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Numerical study of the kinetics of unimolecular heterogeneous reactions onto planar surfaces

V. Skakauskas · P. Katauskis

Abstract   In this paper we investigate two-dimensional in space mathematical models of the kinetics of unimolecular heterogeneous reactions proceeding onto planar surfaces. The models are based on Langmuir-type kinetics of the adsorption, desorption, and reaction including the surface diffusion of the adsorbate, surface diffusion of the product before its desorption, and slow desorption of the product from the adsorbent. It is also assumed that the reactant diffuses towards an adsorbent from a bounded vessel and the product diffuses from the adsorbent into the same vessel. Diffusivity of all species and kinetic coefficients are constants. The numerical simulation was carried out using the finite difference technique for four models: one model neglects the surface diffusion of the adsorbate and product, the second one includes the surface diffusion of the adsorbate and product, the third of them includes the surface diffusion of the adsorbate and neglects diffusion of the product along the surface, and the last one neglects the surface diffusion of the adsorbate and includes diffusion of the product along the adsorbent. By changing input parameters effects of the surface diffusion of the adsorbate and product and the slow desorption of the product are studied numerically.

Keywords   Heterogeneous reactions · Adsorption · Desorption · Parabolic equations

1 Introduction and formulation of the problem

In order for the catalytic reaction on a surface to occur, one or more of the reactants must diffuse to the catalyst surface (adsorbent) and adsorb onto it forming one or more intermediates (adsorbates). After conversion (reaction) of the adsorbates the

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product must desorb and diffuse away from the adsorbent. Equilibrium properties of different adsorption systems are well covered in literature. Kinetics of Langmuirian adsorption onto planar, spherical, and cylindrical surfaces is studied in [1]. In this case of surfaces the problem is one-dimensional and the assumptions that density of active centers of a surface is constant, an adsorbate cannot diffuse along the surface, and the pool of the reactant diffusing towards the adsorbent is large enough (i.e. the *volume of a vessel* containing the reactant is *infinite*) let authors of this paper to derive a nonlinear Volterra type integral equation for the surface coverage, which they solved numerically. In [1], it is also given a survey of papers devoted to diffusion limited adsorption process in which the adsorption process is assumed to be very fast compared with the transport rate by diffusion. In the case where density of a reactant at the surface is given, the surface diffusion on an adsorbate is considered in [2].

In the case where diffusion of the reactant in a volume at the surface is neglected, unimolecular and bimolecular surface reactions proceeding on the surfaces with heterogeneous active centers are studied in [3–5] by using Monte Carlo simulations.

A common feature of the previous reports dealing with adsorption and surface reactions is that the *desorption of the product* is assumed to be *instantaneous*.

In the present paper we consider two-dimensional in space four one-molecular reaction models given in [6]. All these models include the reactant diffusion towards the adsorbent from a *bounded vessel*, its adsorption onto and desorption from the adsorbent, the conversion of the adsorbate into a product, *slow desorption of the product* and its diffusion away from the adsorbent. In addition we take (or do not) into account the surface diffusion of the adsorbate and reaction product before it desorbs from the surface. In the first of these four models, we neglect the surface diffusion of the adsorbate and product. The second one includes the diffusion of the adsorbate and the product along the adsorbent. The third of them includes the surface diffusion of the adsorbate and neglects the diffusion of the product along the surface. At last in the fourth model, we neglect the surface diffusion of the adsorbate and include the diffusion of the product along the surface.

The existence and uniqueness theorems for models neglecting the surface diffusion of the adsorbate and product and including instantaneous or slow desorption of the product are given in [7] and [8]. Results of numerical solving of the same models are discused in [9].

Let reactant A and product B of concentrations $a(t, x)$ and $b(t, x)$ occupy bounded domain Ω with surface $\partial\Omega = S_1 \cup S_2$. Here t is time, $x \in \Omega$ is a position, S_2 is a surface of the adsorbent K, and $S_1 = \partial\Omega \setminus S_2$. Let the constant s be the surface density of the active sites of S_2 and $u_1 s$ and $u_2 s$ be the densities of active sites occupied by molecules of the adsorbate AK and product B, respectively. Obviously $u_k < 1$, $k = 1, 2$, and $u_1 + u_2 \le 1$. Then neglecting the diffusion of the adsorbate and product along the surface and using the Langmuir kinetic law we get the equations

$$\partial_t u_1 = k_f (1 - u_1 - u_2) a|_{S_2} - (k_r + k) u_1, \quad u_1(0, x) = u_{10}(x), \quad x \in S_2, \quad (1)$$
$$\partial_t u_2 = k u_1 - k_{r1} u_2, \quad u_2(0, x) = u_{20}(x), \quad x \in S_2. \quad (2)$$

Here k_f and k_r are the adsorption and desorption rate constants of the reactant A, k is the reaction rate constant and k_{r1} is the desorption rate constant of the product B, u_{10} and u_{20} are the initial distributions.

In the case where the diffusion of the adsorbate AK and product B along the surface is taken into account, we have the equations

$$\partial_t u_1 = k_f(1 - u_1 - u_2)a|_{S_2} - (k_r + k)u_1 + \kappa_1 \Delta u_1,$$
$$u_1(0, x) = u_{10}(x), \quad x \in S_2, \quad \partial_n u_1|_{S_1 \cap S_2} = 0, \tag{3}$$
$$\partial_t u_2 = k u_1 - k_{r1} u_2 + \kappa_2 \Delta u_2,$$
$$u_2(0, x) = u_{20}(x), \quad x \in S_2, \quad \partial_n u_2|_{S_1 \cap S_2} = 0. \tag{4}$$

Here Δ is the Laplace operator defined on S_2, κ_1 and κ_2 are the surface diffusion coefficients of the adsorbate and product, $\partial_n u_1$ and $\partial_n u_2$ are the outward normal derivatives.

If we neglect the diffusion of the adsorbate or the product along the surface we have Eqs. (1) and (4) or (3) and (2).

The diffusion of the reactant A and product B is described by the systems

$$\begin{cases} \partial_t a = \kappa_a \Delta a, \quad x \in \Omega, \ t > 0, \\ \partial_n a|_{S_1} = 0, \quad t > 0, \\ \kappa_a \partial_n a|_{S_2} = -k_f s(1 - u_1 - u_2)a|_{S_2} + k_r s u_1, \quad t > 0, \\ a(0, x) = a_0(x), \quad x \in \Omega \end{cases} \tag{5}$$

and

$$\begin{cases} \partial_t b = \kappa_b \Delta b, \quad x \in \Omega, \ t > 0, \\ \partial_n b|_{S_1} = 0, \quad t > 0, \\ \kappa_b \partial_n b|_{S_2} = k_{r1} s u_2, \quad t > 0, \\ b(0, x) = b_0(x), \quad x \in \Omega. \end{cases} \tag{6}$$

Here κ_a and κ_b are the diffusion coefficients, $\partial_n a$ and $\partial_n b$ are the outward normal derivatives.

Systems (5) and (6) with one pair conditions of the set (1) and (2), (3) and (4), (1) and (4), (3) and (2) possess the mass conservation law

$$\int_\Omega (a + b)\, dx + \int_{S_2} s(u_1 + u_2)\, dx = \int_\Omega (a_0 + b_0)\, dx + \int_{S_2} s(u_{10} + u_{20})\, dx. \tag{7}$$

If we use the steady-state approximation of conditions (1) and (2) we get the Langmuir isotherms [10]

$$u_1 = \frac{k_f a|_{S_2}}{k_f(1 + k/k_{r1})a|_{S_2} + k_r + k},$$

$$u_2 = \frac{k k_f k_{r1}^{-1} a|_{S_2}}{k_f (1 + k/k_{r1}) a|_{S_2} + k_r + k}.$$

A lot of papers (see, e.g. [11–13] and literature therein) is devoted to modification of isotherms of this type to more accurately describe the experimental observations.

2 Numerical algorithms

Using the dimensionless variables $\bar{t} = t/T, \bar{x}_1 = x_1/l, \bar{x}_2 = x_2/l, \bar{a} = a/a_*, \bar{b} = b/a_*, \bar{a}_0 = a_0/a_*, \bar{b}_0 = b_0/a_*$ and constants $\bar{s} = s/a_* l, \bar{k}_f = k_f T a_*, \bar{k}_r = k_r T, \bar{k}_{r1} = k_{r1} T, \bar{k} = k T, \bar{\kappa}_a = \kappa_a T/l^2, \bar{\kappa}_b = \kappa_b T/l^2, \bar{\kappa}_1 = \kappa_1 T/l^2, \bar{\kappa}_2 = \kappa_2 T/l^2$, where T, l, and a_* are the characteristic dimensional units, we rewrite Eqs. (1–7) in the same form with t, x_1, x_2, a, b, a_0, b_0, k_f, k_r, k_{r1}, k, s, $\kappa_a, \kappa_b, \kappa_1$, and κ_2 replaced by $\bar{t}$, $\bar{x}_1$, $\bar{x}_2$, $\bar{a}$, $\bar{b}$, $\bar{a}_0$, $\bar{b}_0$, $\bar{k}_f$, $\bar{k}_r$, $\bar{k}_{r1}$, $\bar{k}, \bar{s}, \bar{\kappa}_a, \bar{\kappa}_b, \bar{\kappa}_1$, and $\bar{\kappa}_2$, respectively. For simplicity in what follows, we omit the bar and treat Eqs. (1–7) as dimensionless.

To get the numerical solution of problem (5) and (6) with one pair conditions of the set (1) and (2), (3) and (4), (1) and (4), (3) and (2) we use the finite-difference schemes and consider two-dimensional domain $\overline{\Omega} = [0, 1] \times [0, 1]$ with $S_2 = \{(x_1, x_2) : x_1 \in [0, 1], x_2 = 0\}$.

Assume that $t_k = k\tau, t_{k+1/2} = (k + 1/2)\tau, 0 \le k \le M, \tau = T/M, x_{1i} = ih_1, 0 \le i \le N_1, h_1 = 1/N_1; x_{2j} = jh_2, 0 \le j \le N_2, h_2 = 1/N_2$. Set $a_{ij}^k = a(t_k, x_{1i}, x_{2j}), b_{ij}^k = b(t_k, x_{1i}, x_{2j}), u_{1i}^k = u_1(t_k, x_{1i}), u_{2i}^k = u_2(t_k, x_{1i})$ and $a_{ij}^{k+1/2} = a(t_{k+1/2}, x_{1i}, x_{2j}), b_{ij}^{k+1/2} = b(t_{k+1/2}, x_{1i}, x_{2j})$.

Let the difference operators Λ_1 and Λ_2 be defined by $\Lambda_1 v_{ij} = (v_{i-1,j} - 2v_{ij} + v_{i+1,j})/h_1^2, \Lambda_2 v_{ij} = (v_{i,j-1} - 2v_{ij} + v_{i,j+1})/h_2^2$.

To approximate the differential problems (5) and (6) the alternating directions implicit method [14] is used. We write the following difference scheme to problem (5):

$$a_{ij}^{k+1/2} - \frac{\tau\kappa_a}{2}\Lambda_1 a_{ij}^{k+1/2} = a_{ij}^k + \frac{\tau\kappa_a}{2}\Lambda_2 a_{ij}^k,$$
$$i = 1, 2, \ldots, N_1 - 1; \; j = 1, 2, \ldots, N_2 - 1, \tag{8}$$
$$a_{0j}^{k+1/2} = a_{1j}^{k+1/2}, \quad a_{N_1 j}^{k+1/2} = a_{N_1-1,j}^{k+1/2}, \quad j = 1, 2, \ldots, N_2 - 1, \tag{9}$$

and

$$a_{ij}^{k+1} - \frac{\tau\kappa_a}{2}\Lambda_2 a_{ij}^{k+1} = a_{ij}^{k+1/2} + \frac{\tau\kappa_a}{2}\Lambda_1 a_{ij}^{k+1/2},$$
$$i = 1, 2, \ldots, N_1 - 1; \; j = 1, 2, \ldots, N_2 - 1, \tag{10}$$
$$a_{i0}^{k+1} = \frac{\kappa_a}{\kappa_a + h_2 s k_f (1 - u_{1,i}^k - u_{2,i}^k)} a_{i1}^{k+1} + \frac{h_2 s k_r u_{1,i}^k}{\kappa_a + h_2 s k_f (1 - u_{1,i}^k - u_{2,i}^k)},$$
$$i = 1, 2, \ldots, N_1 - 1, \tag{11}$$
$$a_{iN_2}^{k+1} = a_{iN_2-1}^{k+1}, \quad i = 1, 2, \ldots, N_1 - 1, \tag{12}$$
$$a_{0j}^{k+1} = a_{1j}^{k+1}, \quad a_{N_1 j}^{k+1} = a_{N_1-1,j}^{k+1}, \quad j = 1, 2, \ldots, N_2 - 1, \tag{13}$$

for all $k = 0, 1, \ldots, M - 1$, with the discrete initial condition

$$a_{ij}^0 = a_{0,ij}, \quad i = 0, 1, \ldots, N_1; \; j = 0, 1, \ldots, N_2. \tag{14}$$

The difference scheme to problem (6) differs from that to problem (5) by the approximation of the boundary condition at $x_2 = 0$ and diffusion coefficient.

To get the discrete form of Eq. (3) we use the finite-difference scheme

$$
\begin{aligned}
&u_{1,i}^{k+1} - \tau \kappa_1 \Lambda_1 u_{1,i}^{k+1} = u_{1,i}^k + 0.5\tau \big[k_f (1 - u_{1,i}^k - u_{2,i}^k) a_{i0}^{k+1} - (k_r + k) u_{1,i}^k \\
&\quad + k_f (1 - u_{1,i}^{k-1} - u_{2,i}^{k-1}) a_{i0}^k - (k_r + k) u_{1,i}^{k-1} \big], \quad i = 1, 2, \ldots, N_1 - 1, \\
&u_{1,0}^{k+1} = u_{1,1}^{k+1}, \quad u_{1,N_1}^{k+1} = u_{1,N_1-1}^{k+1}, \quad k = 1, 2, \ldots, M - 1, \\
&u_{1,i}^0 = u_{10,i}, \quad i = 0, 1, \ldots, N_1.
\end{aligned} \tag{15}
$$

When $\kappa_1 = 0$ from (15) we have the explicit scheme for solving the problem (1). The values of u_2 at each time layer are calculated by the scheme

$$
\begin{aligned}
&u_{2,i}^{k+1} - \tau \kappa_2 \Lambda_1 u_{2,i}^{k+1} = u_{2,i}^k + 0.5\tau \big[k(u_{1,i}^k + u_{1,i}^{k-1}) - k_{r1}(u_{2,i}^k + u_{2,i}^{k-1}) \big], \\
&\quad i = 1, 2, \ldots, N_1 - 1, \\
&u_{2,0}^{k+1} = u_{2,1}^{k+1}, \quad u_{2,N_1}^{k+1} = u_{2,N_1-1}^{k+1}, \quad k = 1, 2, \ldots, M - 1, \\
&u_{2,i}^0 = u_{20,i}, \quad i = 0, 1, \ldots, N_1,
\end{aligned} \tag{16}
$$

which approximates Eq. (4) if $\kappa_2 \neq 0$ and Eq. (2) if $\kappa_2 = 0$. In the first time layer the right-hand sides of (15) and (16) are $u_{10,i} + 0.5\tau[k_f(1 - u_{10,i} - u_{20,i})a_{i0}^1 - (k_r+k)u_{10,i}]$ and $u_{20,i} + 0.5\tau(ku_{10,i} - k_{r1}u_{20,i})$.

Differential problems (5) and (6) include complex nonlinear boundary conditions on S_2. This fact forces us to construct a complicated difference scheme. Difference schemes (15) and (16) to problems (1–4) were constructed taking into account discretizations of parabolic equations for a and b made by using alternating direction implicit scheme and approximations of the boundary conditions on S_2. In the case where $\partial_{x_2} a_0(x)|_{x_2=0;1} = \partial_{x_2} b_0(x)|_{x_2=0;1} = 0$, this allows to prove that the difference solutions satisfy the discrete analogue of the mass conservation law (7). From (8–16) and the difference scheme for function b we get:

$$
\begin{aligned}
&h_1 h_2 \sum_{i=1}^{N_1-1} \sum_{j=1}^{N_2-1} (a_{ij}^{k+1} + b_{ij}^{k+1}) + h_1 s \sum_{i=1}^{N_1-1} (u_{1,i}^{k+1} + u_{2,i}^{k+1}) \\
&\quad = h_1 h_2 \sum_{i=1}^{N_1-1} \sum_{j=1}^{N_2-1} (a_{ij}^k + b_{ij}^k) + h_1 s \sum_{i=1}^{N_1-1} (u_{1,i}^k + u_{2,i}^k)
\end{aligned} \tag{17}
$$

for each $k = 0, 1, 2, \ldots$. The approximation resulted with the systems of linear algebraic equations with a tridiagonal matrix. Systems having such type of matrix are solved effectively by using the elimination method [14]. Matrices of problems (8), (9)

for fixed k and j, (10–12) for fixed k and i, and problems (15) and (16) for $\kappa_1 \neq 0$ and $\kappa_2 \neq 0$ are tridiagonal. In this work the digital simulation was carried out using a software developed by the authors in C++ programming language. The numerical experiments for different values of h_1, h_2 and τ show that the difference schemes are stable.

3 Numerical results

Numerical results of dimensionless solutions are illustrated in Figs. 1–15 for $\overline{\Omega} = [0, 1] \times [0, 1]$, $S_2 = \{(x_1, x_2) : x_1 \in [0, 1], x_2 = 0\}$, $\kappa_a = \kappa_b = 0.1$, $s = 10$, $u_{10} = u_{20} = b_0 = 0$,

$$a_0 = 20(\exp(-2x_1) - \exp(-2))/(1 - \exp(-2)).$$

Usually surfaces are not homogeneous and constants $k_f, k_r, k, k_{r1}, \kappa_1$, and κ_2 depend on many factors including processing of surfaces. Therefore experimental observations of their values may be different. For all calculations we used the following values of data:

$$
\begin{aligned}
&T = 1\,\text{s}, \quad l = 10^{-1}\,\text{cm}, \quad s = 10^{-11}\,\text{mol cm}^{-2}, \\
&a_* = 10^{-11}\,\text{mol cm}^{-3}, \quad k_f \in [10^9, 10^{11}]\,\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}, \\
&k_r, k, k_{r1} \in [10^{-2}, 1]\,\text{s}^{-1}, \quad \kappa_a, \kappa_b \in [5 \times 10^{-7}, 10^{-3}]\,\text{cm}^2\,\text{s}^{-1}, \\
&\kappa_1, \kappa_2 \in [5 \times 10^{-3}, 5 \times 10^{-2}]\,\text{cm}^2\,\text{s}^{-1}.
\end{aligned}
\tag{18}
$$

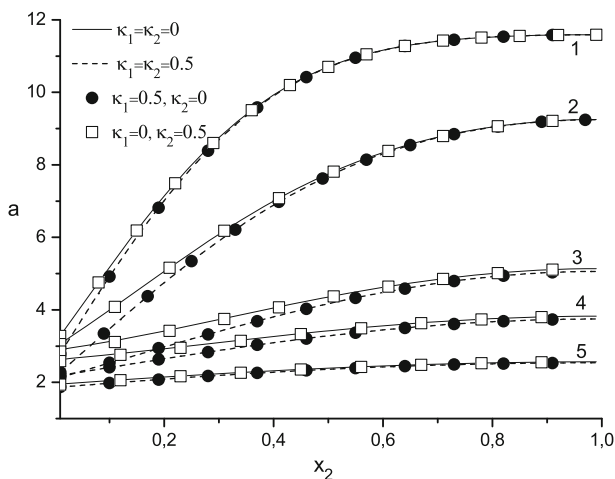Values of s, k_f, k_r, and κ_a were used in [1]. Values of constants that we use are given in captions.

Fig. 1 Time evolution of $a(t, 0, x_2)$ for $k_f = 0.2, k_r = 1, k_{r1} = 0.1, k = 0.1$. Values of time t: 0.5 (1), 1 (2), 3 (3), 5 (4), 10 (5)
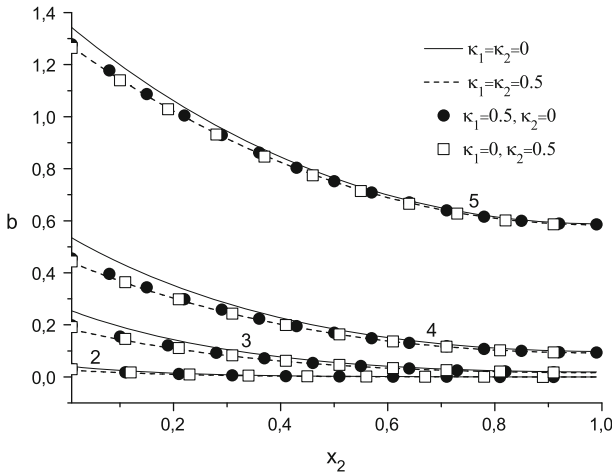
Fig. 2 Time evolution of $b(t, 0, x_2)$ for $k_f = 0.2, k_r = 1, k_{r1} = 0.1, k = 0.1$. Values of time t: 1 (2), 3 (3), 5 (4), 10 (5)
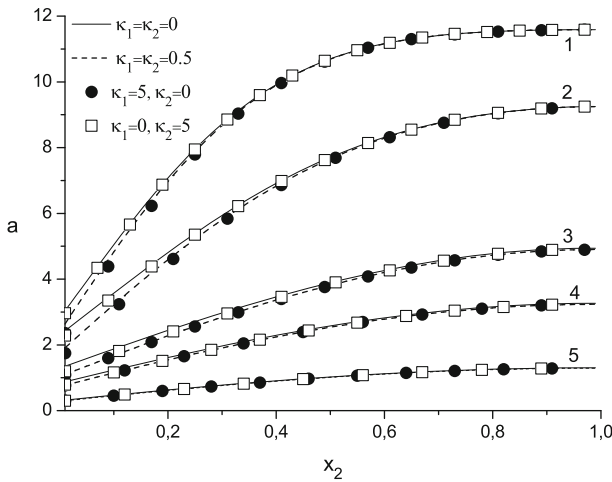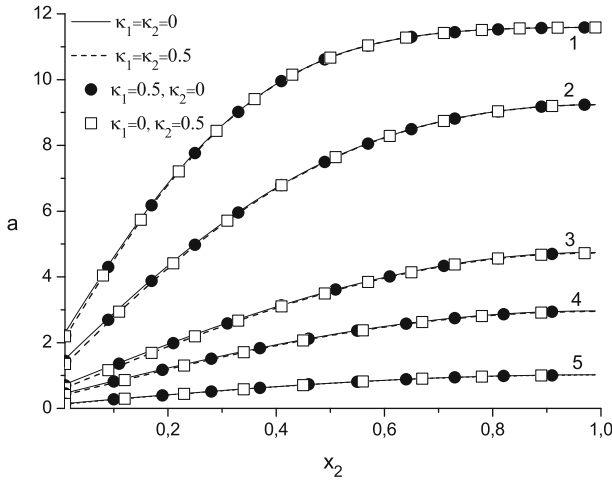

Fig. 3 Comparison of values of function $a(t, 0, x_2)$ for $k_f = 0.2, k_r = 1, k_{r1} = 0.1, k = 1$. Values of time are the same as in Fig. 1

Curves 1–5 in Figs. 1–7 are plotted for $t = 0.5, 1, 3, 5, 10$, respectively.

Figure 1 demonstrates the behavior of function $a(t, 0, x_2)$ from all four models versus x_2 for five values of t and $k_f = 0.2, k_r = 1, k_{r1} = 0.1$, and $k = 0.1$. For large $t \geq 10$ values of $a(t, 0, x_2)$ from all models approximately are the same. For $t \in [0.5, 10]$ curves with $\kappa_1 = \kappa_2 = 0$ and $\kappa_1 = 0, \kappa_2 = 0.5$ approximately coincide and so do curves with $\kappa_1 = \kappa_2 = 0.5$ and $\kappa_1 = 0.5, \kappa_2 = 0$. This means that the diffusion of the product along the adsorbent before its desorption influences the behavior of $a(t, 0, x_2)$ weakly.

Fig. 4 Comparison of graphs of $a(t, 0, x_2)$ for $k_f = 0.2$, $k_r = 1$, $k_{r1} = 0.1$, $k = 10$. Values of time are the same as in Fig. 1
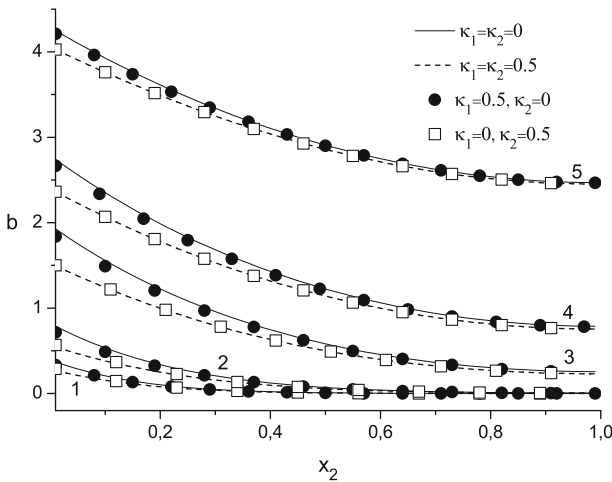

Fig. 5 Graphs of function $b(t, 0, x_2)$ for $k_f = 0.2$, $k_r = 1$, $k_{r1} = 0.1$, $k = 10$. Values of time are the same as in Fig. 1

Figure 2 illustrates the behavior of $b(t, 0, x_2)$ from all models. Curves with $\kappa_1 = \kappa_2 = 0.5$, $\kappa_1 = 0.5$ and $\kappa_2 = 0$, or $\kappa_1 = 0$ and $\kappa_2 = 0.5$ approximately coincide and differ from those with $\kappa_1 = \kappa_2 = 0$. This figure also shows that the diffusion of the adsorbate and product before its desorption impedes the growth of $b(t, 0, x_2)$ in time.

Figure 3 demonstrates the behavior of $a(t, 0, x_2)$ from all models for $k_f = 0.2$, $k_r = 1$, $k_{r1} = 0.1$, and $k = 1$. Curves with $\kappa_1 = \kappa_2 = 0$ and $\kappa_1 = 0$, $\kappa_2 = 5$ approximately coincide, but curve with $\kappa_1 = 5$, $\kappa_2 = 0$ for $t \in [0.5, 3)$ is below that with $\kappa_1 = \kappa_2 = 0.5$. Curves with at least one positive κ_1 or κ_2 are below those with $\kappa_1 = \kappa_2 = 0$. We also see that for $t \in [0.5, 1]$ curves with $\kappa_1 = 5$, $\kappa_2 = 0$ are below
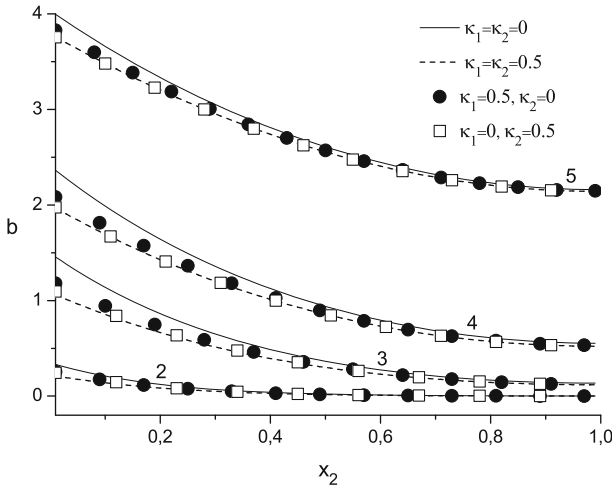
Fig. 6 Graphs of function $b(t, 0, x_2)$ for $k_f = 0.2, k_r = 0.1, k_{r1} = 0.1, k = 1$. Values of time t: 1 (2), 3 (3), 5 (4), 10 (5)
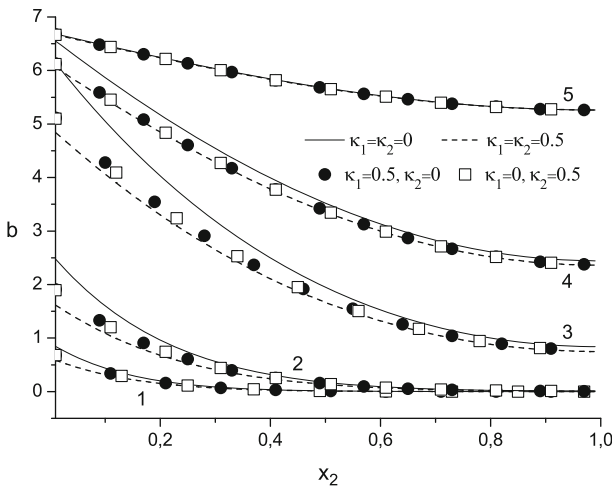

Fig. 7 Graphs of function $b(t, 0, x_2)$ for $k_f = 0.2, k_r = 0.1, k_{r1} = 1, k = 1$. Values of time are the same as in Fig. 1

those with $\kappa_1 = \kappa_2 = 0.5$. This means that as in the case of Fig. 1 the diffusion of the product along the adsorbent before its desorption influences the behavior of $a(t, 0, x_2)$ weakly. From Figs. 1 and 3 we also can see that, for $t > 3$, $a(t, 0, x_2)$ decreases as k increases.

Figures 4 and 5 illustrate the behavior of $a(t, 0, x_2)$ and $b(t, 0, x_2)$ from all models for $k_f = 0.2, k_r = 1, k_{r1} = 0.1$, and $k = 10$. We see approximate coincidence of curves of $a(t, 0, x_2)$ and difference of curves of $b(t, 0, x_2)$. Curves of $b(t, 0, x_2)$ with $\kappa_1 = \kappa_2 = 0.5$ and $\kappa_1 = 0, \kappa_2 = 0.5$ approximately coincide, and so do curves with
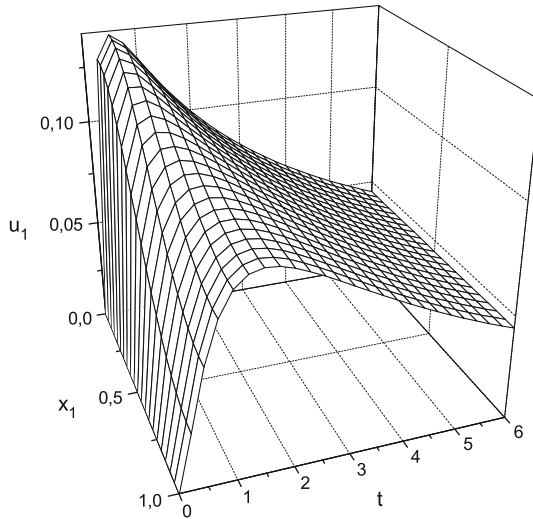
Fig. 8 Function $u_1(t, x_1)$ for $k_f = 0.2, k_r = 1, k_{r1} = 1, k = 1, \kappa_1 = \kappa_2 = 0.5$
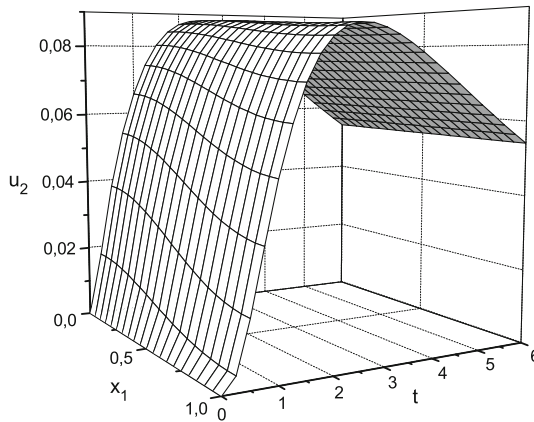

Fig. 9 Function $u_2(t, x_1)$ for $k_f = 0.2, k_r = 1, k_{r1} = 1, k = 1, \kappa_1 = \kappa_2 = 0.5$

$\kappa_1 = \kappa_2 = 0$ and $\kappa_1 = 0.5, \kappa_2 = 0$. This means that the dependence $b(t, 0, x_2)$ on k is strong.

Figures 6 and 7 demonstrate the behavior of $b(t, 0, x_2)$ for $k_f = 0.2, k_r = 0.1, k = 1$, and $k_{r1} = 0.1$ (Fig. 6) and $k_{r1} = 1$ (Fig. 7). The different behavior of $b(t, 0, x_2)$ can be explained by the fact that for large k_{r1} we have the case of an instantaneous desorption of the product from the adsorbent. Calculations show that the increase of k_{r1} increases $b(t, 0, x_2)$ but practically does not influence the behavior of $a(t, 0, x_2)$.

Figures 8 and 9 exhibit graphs of functions u_1 and u_2 for $k_f = 0.2, k_r = 1, k_{r1} = 1$, and $k = 1$. Times $t_1(x_1)$ and $t_2(x_1)$ of maximal values of u_1 and u_2 depend on data $k_f, k_r, k_{r1}, k\kappa_1, \kappa_2, \kappa_a, \kappa_b$, and s. Graphs show that $t_1(x_1) < t_2(x_1)$. Calculations
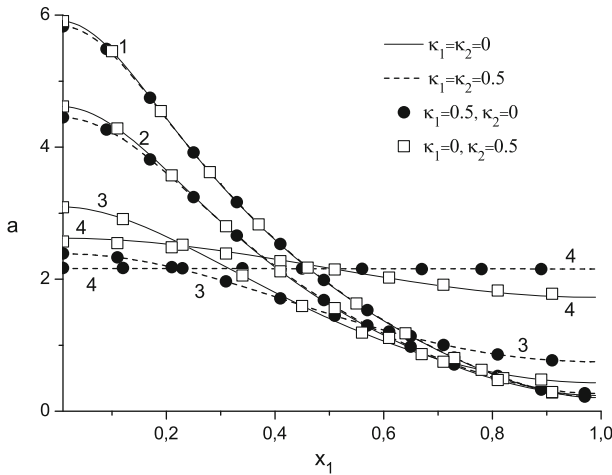
Fig. 10 Comparison of values of function $a(t, x_1, 0)$ for $k_f = 0.2$, $k_r = 1$, $k_{r1} = 0.1$, $k = 0.1$, and four values of time t: 0.05 (1), 0.1 (2), 0.5 (3), 5 (4)
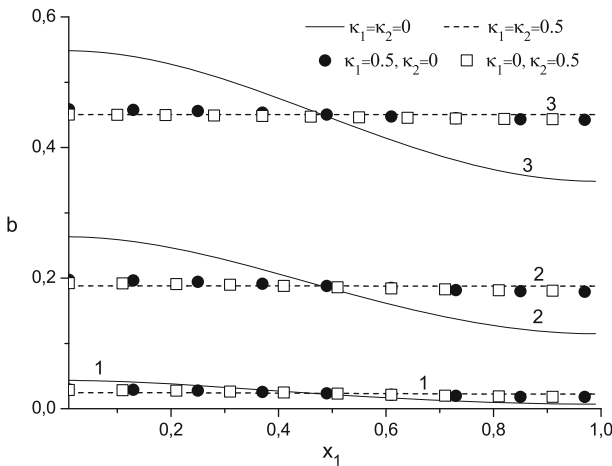

Fig. 11 Comparison of values of function $b(t, x_1, 0)$ for $k_f = 0.2$, $k_r = 1$, $k_{r1} = 0.1$, $k = 0.1$, and three values of time t: 1 (1), 3 (2), 5 (3)

show that, in the case of small $t_2(x_1) - t_1(x_1)$, u_2 influences the behavior of a more significantly. In the other cases this influence is small.

Figures 10 and 11 demonstrate the behavior of $a(t, x_1, 0)$ and $b(t, x_1, 0)$ for $k_f = 0.2$, $k_r = 1$, $k = 0.1$, and $k_{r1} = 0.1$. For $t \in [0.5, 5]$ curves of $a(t, x_1, 0)$ with $\kappa_1 = \kappa_2 = 0.5$ and curves $\kappa_1 = 0.5$, $\kappa_2 = 0$ approximately coincide and so do curves with $\kappa_1 = \kappa_2 = 0$ and $\kappa_1 = 0$, $\kappa_2 = 0.5$. This means that κ_2 influences the behavior of $a(t, x_1, 0)$ weakly. But the diffusion of the adsorbate or product along the surface influences the behavior of b significantly.

Figures 12–15 demonstrate the graphs of a and b for $t = 0.5$, $k_f = 0.2$, $k_r = 1$, $k_{r1} = 0.1$, $k = 1$, and $\kappa_1 = \kappa_2 = 0.5$ (Figs. 12, 13), $\kappa_1 = \kappa_2 = 0$ (Figs. 14, 15).
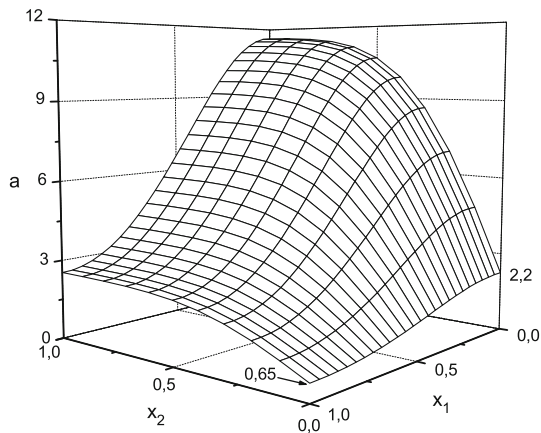
Fig. 12 Graph of function $a(0.5, x_1, x_2)$ for $k_f = 0.2$, $k_r = 1$, $k_{r1} = 0.1$, $k = 1$, $\kappa_1 = \kappa_2 = 0.5$
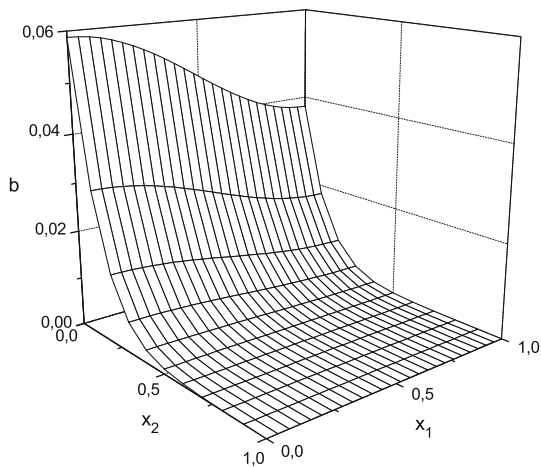

Fig. 13 Graph of function $b(0.5, x_1, x_2)$ for $k_f = 0.2$, $k_r = 1$, $k_{r1} = 0.1$, $k = 1$, $\kappa_1 = \kappa_2 = 0.5$

We see that the qualitative behavior of a depends on κ_1, κ_2 slightly, but their influence on b for small x_2 is strong.

4 Conclusions

We examined numerically four models of unimolecular heterogeneous reactions. In one of them we neglect the surface diffusion of adsorbate and product before its desorption from the adsorbent. The other includes the surface diffusion of adsorbate and product before its desorption from the adsorbent. In third model we neglect only the surface diffusion of the product before its desorption from the adsorbent, while in the fourth one we neglect only the adsorbate diffusion.
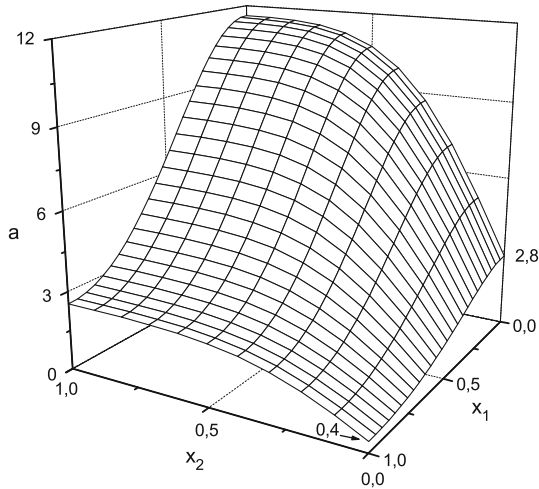
Fig. 14 Graph of function $a(0.5, x_1, x_2)$ for $k_f = 0.2, k_r = 1, k_{r1} = 0.1, k = 1, \kappa_1 = \kappa_2 = 0$
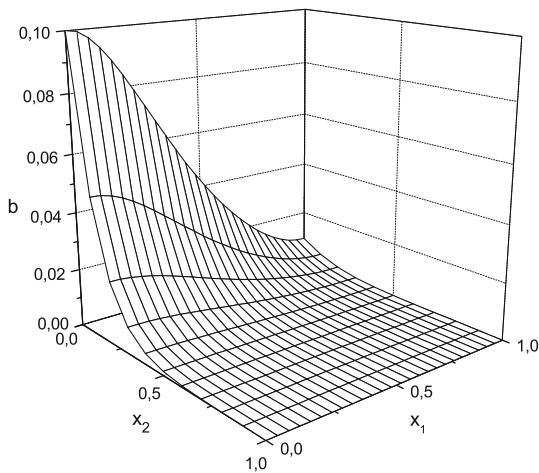

Fig. 15 Graph of function $b(0.5, x_1, x_2)$ for $k_f = 0.2, k_r = 1, k_{r1} = 0.1, k = 1, \kappa_1 = \kappa_2 = 0$

Numerical calculations show that:

The surface diffusion only of the product before its desorption influences the concentration of the reactant A weakly, but it influences the concentration of the product B essentially;

Values of a from the first and fourth models and values of a from the second and third models practically coincide for the same value of diffusivity κ_1;

The increase of reaction rate constant k increases b, the increase of desorption rate constant k_r decreases u_2 and, hence, it decreases b, the increase of product desorption rate constant k_{r1} increases b but practically does not influence the behavior of a.

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