

Adsorption of gas mixtures on homogeneous surfaces Extension of Jovanović equation on multilayer adsorption

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The Jovanović equation of multilayer adsorption isotherm on homogeneous surfaces is extended on a case of adsorption from gaseous mixtures. For small partial pressure of components, the proposed equation is reduced to González—Holland adsorption isotherm.

Уравнение Йовановича для многослойной адсорбционной изотермы на гомогенных поверхностях было приспособлено и для случая адсорбции из газообразных смесей. Для небольших парциальных давлений компонент предлагаемое уравнение было приведено к адсорбционной изотерме Гонзалез—Холланда.

From the theoretical papers which have been published on adsorption of gas mixtures only a few of them consider the multilayer adsorption [1—8]. The reason for this is the well-known difficulty in formulating a sound theoretical description of multilayer adsorption in the case of pure gases. In [1—4] the BET adsorption model was extended to adsorption of gas mixtures on homogeneous surfaces. It follows from the papers [1—4] that exact extension of BET equation to mixed-gas adsorption leads to very complicated expression. This expression assumes exceptionally simple form in the case of constancy of y_i , where y_i is the mole fraction of the i -th gas in the bulk phase [4]. For $y_i = \text{const}$, the BET model gives the following adsorption isotherm for binary gas mixtures [4]

$$\Theta_M = (1 - x)^{-1} \frac{\bar{c}x}{1 - x + \bar{c}x}, \quad (1)$$

where

$$\bar{c} = (x_1 + x_2)^{-1} (c_1 x_1 + c_2 x_2), \quad (2)$$

$$x = x_1 + x_2, \quad (3)$$

and

$$x_i = y_i p / p_{0i}; \quad i = 1, 2. \quad (4)$$

In the above Θ_M is the relative multilayer surface coverage; c_1 and c_2 are the BET constants for pure gases 1 and 2, respectively; p_{01} and p_{02} are the saturation vapour pressures of the components 1 and 2, respectively; and, p is the total pressure of gaseous mixture.

Arnold [4] examined eqn (1) using the experimental adsorption data of nitrogen—oxygen mixture on anatase at 78 K. These data were measured for different percentage content of oxygen in mixture: 15, 30, 50, 70, and 85%. Thus, the mole fractions of oxygen and nitrogen in the bulk phase were constant for the given content of oxygen in mixture. It follows from [4] that eqn (1) gives poor agreement with experimental data. The reason of this is imperfection of the customary BET equation.

Interesting model for multilayer adsorption of gas mixtures on homogeneous surfaces has been recently proposed by *Gonzalez and Holland* [5, 6]. An additional assumption to the BET ones was made by them, which led to a simple form of bilayer adsorption isotherm of n -component gas mixture [5]

$$\Theta_M = \left(1 + \sum_{i=1}^n a_{2i} p_i\right) \frac{\sum_{i=1}^n a_{1i} p_i}{1 + \sum_{i=1}^n a_{1i} p_i}, \quad (5)$$

where p_i is the partial pressure of the i -th gas, a_{1i} and a_{2i} are the constants connected with the molecular partition functions of the i -th gas for molecules adsorbed in the first and second layer, respectively. In [8], the adsorption isotherm (5) has been generalized to adsorption of binary gas mixtures on heterogeneous surfaces.

In a number of recent papers describing the physical adsorption of pure gases on solids, the *Jovanović's* adsorption model [9, 10] was widely discussed [11—15]. It follows that for many adsorption systems the *Jovanović* adsorption isotherms give satisfactory agreement with the experimental data in a wide range of adsorbate pressures.

Recently, the *Jovanović* monolayer adsorption isotherm [9] on homogeneous surfaces has been extended to adsorption of gas mixtures [16]. According to [16] the monolayer surface coverage Θ for n -component gas mixture can be expressed as follows

$$\Theta = 1 - \exp\left(-\sum_{i=1}^n a_{1i} p_i\right). \quad (6)$$

Eqn (6) for binary gas mixtures assumes the form

$$\Theta = 1 - \exp(-a_{11}p_1 - a_{12}p_2). \quad (7)$$

The last equation has been adopted to describe the monolayer adsorption of binary gas mixtures on patchwise heterogeneous surfaces [17]. In both, homogeneous and heterogeneous approximations, eqns (6) and (7) will predict the adsorption equilibria of many gas mixtures by means of the pure-gas adsorption parameters.

In this paper the possibilities of extension of the monolayer isotherms (6) and (7) to multilayer mixed-gas adsorption on homogeneous surfaces will be discussed. It will be shown that a simple equation of adsorption isotherm can be obtained by means of the Gonzalez and Holland expression (5).

The analytical form of eqn (5) may be presented by formula

$$\Theta_M = g(p_1, p_2, \dots, p_n) \Theta(p_1, p_2, \dots, p_n), \quad (8)$$

where $g(p_1, p_2, \dots, p_n)$ is a function describing the formation of mixed n -component multilayer. The form (8) of multilayer adsorption isotherm of gas mixtures is similar to multilayer isotherms of pure gases [18].

For the Jovanović adsorption model [9, 14] the function $g(p_1, p_2, \dots, p_n)$ may be expressed by equation

$$g(p_1, p_2, \dots, p_n) = \exp\left(\sum_{i=1}^n a_{2i}p_i\right). \quad (9)$$

Using eqns (8), (6), and (9) we obtain the following adsorption isotherm

$$\Theta_M = \exp\left(\sum_{i=1}^n a_{2i}p_i\right) \left[1 - \exp\left(-\sum_{i=1}^n a_{1i}p_i\right)\right] \quad (10)$$

for n -component mixtures, which in the case of binary gas mixtures assumes the following form

$$\Theta_M = \exp(a_{21}p_1 + a_{22}p_2) [1 - \exp(-a_{11}p_1 - a_{12}p_2)]. \quad (11)$$

It can be easily shown that the Gonzalez and Holland adsorption isotherm (5) is the special case of eqn (10), when the partial pressures p_i ($i = 1, 2, \dots, n$) tend to zero.

The mixed-gas adsorption isotherms are frequently measured at certain parameter which is kept constant [4, 19, 20].

In the introduction it was mentioned, that the mixed-gas adsorption isotherms assume very simple forms for $y_i = \text{const}$. Then, in eqns (5), (6), (9), and (10) the expressions

$$\sum_{i=1}^n a_{ki} p_i \quad \text{for } k = 1, 2$$

can be replaced by

$$p \sum_{i=1}^n a_{ki} y_i = \bar{a}_k p.$$

In the above

$$\sum_{i=1}^n a_{ki} y_i$$

can be treated as a certain mean parameter \bar{a}_k ; whereas $p = \sum_{i=1}^n p_i$.

Thus, for $y_i = \text{const}$ ($i = 1, 2, \dots, n$) eqn (10) can be rewritten as follows

$$\Theta_M = \exp(\bar{a}_2 p) [1 - \exp(-\bar{a}_1 p)]. \quad (12)$$

Then, the total surface coverage Θ_M (12) is the function of the total pressure only. Equation (12) is formally identical with the multilayer adsorption isotherm of the i -th gas.

Let us consider now eqn (12) for describing the nitrogen—oxygen adsorption on anatase [4]. It was mentioned earlier that BET eqn (1) describes unsatisfactorily this adsorption system.

Assuming *Jovanović's* simplifications [10], eqn (12) for binary gas mixtures can be expressed in the following linear form

$$\ln N = \ln N_0 + \bar{a}_2 p \quad \text{for } p/p_0 > 0.25, \quad (13)$$

where

$$1/p_0 = y_1/p_{01} + y_2/p_{02} \quad (14)$$

and

$$\Theta_M = N/N_0. \quad (15)$$

The experimental data of nitrogen—oxygen adsorption on anatase [4] were plotted according to eqn (13) by *Jovanović* [10]. It follows from *Jovanović's* paper [10] that the plots (13) for these adsorption systems showed excellent linear behaviour. This result indicates that both eqns (13) and (10) should give satisfactory agreement with experimental data for many adsorption systems. Evidently, the mixed-gas adsorption systems should satisfy the assumptions of *Jovanović* adsorption model [9].

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