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On a mathematical model of dissociative adsorption and associative desorption*

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Abstract. A mathematical model of dissociative adsorption and associative desorption for diatomic molecules is considered. The model is described by a system of parabolic and ordinary differential equations. The existence and uniqueness theorem of the classical solution is proved.

Keywords: Parabolic and ordinary differential equations, surface reactions.

1 Introduction

According to Langmuir a unimolecular heterogeneous catalytic reaction can be modeled by the reaction of the Michaelis–Menten type

$$A + K \underset{\kappa_1}{\overset{\kappa}{\rightleftarrows}} AK \overset{\kappa_2}{\to} B,$$

where κ and κ_1 are adsorption and desorption rate constants, κ_2 is a constant of adsorbate and catalyst compound AK reaction (conversion into product B) rate. When the adsorbate diffusion is not taken into account, reactant diffuses to a surface from a bounded domain and product desorption is fast or slow the existence and uniqueness theorems of classical solutions are proved in [2] and [1], respectively. In [6], these problems are solved numerically. The case where the reactant diffuses in an unbounded domain, the adsorbent is planar, cylindrical or spherical, the adsorbate cannot diffuse along the catalyst surface and desorption of the product is instantaneous is considered in [3]. Authors of this paper reduce the problem into a nonlinear Voltera-type integral equation, which they solve numerically. In [7], taking into account the surface diffusion of the adsorbate and product (before its slow desorption) unimolecular surface reactions are examined numerically.

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2 Statement of the problem

In [4], a model of dissociative adsorption and associative desorption for a diatomic reactant is presented. This process is modeled by formula

$$A_2 + 2K \underset{\tilde{\kappa}_1}{\overset{\tilde{\kappa}}{\rightleftarrows}} 2AK, \tag{1}$$

where $\tilde{\kappa}$ and $\tilde{\kappa}_1$ are adsorption and desorption rate constants. According to this scheme a diatomic molecule of the reactant A_2 interacts with two active sites of the catalyst K forming adsorbate $2AK$ which during desorption releases two active sites.

Suppose, the reactant occupies a bounded domain $\Omega \subset \mathbb{R}^p$, $p \geqslant 3$, $a = a(x,t)$ is the concentration of reactant at the point $x \in \Omega$ at time t, $S := \partial\Omega$ is $p-1$ dimension surface, S_2 is a closed part of surface S of the same dimension (surface of the adsorbent), $S_1 = S \backslash S_2$. Let $\rho = \rho(x)$ be a concentration of active sites of a surface S at point $x \in S$, $\rho \in C(S)$, $\rho(x) \geqslant 0$ for $x \in S$, $\rho(x) = 0$, for $x \in S_1$. Suppose, $\rho\theta = \rho(x)\theta(x,t)$ is a concentration of active sites of a surface occupied by the adsorbate (then $\rho(x)(1-\theta(x,t))$ is a concentration of free active sites of surface S) at the point $x \in S_2$ at time t. From (1) and the law of mass action we have Cauchy problem for function θ

$$\theta' = a\kappa\rho(1-\theta)^2 - \kappa_1\rho\theta^2, \quad t \in (0,T],\ \theta|_{t=0} = \theta_0(x),\ x \in S_2, \tag{2}$$

where $\theta' = d\theta/dt$, $\kappa = 2\tilde{\kappa}$, $\kappa_1 = 2\tilde{\kappa}_1$, $0 \leqslant \theta_0(x) < 1$, $\forall x \in S_2$.

Note that this equation is nonlinear with respect to θ, while the corresponding equation for θ used in [2, 1] is linear.

The diffusion of reactant A_2 can be described by the problem

$$\begin{cases} a_t - k\Delta a = 0, & x \in \Omega,\ t \in (0,T), \\ k\partial a/\partial n = 0, & x \in S_1,\ t \in (0,T), \\ k\partial a/\partial n + \kappa a\rho^2(1-\theta)^2 = \kappa_1\rho^2\theta^2, & x \in S_2,\ t \in (0,T], \\ a|_{t=0} = a_0(x), & x \in \overline{\Omega}, \end{cases} \tag{3}$$

where $a_t = \partial a/\partial t$, $k = \mathrm{const} > 0$ is a diffusion coefficient, $\Delta a = \sum_{i=1}^n a_{x_i x_i}$, $\partial a/\partial n$ is the outward normal derivative to S, $a_0 = a_0(x)$ is the initial concentration of reactant at point $x \in \overline{\Omega}$.

Hence, mathematical model of dissociative adsorption and associative desorption for diatomic molecules is a coupled system (2) and (3).

3 Main results

Suppose, that surface S and known functions a_0, θ_0 and ρ satisfy following conditions:

Assumption 1.

1. $S \in C^{1+\alpha}$, $\alpha \in (0,1)$,

2. $S = S_1 \cup S_2$, S_2 is a closed part of surface S of $n-1$ dimension.

Assumption 2.

1. $a_0 \in C(\overline{\Omega})$, $a_0(x) \geqslant 0$, $\forall x \in \overline{\Omega}$,
2. $\theta_0 \in C(S_2)$, $0 \leqslant \theta_0(x) < 1$, $\forall x \in S_2$,
3. $\rho \in C(S_2)$,
4. a_0 is a continuously differentiable function in any neighbourhood of surface S.

Definition 1. We say that functions a and θ are classical solutions to (2), (3), if

1. $a \in C^{2,1}(\Omega \times (0,T]) \cap C(\overline{\Omega} \times [0,T])$,
2. $\theta \in C^{0,1}(S_2 \times (0,T]) \cap C(\overline{S}_2 \times [0,T])$,
3. $\partial a/\partial n \in C(S_1 \times [0,T]) \cup C(S_2 \times [0,T])$.

The main result of the present paper is the following theorem:

Theorem 1. *Let surface S and known functions a_0, θ_0 and ρ satisfy conditions of Assumptions* 1 *and* 2*. Then problem* (2), (3) *has a unique classical solution.*

The proof of this theorem is based on the heat potential theory and a priori estimates of solutions to problem (2), (3). We prove the following proposition.

Lemma 1. *Let $a \in C(S_2 \times [0,T])$, $a(x,t) \geqslant 0$, $\forall (x,t) \in S_2 \times [0,T]$, $\theta_0 \in C(S_2)$, $0 \leqslant \theta_0(x) < 1$, $\forall x \in S_2$ and θ be a solution of Cauchy problem* (2)*. Then*

$$0 \leqslant \theta(x,t) < 1, \quad \forall x \in S_2,\ t \in [0,T]. \tag{4}$$

Proof. We multiply equation (2) by $e^{\int_0^t \kappa_1 \rho\theta(x,s)\,ds}$ and rewrite it as follows

$$\big(\theta(x,t)e^{\int_0^t \kappa_1\rho(x)\theta(x,s)\,ds}\big)' = \kappa\rho(x)a(x,t)\big(1-\theta(x,t)\big)^2 e^{\int_0^t \kappa_1\rho(x)\theta(x,s)\,ds}.$$

By integrating latter equation from 0 to t, we get the integral equation

$$\begin{aligned}\theta(x,t) = {}&\theta_0(x)e^{-\int_0^t \kappa_1\rho(x)\theta(x,s)\,ds}\\ &+ e^{-\int_0^t \kappa_1\rho(x)\theta(x,s)\,ds}\int_0^t \kappa\rho(x)a(x,\tau)\big(1-\theta(x,\tau)\big)^2 e^{\int_0^\tau \kappa_1\rho(x)\theta(x,s)\,ds}\,d\tau.\end{aligned}$$

Similarly, we multiply equation (2) by $e^{\int_0^t \kappa\rho(x)a(x,s)(1-\theta(x,s))\,ds}$ and get the integral equation

$$\begin{aligned}\theta(x,t) = {}&1 - \big(1-\theta_0(x)\big)e^{-\int_0^t \kappa\rho(x)a(x,s)(1-\theta(x,s))\,ds}\\ &- e^{-\int_0^t \kappa\rho(x)a(x,s)(1-\theta(x,s))\,ds}\int_0^t \kappa_1\rho(x)\theta^2(x,s)e^{\int_0^\tau \kappa\rho(x)a(x,s)(1-\theta(x,s))\,ds}\,d\tau.\end{aligned}$$

According to these integral equations and conditions of lemma, estimates (4) are true. Lemma is proved.

Corollary 1. *Let θ be a solution of Cauchy problem* (2)*. Then*

$$\left(\frac{\theta(x,t)}{1-\theta(x,t)}\right)^2 \leqslant \max\left\{\max_{x\in S_2}\left(\frac{\theta_0(x)}{1-\theta_0(x)}\right)^2, \frac{\kappa}{\kappa_1}m\right\}, \tag{5}$$

where $m = \max_{(x,t)\in S_2\times[0,T]} a(x,t)$*.*

Proof. Set

$$u = \frac{\theta}{1-\theta}.$$

Then Cauchy problem (2) can be rewritten:

$$u' = \kappa\rho a - \kappa_1\rho u^2, \qquad u|_{t=0} = \frac{\theta_0(x)}{1-\theta_0(x)}.$$

For any fixed value $x \in S_2$ function $u \in C[0,T]$. Hence, there exists a point $t^* \in [0,T]$ at which function u has its maximum value. If $t^* = 0$, then

$$u(x,t) \leqslant u(x,0) = \frac{\theta_0(x)}{1-\theta_0(x)}, \quad \forall t \in [0,T].$$

If $t^* > 0$, then $u'(x,t^*) \geqslant 0$, and

$$u^2(x,t) \leqslant u^2(x,t^*) \leqslant \frac{\kappa a(x,t)}{\kappa_1} \leqslant \frac{\kappa m}{\kappa_1}, \quad \forall t \in [0,T],$$

where $m = \max_{x\in S_2,\, t\in[0,T]} a(x,t)$. According to these inequalities, estimate (5) is true.

Lemma 2. *Let $\theta \in C(S_2\times[0,T])$, $0 \leqslant \theta(x,t) < 1$, $\forall x \in S_2$, $t \in [0,T]$. Moreover, let $a_0 \in C(\overline{\Omega})$, $a_0(x) \geqslant 0$, $\forall x \in \overline{\Omega}$ and a be a classical solution to problem* (3)*. Then*

$$0 \leqslant a(x,t) \leqslant \max\left\{\max_{x\in\overline{\Omega}} a_0(x), \max_{x\in S_2,\, t\in[0,T]} \frac{\kappa_1}{\kappa}\left(\frac{\theta(x,t)}{1-\theta(x,t)}\right)^2\right\}, \tag{6}$$

for all $x \in \overline{\Omega}$, $t \in [0,T]$.

Proof. Let the conditions of lemma be satisfied and a be a classical solution of problem (3). Then

$$\begin{gathered}
a_t - k\Delta a = 0, \quad x \in \Omega,\ t \in (0,T), \\
k\partial a/\partial n = 0, \quad x \in S_1,\ t \in [0,T], \\
k\partial a/\partial n + \kappa\rho^2(1-\theta)^2 a = \kappa_1\rho^2\theta^2 \geqslant 0, \quad x \in S_2,\ t \in [0,T], \\
a|_{t=0} = a_0(x) \geqslant 0, \quad x \in \overline{\Omega}.
\end{gathered}$$

By using the positivity lemma (see [5, Lemma 2.1, p. 54]), we get, that $a(x,t) \geqslant 0$ $\forall (x,t) \in \overline{\Omega}\times[0,T]$.

Set

$$A = \max\left\{ \max_{x\in\overline{\Omega}} a_0(x), \max_{x\in S_2,\, t\in[0,T]} \frac{\kappa_1}{\kappa}\left(\frac{\theta(x,t)}{1-\theta(x,t)}\right)^2 \right\}$$

and $p = A - a$. Then

$$\begin{gathered} p_t - k\Delta p = 0, \quad x\in\Omega,\ t\in(0,T), \\ k\partial p/\partial n = 0, \quad x\in S_1,\ t\in[0,T], \\ k\partial p/\partial n + \kappa\rho^2(1-\theta)^2 p = \kappa\rho^2(1-\theta)^2\left(A - \frac{\kappa_1}{\kappa}\left(\frac{\theta}{1-\theta}\right)^2\right) \geqslant 0, \\ p|_{t=0} = A - a_0(x) \geqslant 0, \quad x\in\overline{\Omega}. \end{gathered}$$

According to positivity lemma, we can state, that $p(x,t)\geqslant 0$, $\forall x\in\overline{\Omega}$, $t\in\times[0,T]$. Hence, $a(x,t)\leqslant A$ and Lemma 2 is proved.

Remark 1. This lemma can also be proved using the same technique as in [2].

The proof of uniqueness of the classical solution is analogous to the proof of the same proposition in [2] (with trivial changes).

Now we give the scheme for the proof of the existence of the classical solution.

Let $\Omega_0 = \Omega$, if $a_0 = 0$ in any neighbourhood of surface S, and $\Omega_0 \supset \overline{\Omega}$, if a_0 is continuously differentiable in any neighbourhood of surface S. In the last case, we extend function a_0 on $\Omega_0 \setminus \overline{\Omega}$ preserving the same smoothness.

Let

$$a_i(x,t) = \int_0^t\int_S \Gamma(x,t,\xi,\tau)\varphi_i(\xi,\tau)\,dS_\xi\,d\tau + \int_{\Omega_0}\Gamma(x,t,\xi,0)a_0(\xi)\,d\xi, \quad i=1,2,\ldots$$

be a solution to problem (3) with $\theta=\theta_{i-1}$ and θ_i a solution to problem (2) with $a=a_i$, where

$$\Gamma(x,t,y,\tau) = \frac{1}{(4\pi k(t-\tau))^{n/2}} e^{-\frac{|x-y|^2}{4k(t-\tau)}}, \quad t>\tau,$$

is a fundamental solution to heat transfer equation (3) and φ_i is a solution to the integral equation

$$\begin{aligned} &\frac{1}{2}\varphi_i(\eta,t) + \int_0^t\int_S\left(\frac{\partial\Gamma(\eta,t,\xi,\tau)}{\partial n_\eta} + \frac{1}{k}\sigma(\eta,t,\theta_{i-1})\Gamma(\eta,t,\xi,\tau)\right)\varphi_i(\xi,\tau)\,dS_\xi\,d\tau \\ &\quad = \frac{1}{k}\psi(\eta,t,\theta_{i-1}) - \int_{\Omega_0}\left(\frac{\partial\Gamma(\eta,t,\xi,0)}{\partial n_\eta} + \frac{1}{k}\sigma(\eta,t,\theta_{i-1})\Gamma(\eta,t,\xi,0)\right)a_0(\xi)\,d\xi \end{aligned}$$

in cylinder $S\times[0,T]$,

$$\sigma(x,t,\theta) = \begin{cases} 0, & \text{if } (x,t)\in S_1\times[0,T], \\ \kappa\rho^2(x)(1-\theta(x,t))^2, & \text{if } (x,t)\in S_2\times[0,T], \end{cases}$$

$$\psi = \psi(x,t,\theta) = \begin{cases} 0, & \text{if } (x,t)\in S_1\times[0,T], \\ \kappa_1\rho^2(x)\theta^2(x,t)g(x,\theta(x,t)), & \text{if } (x,t)\in S_2\times[0,T]. \end{cases}$$

Finally, we get sequences: $\{a_i\}_{i=1}^{\infty}$, $\{\theta_i\}_{i=1}^{\infty}$. Similarly as in [2], we prove that sequence $\{a_i\}_{i=1}^{\infty}$ converges uniformly to its limit function a, $a \in C^{2,1}(\Omega \times (0,T]) \cap C(\overline{\Omega} \times [0,T])$ and this function is a classical solution to problem (3), sequence $\{\theta_i\}_{i=1}^{\infty}$ converges uniformly to its limit function θ, $\theta \in C([0,T] \times S_2)$, $\theta' \in C((0,T] \times S_2)$ and θ is a solution to Cauchy problem (2).

References

[1] A. Ambrazevičius. Exsistence and uniqueness theorem to a unimolecular heterogeneous catalytic reaction model. *Nonl. Anal.: Modell. Contr.*, **15**(4):405–421, 2010.

[2] A. Ambrazevičius. Solvability of a coupled system of parabolic and ordinary differential equations. *Centr. Eur. J. Math.*, **8**(3):537–547, 2010.

[3] J. Kankare and I.A. Vinokurov. Kinetics Langmuirian adsorption onto planar, spherical, and cilindrical surfaces. *Langmuir*, **15**:5591–5599, 1999.

[4] M.A. Lieberman. The langmuir isotherm and the standard model of ion-assisted etching. *Plasma Sources Sci. Technol.*, **18**:014002 (5pp), 2009.

[5] C.V. Pao. *Nonlinear Parabolic and Elliptic Equations.* Plenum Press, New York and London, 1992.

[6] V. Skakauskas and P. Katauskis. Numerical solving of coupled systems of parabolic and ordinary differential equations. *Nonl. Anal.: Modell. Contr.*, **15**(3):351–360, 2010.

[7] V. Skakauskas and P. Katauskis. Numerical study of the kinetics of unimolecular heterogeneous reactions onto planar surfaces. *J. Math. Chem.*, **50**(1):141–154, 2012.

REZIUMĖ

Apie vieną disociatyviosios adsorbcijos ir asociatyviosios desorbcijos matematinį modelį

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Nagrinėjamas dviatomių molekulių disociatyviosios adsorbcijos ir asociatyviosios desorbcijos matematinis modelis, aprašomas susieta parabolinių ir paprastųjų diferencialinių lygčių sistema. Įrodoma klasikinio sprendinio egzistavimo ir vienaties teorema.

Raktiniai žodžiai: Parabolinės ir paprastosios diferencialinės lygtys, paviršinės reakcijos.