}$$

$$K_{\mathrm{C}\infty} \equiv C_{j\infty}(1 - R_\mathrm{C0}) \approx C_{01} - C_{02}R_\mathrm{C0}, \tag{1.11}$$

$$K_{T\infty} \equiv T_\infty(1 - R_{T0}) \approx T_{01} - T_{02}R_{T0}. \tag{1.12}$$

We calculate experimental conditions, taking into account that, from expressions (1.2)–(1.4), two equilibrium conservation laws follow: $q(A_\infty + B_\infty + C_\infty)/q_0 = A_0 + B_0 + C_0 = \mathrm{const}_1$ and $qQ_1A_\infty - qQ_2C_\infty + (q + \alpha)T_\infty = q_0Q_1A_0 - q_0Q_2C_0 + q_0T_0 + \alpha T_x = \mathrm{const}_2$. Let the parameters take the following values: nonlinearity vector, $a = b = c = 1$; rate constants and activation energies of steps, $k_{10} = 1$, $k_{-10} = 0$, $k_{20} = 1$, and $k_{-20} = 0$ and $E_1 = E_2 = 2$; flow rates, $q_0 = 1$ and $q = 1$; temperatures, $T_0 = 300$ and $T_x = 200$; and other parameters, $R = 2$, $\alpha = 1$, $Q_1 = 1$, $Q_2 = 1$, $A_0 = 1$, $B_0 = 0$, and $C_0 = 0$. Then, $\mathrm{const}_1 = 1$ and $\mathrm{const}_2 = 501$, $A_\infty \approx 0.40$, $B_\infty \approx 0.26$, $C_\infty \approx 0.34$, and $T_\infty \approx 250.5$. We choose the initial conditions for a pair of experiments, e.g., $A_{01} = 0.7$, $B_{01} = 0.2$, then $C_{01} = \mathrm{const}_1 - A_{01} - B_{01} = 0.1$, $T_{01} = (\mathrm{const}_2 - q_0Q_1A_{01} + q_0Q_2C_{01} - \alpha T_x)/q_0 \approx 300.4$; and $A_{02} = 0.8$, $B_{02} = 0.1$, then $C_{02} = 0.1$, $T_{02} \approx 300.3$ and $K_\mathrm{A0} = 0.07$, $K_{\mathrm{A}\infty} = 0.08$, $K_\mathrm{B0} = 0.13$, $K_{\mathrm{B}\infty} = 0.08$, $K_\mathrm{C0} = -0.12$, $K_{\mathrm{C}\infty} = -0.41$, $K_{T0} \approx -0.93$, and $K_{T\infty} \approx -0.86$. Figure 1 presents quasi-invariants (1.5) and (1.6) for the given

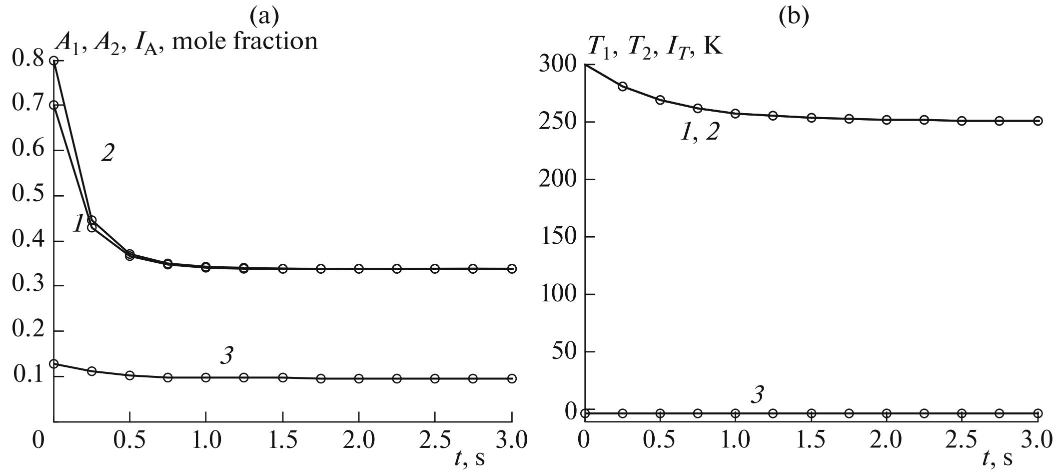

Fig. 2. Kinetic curves: (a) (*1*) $A_1(t)$, (*2*) $A_2(t)$, and (*3*) $I_A(t)$; and (b) (*1*) $T_1(t)$, (*2*) $T_2(t)$, (*3*) $I_T(t)$ for the nonideality vector $a = 2$, $b = 1$, $c = 0$, $A_{01} = 0.7$, $B_{01} = 0.2$, $C_{01} = 0.1$, $A_{02} = 0.8$, $B_{02} = 0.1$, $C_{02} = 0.1$, $T_{01} = 300.4$, and $T_{02} = 300.3$.

nonideality vector that were calculated for this pair of experiments.

Let us carry out a second pair of experiments for the case where the nonideality vector is, e.g., $a = 2$, $b = 1$, and $c = 0$. Then, under the same initial conditions, we obtain $A_\infty \approx 0.34$, $B_\infty \approx 0.28$, $C_\infty \approx 0.38$, $T_\infty \approx 250.5$, $K_{A0} = 0.13$, $K_{A\infty} = 0.1$, $K_{B0} = 0.13$, $K_{B\infty} = 0.09$, $K_{C0} = -0.12$, $K_{C\infty} = -0.46$, $K_{T0} \approx -3.29$, and $K_{T\infty} \approx -2.83$. Figure 2 shows quasi-invariants (1.5) and (1.6) for the new given nonideality vector that were calculated for the same pair of experiments. Figures 1 and 2 demonstrate that the curves $I_A(t)$ and $I_T(t)$ vary within narrower ranges than the respective nonequilibrium reactant concentrations $A_1(t)$, $A_2(t)$ and nonequilibrium temperatures $T_1(t)$, $T_2(t)$ in two experiments; i.e., the former curves are almost time-constant at various nonideality vectors. Note that curves *1* and *2* in Figs. 1b and 2b are virtually coincide because the initial temperatures T_{01} and T_{02} are almost equal.

Thus, we have developed a generalization of the method of multiexperiments for chemical reactions in nonideal systems, which is applicable to various kinetic laws (law of mass action, Marcelin–de Donder law, etc.) in a well-stirred reactor. The method allows one to determine approximate kinetic time invariants (quasi-invariants) of nonlinear multistep chemical reactions in open and closed, isothermal and nonisothermal systems with kinetics of quite a general form; i.e., the method remains valid for any type of nonideality. Such quasi-invariants are combinations of nonequilibrium reactant concentrations measured in two or more experiments that remain almost constant throughout the reaction. Quasi-invariants enable one to predict and study unknown kinetic regularities in reactions occurring under nonideal conditions according to general-form kinetic laws. The developed method expands the range of new tools for solving inverse problems of chemical kinetics and can be used to more adequately identify the mechanisms of chemical reactions and also to increase the efficiency of chemical reactors.

REFERENCES

1. R. Marcelin, Ann. Phys. (N.Y.) **3** (9), 120 (1915).
2. Th. de Donder and P. van Rysselberghe, *Thermodynamic Theory of Affinity: A Book of Principles* (Stanford Univ. Press, Stanford, CA, 1936).
3. P. van Rysselberghe, J. Chem. Phys. **29**, 640 (1958).
4. I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longmans Green, London, 1954).
5. M. Feinberg, Arch. Rat. Mesh. Anal. **46**, 1 (1972).
6. T. A. Akramov, V. I. Bykov, and G. S. Yablonskii, in *Mathematical Problems of the Chemistry* (Vychisl. Tsentr SO AN SSSR, Novosibirsk, 1975), Part 1, p. 206 [in Russian].
7. V. I. Bykov, A. N. Gorban, and V. I. Dimitrov, React. Kinet. Catal. Lett. **12**, 19 (1979).
8. V. I. Bykov, A. N. Gorban, and G. S. Yablonskii, React. Kinet. Catal. Lett. **20**, 261 (1982).
9. A. N. Gorban', V. I. Bykov, and G. S. Yablonskii, Kinet. Katal. **24**, 1239 (1983).
10. G. S. Yablonskii, V. I. Bykov, and A. N. Gorban', *Kinetic Models of Catalytic Reactions* (Nauka, Novosibirsk, 1983) [in Russian].
11. A. N. Gorban', *Bypassing Equilibrium* (Nauka, Novosibirsk, 1984) [in Russian].
12. Yu. S. Snagovskii, Kinet. Katal. **21**, 189 (1980).
13. A. G. Zyskin, Yu. S. Snagovskii, and M. G. Slin'ko, Kinet. Katal. **22**, 1031 (1981).
14. A. G. Zyskin, Yu. S. Snagovskii, and M. G. Slinko, React. Kinet. Catal. Lett. **17**, 257 (1981).
15. Yu. K. Tovbin and A. V. Cherkasov, Teor. Eksp. Khim. **20**, 507 (1984).

16. V. I. Bykov and A. N. Ivanova, Kinet. Katal. **27**, 73 (1986).
17. V. I. Bykov, *Modeling Critical Phenomena in Chemical Kinetics* (URSS, Moscow, 2006) [in Russian].
18. V. I. Bykov and S. B. Tsybenova, *Nonlinear Models of Chemical Kinetics* (URSS, Moscow, 2011) [in Russian].
19. G. S. Yablonsky, D. Constales, and G. B. Marin, Chem. Eng. Sci. **66**, 111 (2011).
20. D. Constales, G. S. Yablonsky, and G. B. Marin, Chem. Eng. Sci. **73**, 20 (2012).
21. V. Kh. Fedotov and N. I. Kol'tsov, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. **59** (5), 72 (2016).
22. B. V. Vol'ter and I. E. Sal'nikov, *Stability of Chemical Reactor Operating Modes* (Khimiya, Moscow, 1972) [in Russian].

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