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Unsteady-State Kinetic Models for Some Typical Catalytic Mechanisms

V. I. Bykov[a] **and E. A. Mamash**[b, *]
[a] *Mendeleev University of Chemical Technology of Russia, Moscow, 125047 Russia*
[b] *Tyva Institute for Exploration of Natural Resources, Siberian Branch,*
Russian Academy of Sciences, Kyzyl, 667007 Russia
**e-mail: m_elena@rambler.ru*

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Abstract—A method of formulating thermodynamically correct expressions for the rates of elementary reactions is suggested for the unimolecular and bimolecular Eley–Rideal mechanisms. This method is based on the lattice gas model and transfer matrix method and provides means to calculate thermodynamic functions containing microlevel parameters, specifically, the energies of the body interactions between particles on the surface of a catalyst. Unsteady-state kinetic models have been constructed for mechanisms of reactions conducted in isothermal perfect- and imperfect-mixing reactors. A qualitative and numerical analysis of these models has been carried out.

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The layer of adsorbate molecules and adsorbent atoms at the gas/solid interface is an open nonideal system exchanging matter and energy both with the gas phase and with the solid [1]. In such a system, there can be nonlinear phenomena, such as steady state multiplicity (SSM), self-oscillations, and spatiotemporal organization [2–7]. These phenomena are observed at all levels, from the nanometer level and on. The microscopic order determines the character of the nonlinear variation of the rates of elementary reactions and, accordingly, the rate of overall catalytic process at the mesoscopic level. The basic microlevel parameter is the energy of interaction between adsorbed particles. In turn, mesoscopic processes can exert an effect on the processes taking place at the micro and nano levels. The nonlinear variations of the reaction rate at the meso and macro levels (kinetic model) fully determine the conditions for stable, safe, and optimal operation of industrial reactors. Therefore, elucidating the correlation between the reaction rate at the micro and nano levels and the reaction rate at the meso and macro levels is very essential for heterogeneous catalysis. The processes occurring at the catalyst surface were demonstrated earlier to be describable using the transfer matrix method [2, 8].

The mathematical models considered here were constructed at the macro level using the lattice gas model nd the transfer matrix method [9–11]. The atomic structure of the surface and microlevel parameters (energies of lateral interparticle interactions on the catalyst surface) were taken into account in calculating of thermodynamic functions (chemical potentials). Since only the one-dimensional lattice gas model can be analytically described, the approach suggested here will be illustrated by the simplest example in which there is a single intermediate; that is, this approach will be applied to the unimolecular and bimolecular Eley–Rideal mechanisms.

Consider the following two simple catalytic mechanisms:

$$\begin{aligned} &A + Z \leftrightarrow AZ, \\ &B + AZ \to Z + AB \end{aligned} \tag{I}$$

and

$$\begin{aligned} &A_2 + 2Z \leftrightarrow 2AZ, \\ &B + AZ \to Z + AB, \end{aligned} \tag{II}$$

where A, B, A_2, and AB are compounds in the gas phase, Z is the catalyst, and AZ is the intermediate. In both mechanisms, the first reaction (adsorption) is reversible and the second reaction is irreversible. The set of reactions (I) corresponds to the unimolecular Eley–Rideal mechanism; the set of reactions (II), to the bimolecular one.

According to the law of surface mass action, the material balance equations in terms of surface coverages for mechanisms (I) and (II) will appear as

$$\frac{d\theta}{dt} = k_a P_A(1-\theta) - k_d\theta - k_R P_B\theta \tag{1}$$

and

$$\frac{d\theta}{dt} = 2k_a P_A(1-\theta)^2 - 2k_d\theta^2 - k_R P_B\theta, \tag{2}$$

where θ is the surface coverage for compound A; k_a, k_d, and k_R are the rate constants of adsorption, desorption, and reaction, respectively; P_A and P_B are the partial pressures of compounds A and B in the gas phase, which will be taken to be constant for the present. In the ideal adsorption layer approximation, the rate constants are independent of the surface coverage and Eqs. (1) and (2) can easily be analyzed. For nonideal systems, the adsorption layer will be considered in terms of the one-dimensional lattice gas model (LGM) and the interaction between particles located in nearest-neighbor lattice sites will be taken into account.

The following expressions for the rate constants of the elementary processes were obtained earlier within the framework of transition state theory and LGM, without taking into the lateral interactions [12]:

(1) monomolecular adsorption and desorption,

$$k_{\mathrm{a}} = k_{\mathrm{a},0}, \quad k_{\mathrm{d}} = k_{\mathrm{d},0}\, \exp(\mu/RT)(1-\theta)/\theta; \tag{3}$$

(2) dissociative adsorption and desorption,

$$\begin{gathered} k_{\mathrm{a}} = k_{\mathrm{a},0}\, P_{00}\big/(1-\theta)^2, \\ k_{\mathrm{d}} = k_{\mathrm{d},0} \exp(2\mu/RT)\, P_{00}\big/\theta^2; \end{gathered} \tag{4}$$

(3) bimolecular reaction of adsorbed species with species from the gas phase,

$$k_{\mathrm{R}} = k_{\mathrm{R},0}(\mu/RT)(1-\theta). \tag{5}$$

In Eqs. (3)–(5), $k_{\mathrm{a},0}$, $k_{\mathrm{d},0}$, and $k_{\mathrm{R},0}$ are the rate constants of adsorption, desorption, and reaction, respectively, at small coverages; $\mu(\theta)$ is the dimensionless chemical potential of the adsorbed molecules of the compound A; ε is the dimensionless energy of the lateral interactions between the nearest neighbors; R is the gas constant; T is absolute temperature; P_{00} is the probability that two nearest-neighbor sites are empty.

In view of Eqs. (3)–(5), Eqs. (1) and (2) will appear as

$$\begin{gathered} \frac{\mathrm{d}\theta}{\mathrm{d}t} = (1-\theta)[k_{\mathrm{a},0}P_{\mathrm{A}} - (k_{\mathrm{d},0}\theta + k_{\mathrm{R},0}P_{\mathrm{B}}) \\ \times \exp\big(\mu(\theta,\varepsilon)/RT\big)], \end{gathered} \tag{6}$$

$$\begin{gathered} \frac{\mathrm{d}\theta}{\mathrm{d}t} = 2P_{00}[k_{\mathrm{a},0}P_{\mathrm{A}} - k_{\mathrm{d},0} \exp\big(2\mu(\theta,\varepsilon)/RT\big)] \\ - k_{\mathrm{R},0}P_{\mathrm{B}} \exp\big(\mu(\theta,\varepsilon)/RT\big)(1-\theta). \end{gathered} \tag{7}$$

Their general form is

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = f\big(\theta, \mu(\theta)\big). \tag{8}$$

In order to solve these equations, it is necessary to determine the chemical potential as a function of surface coverage, i.e., $\mu(\theta)$.

The inverse of the sought relationship— $\mu(\theta)$ isotherm—can be found using the transfer matrix (TM) method [9–11]. This method proved very efficient for a wide variety of models and is the best complement to the rapidly developing statistical (Monte Carlo) modeling of lattice systems [13–15].

We will briefly describe this method as applied to the simplest uniform LGM on a linear chain in which all particles are identical and only the nearest neighbors interact with one another. The thermodynamic Hamiltonian for this system can be written as follows [9]:

$$\beta H_{\mathrm{eff}} = \varepsilon\sum_{i=1}^{N} n_1 n_{i+1} - \mu\sum_{i=1}^{N} n_i. \tag{9}$$

Here, N is the number of sites in the chain; n_i is the occupancy of the ith site, which is 1 if the site is occupied and 0 is the site is empty; $\beta = 1/RT$. The following cyclic boundary conditions are introduced here: $n_{N+1} = n_1$.

By definition, the grand statistical sum for the model can be written as

$$\Xi_N = \sum_{\{n_i\}} \exp\left[-\varepsilon\sum_{i=1}^{N} n_i n_j + \mu\sum_{i=1}^{N} n_i\right]. \tag{10}$$

Here, summation is performed over all possible sets of occupancies. It can readily be seen that the exponential in Eq. (10) is representable as the product of multipliers each depending only on the occupancies of a pair of nearest-neighbor sites:

$$\Xi_N = \sum_{\{n_1\}} \prod_{i=1}^{i=N} T(n_i n_{i+1}), \tag{11}$$

where

$$T(n_i n_{i+1}) = \exp\left[-\varepsilon n_i n_{i+1} + \frac{\mu}{2}(n_i + n_{i+1})\right]. \tag{12}$$

The multiplier $T(n_i n_{i+1})$, considered as a function of the occupancies of nearest-neighbor sites, can take four values.

Let us write these values as a 2 × 2 matrix:

$$\mathbf{T} = \begin{Vmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{Vmatrix} = \begin{Vmatrix} 1 & \exp(\mu/2) \\ \exp(\mu/2) & \exp(-\varepsilon+\mu) \end{Vmatrix}. \tag{13}$$

Here, the first row corresponds to $n_i = 0$; the second row, to $n_i = 1$. Likewise, the first column corresponds to $n_{i+1} = 0$; the second column, to $n_{i+1} = 1$. The matrix **T** is called the transfer matrix.

Since this transfer matrix is symmetrical, it can be diagonalized by homothetic transformation, and, in the $N \to \infty$ limit, the expression for the grand statistical sum for one lattice site will become

$$\begin{aligned} \Xi &= \lim_{N\to\infty} (\Xi_N)^{1/N} = \lim_{N\to\infty} \left(\lambda_1^N + \lambda_2^N\right)^{1/N} \\ &= \lambda_1 \lim_{N\to\infty} \left(1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N\right)^{1/N} = \lambda_1, \end{aligned} \tag{14}$$

where λ_1 and λ_2 are the eigenvalues of the transfer matrix **T**.

Formula (14) provides the basis for use of the transfer matrix method. Proceeding from general relationships of statistical mechanics, we can write an expression for the dimensionless thermodynamic potential per lattice site,

$$\Omega = -\ln\lambda_1 \tag{15}$$

and a thermodynamic relationship for the lattice coverage [16, 17],

$$\theta = -\left(\frac{\partial\Omega}{\partial\mu}\right)_T. \tag{16}$$

Applying formula (16) to the simplest one-dimensional LGM considered, in which all particles are identical and only the nearest neighbors interact, we obtain the isotherm equation for the system (Fig. 1):

$$\theta(\mu) = \frac{1}{2} + \frac{1}{2}\frac{\sinh(\tilde{\mu})}{S}, \tag{17}$$

where $\tilde{\mu} = \frac{\mu - \varepsilon}{2}$, $S = \sqrt{\sinh(\tilde{\mu}) + \exp(\varepsilon)}$, and sinh is hyperbolic sine.

This relationship makes it possible to pass from Eq. (8) to the equation

$$\frac{d\mu}{dt} = g(\mu, \theta(\mu)), \tag{18}$$

that is, after an expression for $\frac{d\theta}{d\mu}$ is derived from Eq. (17), Eqs. (6) and (7) can be rewritten as

$$\frac{d\mu}{dt} = \frac{2S^2[S - \sinh(\tilde{\mu})]}{\sinh(\tilde{\mu})\exp(\varepsilon)} \times \left(k_{a,0}P_A - (k_{d,0} + k_{R,0}P_B)\exp(\mu/RT)\right), \tag{19}$$

$$\frac{d\mu}{dt} = \frac{4S^3}{\cosh(\tilde{\mu})\exp(\varepsilon)} \times \{2P_{00}(\mu/RT)[k_{a,0}P_A - k_{d,0}\exp(2\mu/RT)] - k_{R,0}P_B\exp(\mu/RT)(1-\theta)\}, \tag{20}$$

where cosh is hyperbolic cosine.

In the one-dimensional case considered, the dependence of P_{00} on μ can be analytically expressed using the TM method and the following familiar relationship of statistical mechanics [16, 17]:

$$P_{11} = \frac{\partial\Omega}{\partial\varepsilon}, \tag{21}$$

where P_{11} is the probability that two nearest-neighbor sites of the chain are occupied by adsorbed molecules of the compound A.

With the self-consistency condition

$$P_{10} = P_{01}, \tag{22}$$

where P_{10}, P_{01} is the probability that one of the two nearest-neighbor sites of the chain is empty and the second one is occupied, we obtain, from [12], the following constraints for the probabilities P_{00}, P_{01}, and P_{11}:

$$\begin{aligned} P_{10} + P_{11} &= \theta, \\ P_{00} + 2P_{01} + P_{11} &= 1. \end{aligned} \tag{23}$$

Hence, taking into account Eq. (21) and using the TM method, we obtain

$$P_{00} = 1 - 2\theta + \frac{\partial\Omega}{\partial\varepsilon} = \frac{S - \sinh(\tilde{\mu})}{2e^{\tilde{\mu}}(\cosh(\tilde{\mu}) + S)S}. \tag{24}$$

By solving Eqs. (19) and (20), it is possible to plot the functions θ = θ(*t*) (Fig. 2a) and μ = μ(*t*) (Fig. 2b).

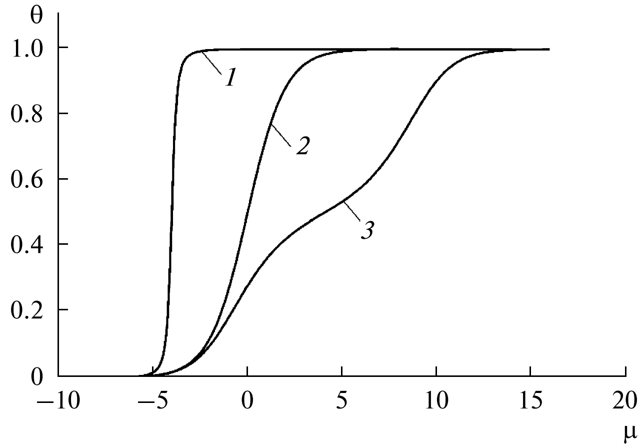

Fig. 1. Surface coverage θ as a function of the chemical potential μ at ε = (*1*) –4, (*2*) 0, and (*3*) 4.

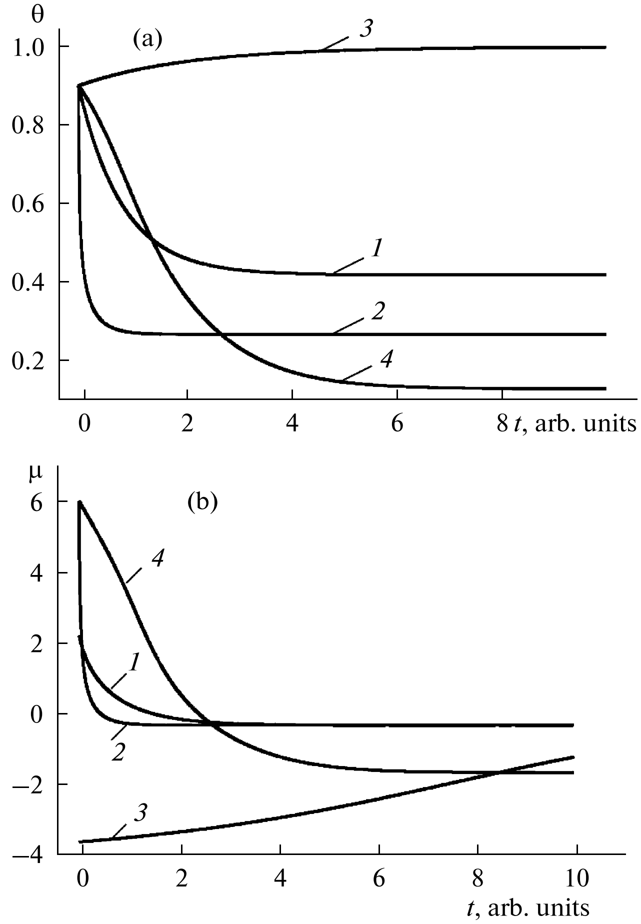

Fig. 2. (a) Surface coverage θ and (b) chemical potential μ as a function of time *t* for Eq. (19) at $k_{a,0} = 0.5$ and $k_{d,0} + k_{R,0} = 0.7$: (*1*) *RT* = 1, ε = 0; (*2*) *RT* = 1, ε = 2; (*3*) *RT* = 1, ε = –5; (*4*) *RT* = 5, ε = 2.

In these equations, we have only microlevel characteristics, such as chemical potential and the energy of lateral interparticle interaction. Of particular interest are dynamic equations for θ that would interrelate microscopic and macroscopic parameters. To set up these equations, we will solve Eq. (17) for chemical potential:

$$\mu := \begin{cases} \varepsilon + \ln\left(1 + 2\theta^* - 2\sqrt{\theta^*(1+\theta^*)}\right), & \theta < 0.5, \\ \varepsilon + \ln\left(1 + 2\theta^* + 2\sqrt{\theta^*(1+\theta^*)}\right), & \theta \ge 0.5, \end{cases} \quad (25)$$

where $\theta^* = \frac{(\theta - 0.5)^2 \exp(\varepsilon)}{\theta - \theta^2}$. Therefore, Eqs. (6) and (7) can be solved without differentiating μ with respect to t.

Now we will analyze Eqs. (6) and (7) at some limiting values of ε.

(1) At $\varepsilon = 0$, there are no lateral interactions between the nearest neighbors and the Langmuir isotherm can be obtained from Eq. (17) or expression (25). Under the assumption that $RT = 1$, Eqs. (6) and (7) will appear as Eqs. (1) and (2), which describe an ideal adsorption layer. The kinetic models constructed for the ideal adsorption layer model using the law of surface mass action have been studied (see, e.g., [7]).

(2) At $\varepsilon \to -\infty$, which means infinitely strong interparticle attraction $\mu \to -\infty$ and we arrive at equations describing monomolecular and dissociative adsorption [12].

(3) At $\varepsilon \to +\infty$ (infinitely strong interparticle repulsion, which is equivalent to the forbiddenness of the nearest neighborhood), $\mu \to +\infty$ if $\theta \ge 0.5$ and $\mu \to \ln\frac{\theta - \theta^2}{(1 - 2\theta)^2}$ if $\theta < 0.5$.

By directly using the TM method, we obtain the following expression for the isotherm:

$$\theta = \frac{1}{2}\frac{\sqrt{1 + 4\exp(\mu)} - 1}{\sqrt{1 + 4\exp(\mu)}}. \quad (26)$$

It is clear from this expression that the limiting coverage is 0.5. As would be expected, if μ is expressed in terms of θ, we will obtain

$$\mu = \ln\frac{\theta - \theta^2}{(1 - 2\theta)^2}, \quad \theta < 0.5. \quad (27)$$

As applied to mechanisms (I) and (II), the equations for surface coverages (Eqs. (6) and (7)) will take the following form:

$$\frac{d\theta}{dt} = (1 - \theta)\left[k_{a,0}P_A - (k_{d,0} + k_{R,0}P_B)\right]\tilde{\theta}, \quad (28)$$

$$\frac{d\theta}{dt} = 2P_{00}\left[k_{a,0}P_A - k_{d,0}\tilde{\theta}^2\right] - k_{R,0}P_B\tilde{\theta}(1 - \theta), \quad (29)$$

where $\tilde{\theta} = \left[\frac{\theta(1 - \theta)}{(1 - 2\theta)^2}\right]^{1/RT}$.

Let us analyze models (6) and (7), which equivalent to (19) and (20), to see whether they allow critical phenomena. Equating the right-hand side of Eq. (6) to zero, we obtain the equality

$$\exp(\mu/RT) = \frac{k_{a,0}P_A}{k_{d,0} + k_{R,0}P_A}. \quad (30)$$

The right-hand side of Eq. (30) is always positive; therefore, there is always only one steady state in this case. A qualitative analysis of the bimolecular Eley–Rideal mechanism, which is described by Eq. (7) or (23), yields more interesting results. The stationarity equation for model (7) is

$$\theta = 1 - \frac{2P_{00}\left[k_{a,0}P_A - k_{d,0}\exp(2\mu/RT)\right]}{k_{R,0}\exp(\mu/RT)} \quad (31)$$

and it does not indicate unambiguously that there is only one steady state. Introducing the generalized parameters

$$A = \frac{k_{a,0}P_A}{k_{R,0}P_B}, \quad B = \frac{k_{d,0}}{k_{R,0}P_B}, \quad (32)$$

we can derive, from equality (31), the following equations for the multiplicity curve of model (7):

$$\begin{cases} B = \dfrac{RT\theta' + \theta - 1}{4\exp(\mu/RT)} + \dfrac{(1 - \theta)P'_{00}}{4\exp(\mu/RT)P_{00}^2} \\ A = B\exp(2\mu/RT) + \dfrac{\exp(\mu/RT)(1 - \theta)}{2P_{00}}. \end{cases} \quad (33)$$

Since the derivative P'_{00} is negative, it follows from the first equation of system (33) that a necessary condition for the existence of multiple steady states in model (7) is that the following inequality is satisfied in some range of μ values:

$$RT\theta' + \theta > 1. \quad (34)$$

Let us see whether this inequality is satisfiable for particular isotherms. If isotherm (17) is realized, then, for a positive ε value, because of the repulsion between the nearest neighbors, the central part of the isotherm is gently sloping and inequality (34) is not satisfies at any μ. The case of $\varepsilon = 0$ corresponds to an ideal adsorption layer, and isotherm (17) becomes the Langmuir isotherm and does not satisfy condition (34) at any μ, again indicating the absence of critical phenomena.

The negative values of ε correspond to matter condensation, and the shape of the isotherm in this case is determined by the attraction between the nearest neighbors. As a consequence, inequality (34) is satisfied in some interval (Fig. 3). However, a numerical experiment carried our for a set of negative ε values (–4, –5, –6, –8) did not reveal steady state multiplicity in the one-dimensional LGM.

Now we will consider an LGM on a square lattice and will take into account the interaction both between the nearest neighbors (ε_1) and between next-to-nearest neighbors (ε_2). In the case of repulsion between the former and attraction between the latter, it is possible to select model parameters such that, in the region where condition (34) is satisfied, the multiplicity curve (33) will come to the positive half-plane and Eq. (7) will describe multiple steady states. For example, at $\varepsilon_1 = 2$ and $\varepsilon_2 = -2$, the isotherm for the two-dimensional LGM intersects curve (31) at three points representing three steady states (Fig. 4). This fact, as well as the existence of a plateau in the central

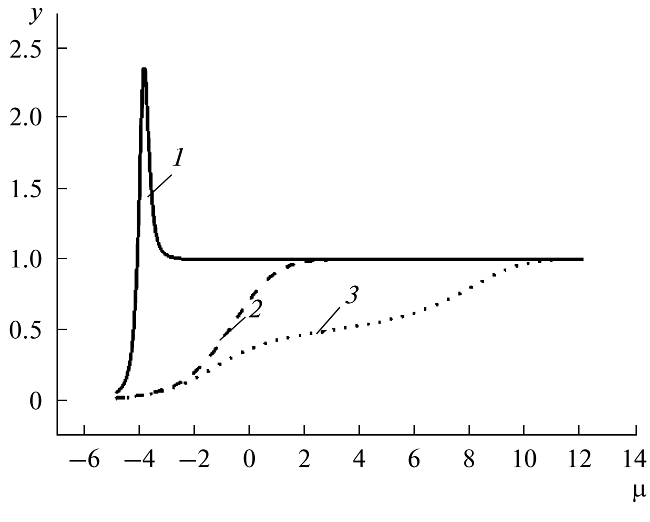

Fig. 3. Plot of $y = RT\theta'(\mu) + \theta(\mu)$ at $RT = 1$ and ε = (*1*) −4, (*2*) 0, and (*3*) 4.

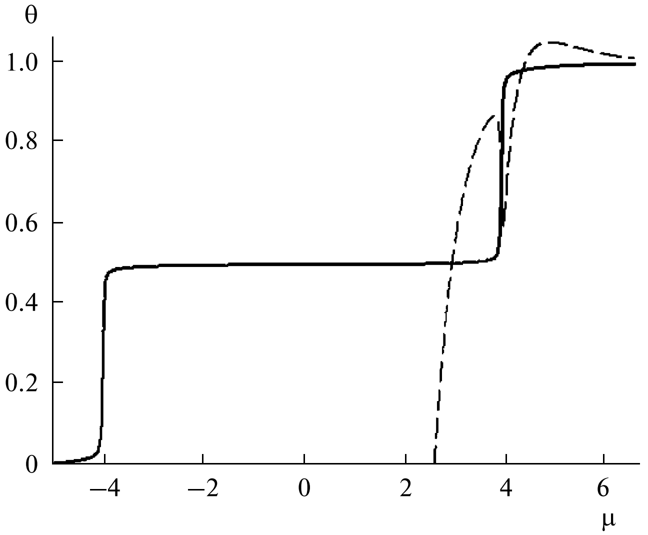

Fig. 4. Isotherm in the two-dimensional LGM at $\varepsilon_1 = 2$ and $\varepsilon_2 = -1$ (solid line) and relationship (31) (dashed line).

part of the isotherm, correlates with the phase diagram of the system, specifically, the appearance of an ordered C(2 × 2) phase, or a "chessboard."

The significance of taking into account the microlevel parameters increases with an increasing complexity of the system. We also studied nonideal models of mechanisms (I) and (II) in an isothermal perfect-mixing reactor, where these models with expressions (3)–(5) and (17) taken into account are described, respectively, by the following systems of ordinary differential equations:

$$\begin{gathered}\frac{\mathrm{d}\mu}{\mathrm{d}t} = \frac{2S^2[S - \sinh(\tilde{\mu})]}{\cosh(\tilde{\mu})\exp(\varepsilon)} \\ \times\left[k_{\mathrm{a},0}P_{\mathrm{A}} - (k_{\mathrm{d},0} + k_{\mathrm{R},0}P_{\mathrm{B}})\exp(\mu/RT)\right], \\ \frac{\mathrm{d}P_{\mathrm{A}}}{\mathrm{d}t} = \frac{P_{\mathrm{A},0} - P_{\mathrm{A}}}{\tau_{\mathrm{R,A}}} \\ + P^*\left[k_{\mathrm{d},0}\exp(\mu/RT) - k_{\mathrm{a},0}P_{\mathrm{A}}\right](1-\theta), \\ \frac{\mathrm{d}P_{\mathrm{B}}}{\mathrm{d}t} = \frac{P_{\mathrm{B},0} - P_{\mathrm{B}}}{\tau_{\mathrm{R,B}}} - P^*P_{\mathrm{B}}k_{\mathrm{R},0}\exp(\mu/RT)(1-\theta),\end{gathered} \tag{35}$$

$$\begin{gathered}\frac{\mathrm{d}\mu}{\mathrm{d}t} = \frac{4S^3}{\sinh(\tilde{\mu})\exp(\varepsilon)}\left\{2P_{00}\left[k_{\mathrm{a},0}P_{\mathrm{A}} - k_{\mathrm{d},0}\exp(2\mu/RT)\right]\right. \\ \left. - k_{\mathrm{R},0}P_{\mathrm{B}}\exp(\mu/RT)(1-\theta)\right\}, \\ \frac{\mathrm{d}P_{\mathrm{A}_2}}{\mathrm{d}t} = \frac{P_{\mathrm{A}_2,0} - P_{\mathrm{A}_2}}{\tau_{\mathrm{R,A}}} \\ + P_{00}P^*\left[k_{\mathrm{d},0}\exp(2\mu/RT) - k_{\mathrm{a},0}P_{\mathrm{A}}\right], \\ \frac{\mathrm{d}P_{\mathrm{B}}}{\mathrm{d}t} = \frac{P_{\mathrm{B},0} - P_{\mathrm{B}}}{\tau_{\mathrm{R,B}}} - P^*P_{\mathrm{B}}k_{\mathrm{R},0}\exp(\mu/RT)(1-\theta).\end{gathered} \tag{36}$$

Here, $\tau_{\mathrm{R,A}}$ and $\tau_{\mathrm{R,A}_2}$ are the mean gas A – surface and gas A_2 – surface contact times, $\tau_{\mathrm{R,B}}$ is the mean gas B–surface contact time, $P_{\mathrm{A},0}$ and $P_{\mathrm{A}_2,0}$ are the pressures of gases A and A_2 at the reactor inlet, $P_{\mathrm{B},0}$ is the gas B pressure at the reactor inlet, $P^* = Sn_0RT/N_0V$ (S is the catalyst surface area, V is the reactor volume, N_0 is Avogadro's number, and n_0 is the adsorption site density), and the other variables and parameters have the same meaning as in the above formulas.

An analysis of the stationarity equations and of multiplicity curves for systems (35) and (36), which is similar to the analysis of model (7), also leads to inequality (34); however, in this case this criterion is only a necessary, not sufficient, condition for the existence of multiple steady states. The fulfillment of this multiplicity criterion was discussed earlier [2, 3]. As was noted above, for isotherm (17) for the one-dimensional LGM, condition (34) is satisfied in the case of a negative ε value, i.e., in the case of attraction between the nearest neighbors. Therefore, there can be steady state multiplicity in systems (35) and (36) even in this simplest case.

From the physicochemical standpoint, the steady-state reaction rate versus pressure curve will show a hysteresis in the criterion fulfillment region, which is typical of systems with multiple steady states. The corresponding plot for mechanism (II) is presented in Fig. 5.

It can be demonstrated that all of the above considerations are also true for irreversible adsorption in mechanisms (I) and (II) and, although the systems of equations are simpler in this case, the SSM criterion (34) is, nevertheless, valid. This is further evidence that the microlevel parameters play an important, if not decisive, role in the modeling of kinetic systems.

An analytical description of two-dimensional LGMs is difficult to devise because of the explicit dependence of μ on θ. For this reason, numerical

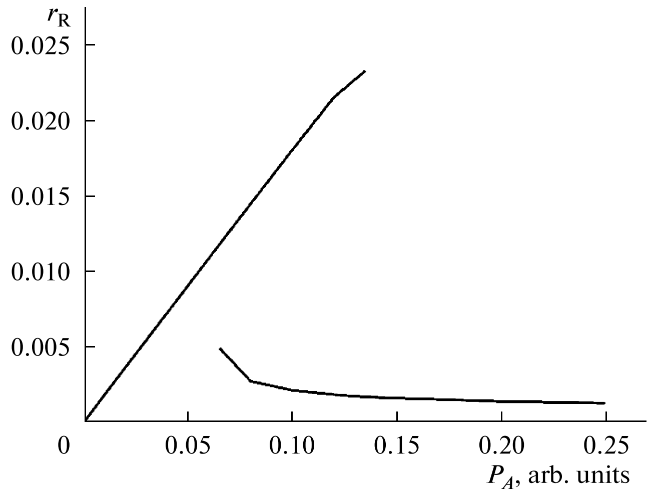

Fig. 5. Steady-state reaction rate r_R as a function of the gas A_2 pressure at the reactor inlet in the region of three steady states for mechanism (II).

algorithms are commonly used (see, e.g., [18]). As was demonstrated using Eq. (7) as an example, passing from the linear LGM to the square-lattice gas model leads only to a qualitative complication of the behavior of the system and, if the pressure constancy condition is abandoned, to the possible existence of three and even five steady states [2, 3]. The approach suggested here can be extended to models with distributed parameters in which the diffusion of intermediates on the catalyst surface is taken into consideration [19]. In addition, the TM method affords an algorithm for constriction and analysis of nonideal models involving two types of intermediates. In this case, it is interesting to examine isotherms as a surface in a three-dimensional space. The shape of these isotherms is determined by the character of the lateral interactions between the adsorbed species. Here, a qualitative complication of the behavior of the system, including the appearance of Andronov–Hopf bifurcations, is again possible.

Thus, we have constructed physicochemically correct unsteady-state models for the simplest catalytic unimolecular and bimolecular Eley–Rideal mechanisms. These models include a microlevel parameter describing surface processes, specifically, the energy of lateral interaction between adsorbed species. Even in the case of the one-dimensional LGM, use of the TM method, which makes it possible to calculate thermodynamic functions involving the energies of lateral interaction between adsorbed species, revealed a number of nontrivial features capable of exerting a qualitative effect on the kinetics of complex processes on the catalyst surface.

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