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ACTIVE SURFACE AND TRANSFER PROCESSES
IN GASODYNAMICS

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In the works [1-5] for the description of gas transfer dynamics in the adsorbate-adsorbent open system we proposed a model in which, unlike the well-known sorption dynamics models, the interactions between adatoms and activated complexes (AC) are explicitly taken into account. The equations of the model for the dimensionless concentrations $\nu(\xi, \tau)$ in gas phase and $\theta(\xi, \tau)$ in sorbent look like:

$$v \frac{\partial \nu}{\partial \xi} + \frac{\partial \nu}{\partial \tau} + \frac{\partial \theta}{\partial \tau} = D \frac{\partial^2 \nu}{\partial \xi^2}, \quad (1)$$

$$0 < \xi < 1, \quad 0 < \tau = \frac{t}{\tau_0} \leq 1,$$

$$\frac{\partial \theta}{\partial \tau} = v_{ads} - v_{des} = \left\{ \frac{\nu}{ap_0} - 1 \right\} \Phi(T, \varepsilon, \varepsilon_1, z, \theta), \quad (2)$$

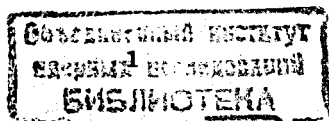
$$\frac{1}{ap_0} = \psi(\theta), \quad (3)$$

$$\nu(\xi, \tau = 0) = 0, \quad \theta(\xi, \tau = 0) = 0, \quad 0 \leq \xi \leq 1, \quad (4)$$

$$\nu(\xi = 0, \tau) = \alpha(\tau) = \nu_0, \quad (5)$$

$$\frac{\partial \nu(1, \tau)}{\partial \xi} = 0, \quad 0 < \tau \leq 1. \quad (6)$$

Here p_0 is the equilibrium pressure corresponding to the surface coverage θ , a is the adsorption coefficient, τ_0 -characteristical sorption time [2,3], v -gas average velocity, D -longitudinal diffusion coefficient, and through the $\Phi(T, \varepsilon, \varepsilon_1, z, \theta)$ we expressed the dependence of the adsorption v_{ads} and desorption v_{des} velocities on the surface coverage rate θ , temperature and the effective adatom-adatom ε , adatom-AC ε_1 interaction parameters. The function $\psi(\theta)$ in (3) is defined by the adsorption isotherms.



The eq.(2) we obtained on the basis of application of the quantum statistical Ising type Hamiltonian,

$$H = -\mu \sum_f N_f - \varepsilon \sum_{(fg)} N_f N_g, \quad (7)$$

to the adsorption and desorption of particles in the open system, which are interacted in the adsorbed states on a homogeneous surface [1,2].

In the works [2,3], within the framework of the proposed model, in three approximations of particle correlation effects, namely, in the molecular field approximation (MFA), quasichemical approximation (QCA) and polynomial fission (PF) the gas isotherms at different values of adatoms interaction parameter $\beta\varepsilon$ ($\beta = (k_B T)^{-1} (eV)^{-1}$) were obtained. The analysis of the calculated gas isotherms shows the essential nonlinear dependence of surface coverage rate θ on the gas concentration ν with the growth $\beta\varepsilon$ (the "strange attractors" regime) [2,3]. In [4], on the basis of the numerical solution the system of eqs.(1)- (6), for one-central physical adsorption a "hidden mechanism" of concentrational wave formation is founded that is owed to the parameter $\beta\varepsilon$. It is worth to note that the concentration jumps exist for the same values of $\beta\varepsilon$, when in the system the strange attractors appear. That is there is a certain correlation between these two regimes. The numerical results for the fixed values of the particles interaction energy ε (eV), such that

$$\beta\varepsilon = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5$$

are shown in the Fig.1 and Fig.2, respectively. The analysis of these results

shows that the adatoms interaction parameter $\beta\varepsilon$ influenced essentially on the surface coverage rates θ_s . Namely, with the increasing of $\beta\varepsilon$ we will come to the more greater saturation values of θ_s (Fig.1). On the contrary, the time τ , necessary to reach such ending saturation θ_s , decreased correspondingly to the same values $\beta\varepsilon$ (Fig.2). Thus, the adatom interactions in the stream+ adsorbate open system results in:

- 1) nonlinear evolutions of gas concentration ν in the stream;
- 2) various equilibrium values of concentration θ_s in the sorbent pores.

The more detailed analysis of these results with the regards of their application to the experimental data on physical adsorption in crystalline zeolites is given in [6]. In this report we generalize the above results assuming stochasticity of the transfer processes in an adsorbing system. This is naturally inasmuch as the transfer processes in many real physical systems goes under the influence of the spatial and temporary inhomogeneities. The stochastic process in the adsorbate- adsorbent open system we simulate by the introducing of the temporary adatom- adatom and adatom-AC random interactions:

$$\varepsilon \rightarrow \varepsilon(\tau) = n(\tau)\varepsilon_0, \quad \varepsilon_1 \rightarrow \varepsilon_1(\tau) = n(\tau)\varepsilon_{10}, \quad (8)$$

$$n(\varepsilon_0, \varepsilon_{10} = const).$$

In expression (8) n is a random variable, which values change in the interval $[0 \div 1]$. Distribution of n is given by the uniform pseudorandom number generator.

The system of nonlinear eqs. (1)-(6) in three approximations to adatoms interactions was solved numerically by difference methods [2,3]. It is worth to note that in the PF and QCA correlation effects are taken into account, but in MFA they are neglected:

a) PF approximation

$$\frac{\partial \theta}{\partial \tau} = \left\{ \frac{\nu}{ap_0} - 1 \right\} \sum_{k=0}^z \frac{y^k}{k!} F_k,$$

$$F_k = \sum_{m=k}^z R_m^k N_m, \quad y = \exp(\beta(\varepsilon_1 - \varepsilon)) - 1,$$

$$R_m^k = A_m^k C_z^m \theta^m (1 - \theta)^{z-m}, \quad N_m = [1 + (ap_0 \exp(\beta \varepsilon m))^{-1}]^{-1},$$

where $A_z^m = \frac{m!}{(z-m)!}$, $C_z^m = \frac{A_z^m}{z!}$ and the adsorption isotherm $\theta = \theta(ap_0)$ will be defined from the equality $F_0 = \theta$.

b) QCA

$$\frac{\partial \theta}{\partial \tau} = \left\{ \nu(1 - \theta)[1 - r + r \exp(-\beta \varepsilon)]^{-z} - \theta \right\} (1 + yr)^z,$$

$$r = \frac{\delta - 1 + 2\theta}{\delta + 1},$$

$$\delta = \sqrt{(1 - 2\theta)^2 + 4\theta(1 - \theta) \exp(\beta \varepsilon)},$$

c) MFA

$$\frac{\partial \theta}{\partial \tau} = \left\{ \nu(1 - \theta) \exp(z\beta \varepsilon \theta) - \theta \right\} (1 + y\theta)^z.$$

The evolutions of concentrations $\nu(\xi, \tau)$ and $\theta(\xi, \tau)$ we analysed in the enough large intervals of time $\tau \gg 1$, ($t \gg \tau_0$) and coordinate $\xi \gg 1$, ($x \gg L$). The calculations were carried out for the difference values of the

parameters $\beta \varepsilon_0$ and $\beta \varepsilon_{10}$. When the parameters $\beta \varepsilon$, $\beta \varepsilon_1$ change very quickly (Fig.3), the system "not catch" to respond to such a variation and we will have the same picture for $\nu(\xi, \tau)$, $\theta(\xi, \tau)$, as $\beta \varepsilon, \beta \varepsilon_1 = const$. Therefore, the random values of $\beta \varepsilon$ and $\beta \varepsilon_1$ were chosen with the some explicit duration $\tau^* = K \Delta \tau$, where $\Delta \tau$ is the discretization step of the difference scheme, and $K \gg 1$ (Fig.4). In Figs.5.1- 5.3 the results of calculations for ten moments of time in the interval $[0 \div 50]$ with the step $\tau = 5.0$ for $\beta \varepsilon_0 = 1.0, 1.5, 2.0$ and $\beta \varepsilon_{10} = 1.5, 2.0, 2.5$ (i.e. $(\delta \varepsilon)_0 = \varepsilon_{10} - \varepsilon_0 = 0.5$) are shown. From the Figs.5.1- 5.3 it is easily to see the irregular evolutions of the concentrations in gas stream and in sorbent. In that points, where one observes the increasing of $\theta(\xi, \tau)$, the concentration in gas phase $\nu(\xi, \tau)$ decreases. The calculation were carried out for $K = 100; 500; 1000; 10000$, and the dynamics of the system in all cases are nearly similar.

Thus, the introducing of the random interactions in the adsorbate- adsorbent open system change essentially the gas transfer dynamics and we observe the stable concentration wave formations in the system.

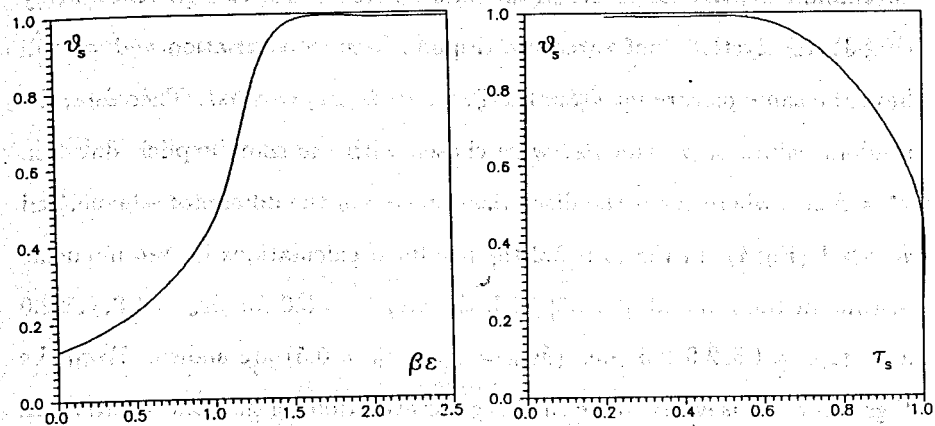


Fig.1

Fig.2

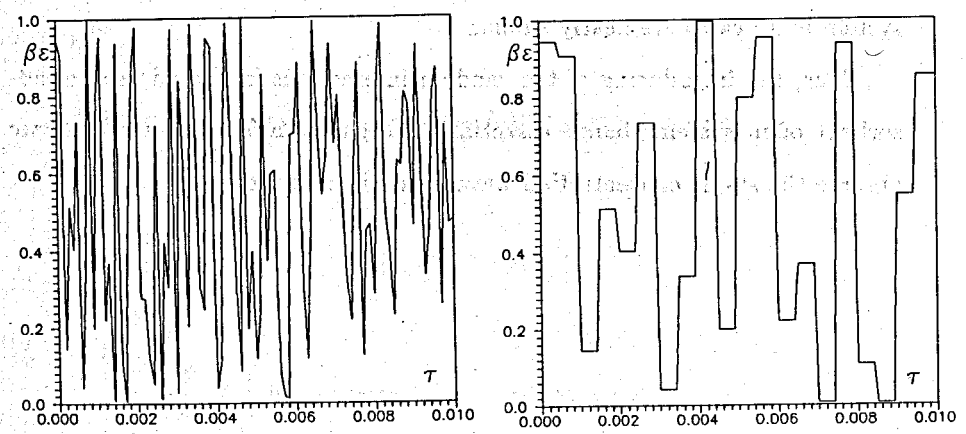


Fig.3

Fig.4

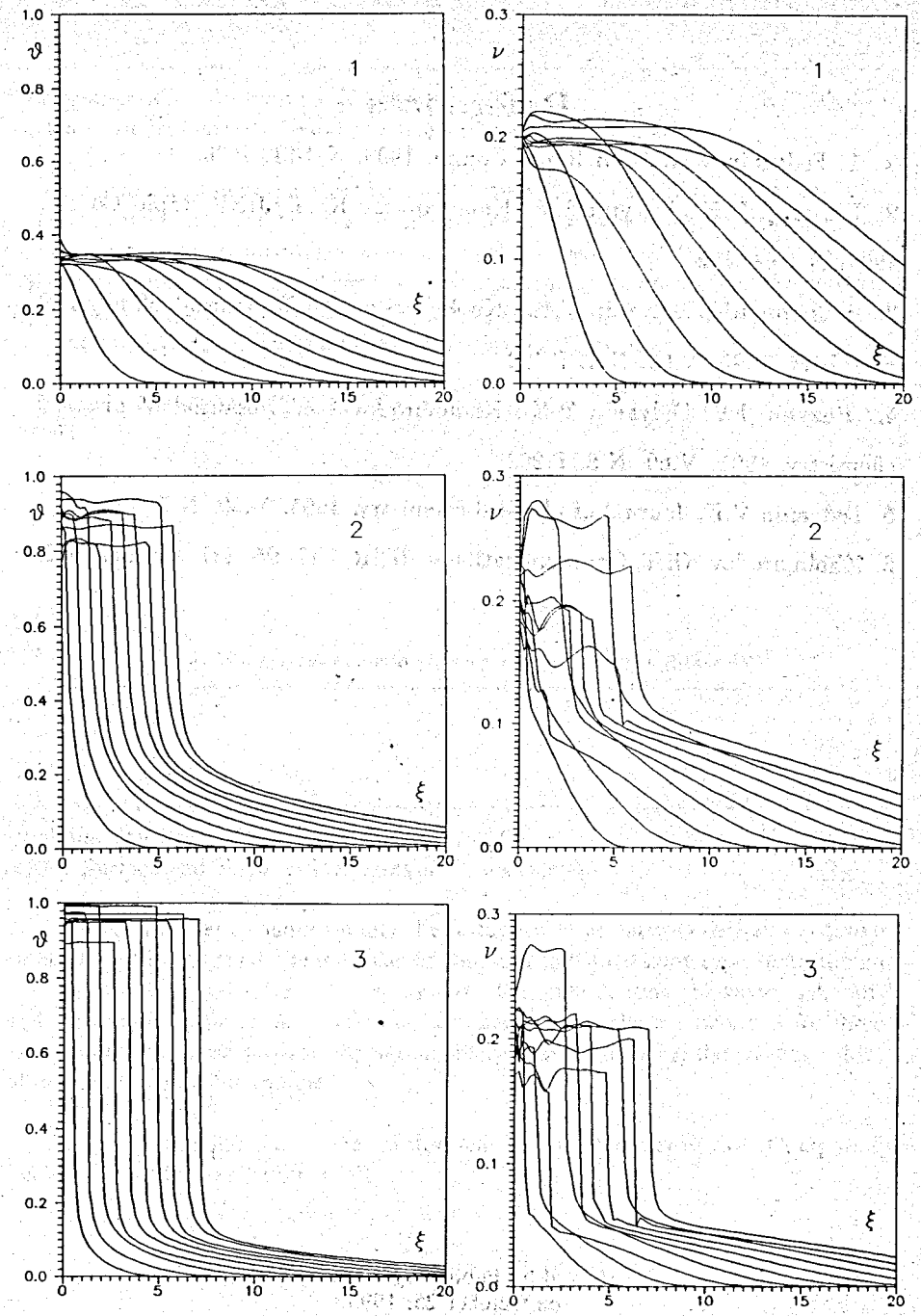


Fig.5.1-5.3

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