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Application of the Statistical Rate Theory of interfacial transport to investigate the kinetics of mixed-gas adsorption onto the energetically homogeneous and strongly heterogeneous surfaces

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ABSTRACT

Kinetics of mixed-gas adsorption by using the Statistical Rate Theory is studied. Applying the adsorption lattice model two cases are investigated: when adsorption occurs like on the homogeneous surface and when energetic heterogeneity of adsorption system can be described by the rectangular adsorption energy distribution function. The model of calculations offers possibility of theoretical prediction of the rate of adsorption/desorption of mixture components by using the single-gas equilibrium and kinetic data. Possible changes of adsorbate concentration near the adsorbing surface are also taken into account. The obtained theoretical expressions were verified using real adsorption systems.

1. Introduction

The use of adsorption phenomenon can be helpful in designing of modern chemical technologies which are friendlier for the environment. One of the examples are the gas separation and purification processes commonly used in industry. A very popular cryogenic method proposed by von Linde in 1895 can be replaced by modern technologies based on the idea of Skarstrom [9]. By passing gas mixture through the adsorption columns and suitably manipulating the pressures and directions of gas flow the mixture can be separated. This technique named Pressure Swing Adsorption (PSA) has been developed lately. In comparison to the Linde method PSA is less energy consuming, involves applying “soft” technological regimes and the purity of separated gases is similar to that obtained by the cryogenic method. PSA systems are controlled by computers so they are fully automated.

Industrial gas separation of gases by adsorption processes is usually based on the equilibrium properties of mixture components. Separation can be also performed by utilizing the kinetics of adsorption/desorption of mixture components. For example, if large differences between adsorption rates of components exist, one of them is quickly removed from a mixture.

In the present paper we focus our attention on the theoretical description of the time dependence of partial surface coverage of gas mixture components. To our knowledge only few papers devoted to this subject can be found [3]. The obtained results can be used in the computer software controlling PSA apparatus. As the conditions of gas separation process change quickly, it is necessary to determine very fast how to change the physical conditions of the process. The accuracy and quickness of this determination have major influence on the purity of separated gases.

As the theoretical tool we use the Statistical Rate Theory (SRT) proposed by Ward et al. [1,2]. SRT has been applied successfully to represent the rates of various interfacial transports, like the rate of gas adsorption at the liquid–gas interface [12–14], hydrogen adsorption by metals [15], electron exchange between ionic isotopes in solution [16], permeation of ionic channels in biological membranes [17], rate of liquid evaporation [18–20] and kinetics of adsorption on energetically heterogeneous surfaces [21–23]. Recently Azizian et al. [27] used SRT approach to study the kinetics of competitive adsorption at the solid/solution interface.

It is still one more reason for which we took interest in the problem of theoretical description of the kinetics of mixed-gas adsorption. Similarly to the adsorption equilibrium, the experimental measurement of adsorption rate of gas mixture components is difficult and time consuming in comparison to analogous measurements for pure gases. Theoretical predictions of mixed-gas adsorption equilibrium have been studied by us recently [4–6]. Generally, to predict theoretically predict the mixed-gas adsorption equilibrium, only information about single-gas isotherms is necessary. Such rule we try to adopt for the case of theoretical description of kinetics of mixed-gas adsorption.

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The present paper shows new theoretical expressions describing the rate of adsorption of mixture components for the case of homogeneous and strongly heterogeneous surfaces. While considering the heterogeneity effects we used the rectangular adsorption energy distribution function and the adsorption isotherms calculated by the Integral Equation approach and Condensation Approximation [6]. Finally, the proposed model of calculations will be verified by using the experimental kinetic data.

2. Kinetics of competitive gas adsorption on the energetically homogeneous surface

The Statistical Rate Theory approach is based on the assumption that adsorption rate is determined by the difference between the chemical potentials in gas and the adsorbed phases. While considering the case when two-component mixture of gases is adsorbed, the adsorption rate of component '1' can be described by the following equation:

$$\frac{d\theta_1}{dt} = K_{gs}\, p_1^{(e)}(1 - \theta_1^{(e)} - \theta_2^{(e)})\left[\exp\left\{\frac{\mu_1^g - \mu_1^s}{kT}\right\} - \exp\left\{\frac{\mu_1^s - \mu_1^g}{kT}\right\}\right] \quad (1)$$

where θ_i is the surface coverage of component '1', t is the time, μ_1^s and μ_1^g are the chemical potentials of given component in adsorbed and gas phases, respectively, K_{gs} is the so-called equilibrium exchange rate. The equilibrium state (e) is defined as the one in which a system isolated at the non-equilibrium pressure p_1 and the coverage θ_1 would evolve.

Theoretical investigations by Panczyk [3] show, that the correct description of the adsorption kinetics should take into account also the change of pressure of gas phase near the surface region. It is due to the fact that the surface removes the particles from near region and, after adsorption, they no longer contribute to the pressure in the slice of gas phase. This effect is growing especially when the adsorption process is fast. Below we show how to determine the expression for pressure change near the surface region. For that purpose we use the model of adsorption system proposed by Panczyk [3] (see Fig. 1).

It can be stated that the time-change of the number of molecules in the near surface region dn/dt is controlled by the bulk gas phase n_0 (the reservoir of the adsorbate) and the molecules which leave the near-surface region through the interface S_G, n_{S_G}, or are captured/released by the surface area S_A, n_{S_A}. Kinetic theory of gases predicts that the number of molecules passing through a given area S_G per unit time reads:

$$n_0 = \frac{S_G}{\sqrt{2\pi mkT}}\, p_0 \quad (2)$$

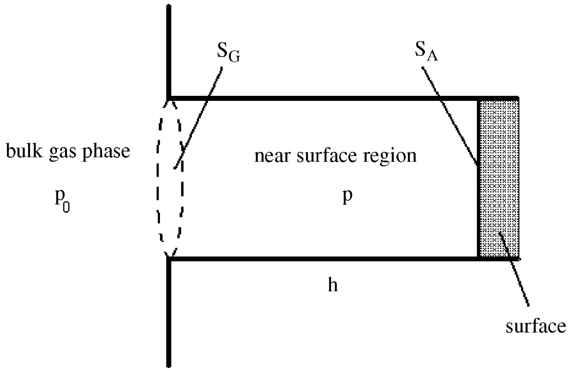

Fig. 1. Model of adsorption system showing different pressure regions during the adsorption process [3].

$$n_{S_G} = \frac{S_G}{\sqrt{2\pi mkT}}\, p \quad (3)$$

Next, the change of the adsorbate concentration in the near-surface region caused by adsorption n_{S_A} can be written:

$$n_{S_A} = \frac{d\theta}{dt} N_0 S_A \quad (4)$$

where N_0 is the number of adsorption centers per unit of surface area. The mass balance should be fulfilled

$$\frac{dn}{dt} = n_0 - n_{S_G} - n_{S_A} \quad (5)$$

By adopting the ideal gas law

$$\frac{dn}{dt} = \frac{dp}{dt}\frac{S_G h}{kT} \quad (6)$$

the pressure changes in the near surface region can be written as follows [3]:

$$\frac{dp}{dt} = \frac{S_G}{\sqrt{2\pi mkT}}(p_0 - p)\frac{kT}{S_G h} - \frac{d\theta}{dt} N_0 S_A \frac{kT}{S_G h} \quad (7)$$

The above equation can be written in the simplified form:

$$\frac{dp}{dt} = \alpha(p_0 - p) - \beta\frac{d\theta}{dt} \quad (8)$$

where α and β are the temperature-dependent parameters and p_0 is the bulk phase pressure of a given component. From the practical point of view α and β can be treated as the best-fit parameters improving agreement between theory and experimental data.

In the simplest case when adsorption occurs like on the energetically homogeneous surface, the chemical potential of component '1' in the adsorbed phase can be expressed as follows:

$$\mu_1^s = kT\ln\frac{\theta_1}{(1 - \theta_1 - \theta_2)K_1} \quad (9)$$

where $K_1 = q_{01}^s \exp\{\varepsilon_1/kT\}$ and q_{01}^s is the molar partition function of the adsorbed molecules.

If we assume that the gas phase is ideal, the chemical potential has the well-known form:

$$\mu_1^g = \mu_{01}^g + kT\ln p_1 \quad (10)$$

To build up a set of equations describing the process of two-component adsorption it is necessary to concentrate on the experimental procedure which is to be described. Rudzinski and Panczyk [7] have considered the three extreme cases:

1. "Volume-dominated"—in the non-equilibrium adsorption process the gas in the gaseous phase above the surface exceeds the amount of adsorbed portion significantly. In that case, after the system is isolated and equilibrated, the gas pressure p does not change much so $p^{(e)} = p$,
2. "Surface-dominated"—in the non-equilibrium process the adsorbed amount strongly prevails the amount of gas in the gas phase. After isolating and equilibrating θ remains practically unchanged i.e. $\theta^{(e)} = \theta$,
3. "Equilibrium-dominated"—the process is carried out under such conditions that the gas/solid system is close to equilibrium. In this case it may assume $\theta^{(e)} = \theta$ and $p^{(e)} = p$.

If we assume that the adsorption process is performed, the volume-dominated model should be used. It implies the following form of the functions $\theta_1^{(e)}$ and $p_1^{(e)}$:

$$1 - \theta_1^{(e)} - \theta_2^{(e)} = (1 + K_1 p_1 + K_2 p_2)^{-1} \quad (11)$$

and $p_i^{(e)} = p_i$.