Analysis of multilayer adsorption of oxygen—nitrogen mixtures on anatase

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A theoretical analysis of multilayer adsorption of a mixture of gases O_2 and N_2 on an amorphous surface of anatase (TiO_2) was carried out. Equations of the theory are based on the lattice-gas model. Intermolecular interactions between the closest neighbors were taken into account in the mean-field approximation. The energy parameters of these interactions were determined from the data on the vapor—liquid equilibrium. The calculation of the mixed adsorption was preceded by the description of multilayer adsorption of individual gases. The model describes adequately the overall and partial isotherms of multilayer adsorption of a mixture of gases provided that (1) the roughness of the adsorbent surface is taken into account in a simplified way and (2) the relationships between the heats of adsorption of the O_2 and N_2 molecules on various sites of the heterogeneous surface of anatase are similar.

Key words: multilayer adsorption, isotherm, mixed adsorption, oxygen/anatase, nitrogen/anatase, lattice model.

Adsorption of a mixture of nitrogen and oxygen has been studied experimentally;[1] however, a model suitable for theoretical description of adsorption of binary mixtures is lacking.[2,3] In the present paper, experimental isotherms of the multilayer adsorption of an $N_2 + O_2$ mixture on an amorphous surface of anatase (TiO_2) have been interpreted using the recently developed theory of multilayer adsorption of mixtures of gases on heterogeneous surfaces,[4,5] based on the lattice-gas model. The theory takes into account local heterogeneities of the surface and pair interactions between the adsorbed molecules as well as interactions of the adsorbed molecules with the substrate at arbitrary distances.

Fundamentals of the lattice-gas model

According to the lattice model, the near-surface layer of a gas—solid interface is broken up into a number of monomolecular layers arranged parallel to the interface plane. The description of the structure of the transition region is based on a strict succession of the layers beginning with the first (surface) layer and ending with the last layer of this region ξ in which molecules are arranged virtually in the same way as in the bulk (here $\xi = L_0/d$, where L_0 is the width of the near-surface region, and d is the average diameter of molecules in the mixture). The space inside each layer is broken up into sites having a characteristic size close to the diameter of the molecules.[4—7] In the present paper we have considered the case where the components of the mixture have approximately identical sizes. The distinctions in the types of sites in the near-surface region are due to the heterogeneity of the surface and to the jump in the density in the near-surface region. The density jump is caused by the interaction of the adsorbent with an adsorbate and occurs in the case of a homogeneous surface as well. If there are dispersion or chemical interactions, their effect extends to a small number of monolayers. The heterogeneity of the surface is associated with the differences in the adsorbate—adsorbent interactions in various sites of the first monolayer. (It is also manifested in the overlying layers, but to a lesser degree.) The type of sites of the near-surface region is characterized by the number of a layer k and by the interaction potential (bond energy) of a molecule i with the adsorbent $Q_q^i(k)$, which is related to the local Langmuir constant: $a_q^i(k) = \hat{a}_q^i(k)\exp[\beta Q_q^i(k)]$, where $\hat{a}_q^i(k)$ is the pre-exponent of the local Langmuir constant; $\beta = (kT)^{-1}$.

Let us denote the number of types of sites located in the layer k by t_k. For each layer we introduce its own distribution functions characterizing the composition of the layer $f_q(k)$ and its structure d_{kn} (qp):

$$\sum_{q=1}^{t_k} f_q(k) = 1, \quad \sum_{q=1}^{t_k} d_{kn}(qp) = 1, \qquad (1)$$

where $f_q(k)$ is the fraction of type q sites located in the layer k, $\xi \geq k \geq 1$; $d_{kn}(qp)$ is the probability of a type p site in the layer n located in the near-surface region near a type q site in the layer k, $n = k, k\pm1$.

Let us denote the molar fraction of the filling of type q sites in the layer k with molecules i by $\theta_q^i(k)$; then the

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partial fillings θ_i of the layer k and of the whole near-surface region with these molecules will be written as

$$\theta_i(k) = \sum_{q=1}^{l_k} f_q(k)\theta_q^i(k), \quad \theta_i = \sum_{k=1}^{\xi}\theta_i(k)L_k/L, \qquad (2)$$

$$L = \sum_{k=1}^{\xi} L_k ,$$

where L_k is the ratio of the number of sites in the layer k to that in the layer ξ in the bulk of the gas phase, which may be dissimilar due to the structural heterogeneity of the surface (for example, due to its roughness) and due to the different structures of the adsorption solution near the surface and in the bulk. The complete filling of the layer k and of the near-surface region as a whole is found in the following way (s is the number of components of the mixture):

$$\theta(k) = \sum_{i=1}^{s}\theta_i(k), \quad \theta = \sum_{i=1}^{s}\theta_i = \sum_{k=1}^{\xi}\theta(k)L_k/L. \qquad (3)$$

The overall number N_i of molecules i and their excess Γ_i in the near-surface region are determined as follows:

$$N_i = L\theta_i N_\xi, \quad \Gamma_i = N_\xi \sum_{k=1}^{\xi}[\theta_i(k) - \theta_i(\xi)]L_k , \qquad (4)$$

where N_ξ is the number of sites in a homogeneous monolayer in the bulk of the gas phase. To calculate the distributions of values (2)—(4) one should know the $\theta_q^i(k)$ values, which are defined by the corresponding algebraic equations. Let us restrict ourselves to the simplest variant of the theory. We shall take into account the interactions between the closest neighboring molecules ε_{ij} (i, j = a, b; where symbol "a" refers to the oxygen molecule, and symbol "b" refers to the nitrogen molecule) in the mean-field approximation and assume that the energy parameters do not depend on the types of sites over which the O_2 and N_2 molecules are located. In this case, the equations for the mixed multilayer adsorption on a heterogeneous surface in the mean-field approximation assume the form

$$a_q^i(k)P_i\theta_q^v(k) = \theta_q^i(k)\exp\left[-\beta\sum_{n=k-1}^{k+1}\sum_{p=1}^{l} Z_{kn}(qp)\sum_{j=1}^{s}\varepsilon_{ij}\theta_p^j(n)\right], \qquad (5)$$

where $\theta_q^v = 1 - \sum_{i=1}^{s}\theta_q^i(k)$, $Z_{kn}(qp) = Z_q(k)d_{kn}(qp)$, and $Z_q(k)$ is the number of neighboring sites surrounding a type q site in the layer k.

The amorphous surface of anatase has a complex structure at the atomic level, which is not known in detail. Based on general considerations concerning amorphous surfaces, the following assumptions were made: (1) the number of various types of sites of a heterogeneous surface is great, and continuous distribution functions $f_k^i(\varepsilon_k^i)$ may be used to specify the composition of each layer of the near-surface region; (2) the sites of various types are distributed randomly; this makes it possible to present $d_{kn}(\varepsilon_1, \varepsilon_2)$, which is the continuous analog ($q \Rightarrow \varepsilon^1$, $p \Rightarrow \varepsilon^2$) of the $d_{kn}(qp)$ discrete functions (1), as $d_{kn}(\varepsilon^1, \varepsilon^2) = f_n(\varepsilon^2)$; (3) the anatase surface is somewhat rough at the atomic level.

The equations of the lattice model[4,5] make it possible to take into account the detailed structure of a rough surface (see Ref. 8), but in order to simplify the calculations, we shall use the following simple variant of the model. We shall consider that in Eqs. (2)—(4), $L_k = L$, but the lattice structure is defined by the quantities Z_{kn} that characterize the average numbers of neighbors in layer n with respect to the layer k ($Z_{k,k+1} = Z_{k,k-1}$, $Z_{kk} = Z - 2Z_{k,k+1}$). In addition, we set Z (the number of neighbors in the lattice structure) equal to 6. Varying the Z_{kk} value (<4) reflects the surface roughness in an averaged way (for a planar adsorbent surface, $Z_{kk} = 4$). Thus we obtain the corresponding set of equations:

$$a_k^i(\varepsilon)P_i = \frac{\theta_k^i(\varepsilon)\exp[-\beta\sum_{n=k-1}^{k+1}Z_{kn}(\varepsilon_{ia}\theta_k^a + \varepsilon_{ib}\theta_k^b)]}{1 - \theta_k^a(\varepsilon) - \theta_k^b(\varepsilon)}, \qquad (6)$$

$$\theta_k^i = \int_{\varepsilon_{k,\min}^i}^{\varepsilon_{k,\max}^i} f_k^i(\varepsilon_k^i)\theta_k^i(\varepsilon_i)\mathrm{d}\varepsilon_i .$$

To calculate the mixed adsorption of O_2 and N_2 one should determine the parameters of the lateral interaction of molecules ε_{ij} and the functions of the distribution of sites in the layers of the near-surface region $f_k^i(\varepsilon_k^i)$ for molecules of various sorts.

Parameters of the lateral interaction

Experimental data[1] on the multilayer adsorption of a mixture of gaseous O_2 and N_2 on an amorphous anatase surface include information concerning mixtures of various compositions (T = 78.2 K): Y_a = 0.149 (I), 0.298 (II), 0.502 (III), 0.702 (IV), and 0.853 (V), where Y_i is the mole fraction of the component i in the gas phase, index "a" refers to the oxygen molecules, and index "b" refers to the nitrogen molecules, $Y_a + Y_b = 1$, and also concerning the pure components (V_m = 288 cm^3 for oxygen and V_m = 305 cm^3 for nitrogen, where V_m is the capacity of a monolayer).

The ε_{ij} parameters were determined using the experimental data on the bulk gas—liquid phase equilibrium of a mixture of oxygen and nitrogen for the same compositions of the gas mixture, for which adsorption was studied. Like the description of adsorption, the calculation of the phase equilibrium can be carried out by using lattice models[9,10]. For a binary mixture consisting of O_2 and N_2, each structure site has three states of occupation: it can be occupied by oxygen (i = a), by nitrogen

(i = b), or be vacant (i = v). Phase equilibrium is described by the equations

$$\mu_g{}^i = \mu_l{}^i,\ i = \text{a, b, v};\ \sum_{i=a}^{v}\theta_\alpha^i = 1,\ \alpha = \text{g, l},$$

where $\theta_\alpha{}^i$ is the fraction of a component i in the α phase, $\mu_\alpha{}^i$ is the chemical potential of the component i in the α phase; in the mean-field approximation we obtain[9]

$$\beta\mu_a{}^i = \beta\mu_a{}^{i,0} + \ln(\theta_a{}^i g_a{}^i), \qquad \mu_g{}^{i,0} = \mu_l{}^{i,0}, \tag{7}$$

$$\ln\gamma_\alpha{}^a = b_{ab}(\theta_\alpha{}^b)^2 + b_{av}(\theta_\alpha{}^v)^2 + \theta_\alpha{}^b\theta_\alpha{}^v(b_{ab} - b_{bv} - b_{av}),$$

$$b_{ab} = Z(\varepsilon_{aa} + \varepsilon_{bb} - 2\varepsilon_{ab})/2.$$

Expressions for $\gamma_\alpha{}^b$ and $\gamma_\alpha{}^v$ can be obtained from the expression for $\gamma_\alpha{}^a$ by cyclic permutation of indices a, b, and v. For pure components, set (7) leads to the known expression[9,11] $\hat{a}_g{}^i p_0{}^{i*} = \exp[-\beta Z\varepsilon_{ii}/2]$, where $p_0{}^{i*}$ is the saturated vapor pressure for the component i. Fixing the $Y_a = \theta_g{}^a/(\theta_g{}^a + \theta_g{}^b)$ value relates $\theta_g{}^a$ to $\theta_g{}^b$, which makes it possible to solve the set of equations (7) and then to calculate partial saturated vapor pressures from the equations of the lattice model: $p_0^i = \theta_\alpha^i \exp[-\beta Z\sum_{j=a}^{v}\varepsilon_{ij}\theta_\alpha^j]/(\hat{a}^i\theta_\alpha^v)$, and also to determine the overall pressure $p_0 = p_0{}^a + p_0{}^b$. The fitted parameters of the model are $\hat{a}_g{}^a$, $\hat{a}_g{}^b$, ε_{aa}, ε_{ab}, and ε_{bb} ($\varepsilon_{iv} = 0$ for i = a, b, v, the interactions with vacancies are equal to zero). After normalization of the $p_0{}^i$ values to $p_0{}^{i*}$, $\hat{a}^a/\hat{a}^b$, ε_{aa}, ε_{ab}, and ε_{bb} remain as the fitted parameters. These values were selected using the data on the vapor—liquid equilibrium[1] for seven compositions of the gas phase (Y_a) including pure components. The $\hat{a}^b$ value was determined as $\hat{a}^b = \exp[-\beta Z\varepsilon_{bb}/2]/p^{b*}{}_{0,exp}$. The following values for these parameters were found: $\hat{a}_g{}^a = 6.77\cdot10^{-5}$ and $\hat{a}_g{}^b = 7.44\cdot10^{-5}$ Torr^{-1}, $\beta\varepsilon_{aa} = 1.470$, $\beta\varepsilon_{ab} = 1.162$, $\beta\varepsilon_{bb} = 0.924$. The accuracy of interpretation of the data on the gas—liquid equilibrium of a mixture of oxygen and nitrogen on anatase for seven gas-phase compositions with these parameters is illustrated by Table 1. Subsequently, these parameters were not varied in the description of individual and partial isotherms of the components of the mixture. Note that the ε_{ij} parameters found are in good agreement with the traditional combination rule $\varepsilon_{ab} = (\varepsilon_{aa}\varepsilon_{bb})^{1/2}$, because the molecular properties of these gases are similar, and the Raoult law is obeyed to a rather high degree of accuracy.[1]

Table 1. Results of the calculation of bulk gas—liquid equilibrium for a mixture of oxygen and nitrogen on anatase (X_l is the concentration of oxygen in the liquid phase)

Y_a	$X_{l,calc}$	$X_{l,exp}$	$p_0/p_0{}^{b*}$(calc.)	$p_0/p_0{}^{b*}$(exp.)
0.000	0.000	0.000	1.000	1.000
0.149	0.430	0.434	0.686	0.692
0.298	0.680	0.677	0.498	0.498
0.502	0.847	0.846	0.357	0.352
0.702	0.932	0.931	0.280	0.277
0.853	0.972	0.971	0.242	0.241
1.000	1.000	1.000	0.214	0.214

Adsorption of individual components

To determine the character of the heterogeneity of the anatase surface, three types of distribution functions were considered: a uniform function $f_k{}^i(\varepsilon_k{}^i) = (\Delta\varepsilon_k{}^i)^{-1}$, $\Delta\varepsilon_k{}^i = \varepsilon^i{}_{k,max} - \varepsilon^i{}_{k,min}$; an exponential function $f_k{}^i(\varepsilon_k{}^i) = \exp(\gamma_i\varepsilon_k{}^i)/m_i$, where γ_i and m_i are the distribution parameter and the normalizing factor for component i; and a Gaussian function $f_k^i(\varepsilon^i{}_k) = \exp[-(\varepsilon^i{}_k - \hat{\varepsilon}^i{}_k)^2/2\sigma^i{}_k]$, where $\hat{\varepsilon}^i{}_k = \varepsilon^i{}_{k,min} + b_i\Delta\varepsilon_k{}^i$ characterizes the position of the function maximum by the b_i ($0 \le b_i \le 1$) parameter, and σ_i is the peak half-width. We assume that $a^i(\varepsilon) = \hat{a}^i\exp[\beta\varepsilon_k{}^i(\varepsilon_k{}^L)]$, where $\varepsilon_k{}^i(\varepsilon_k{}^L)$ is a function that relates the heat of adsorption of the component i to that of a reference component L, for which the distribution function of the adsorbent surface, used for the calculation of the adsorption of the mixture, is constructed. Obviously, when $i = L$, we obtain $\varepsilon_k{}^i(\varepsilon_k{}^L) = \varepsilon_k{}^L$ (see Refs. 13—15). To decrease the number of independent parameters of the model, a power law for the decrease of the adsorbate—adsorbent potential for various layers was used: $\varepsilon_k{}^i = \varepsilon_l{}^i/(k)^{ni}$, where n_i is a parameter. (This potential is an analog of the attracting part of the Lennard—Jones potential 3—9 and 4—10 for planar surfaces. The solid sphere of the lattice sites takes into account the repulsive contribution of the Lennard-Jones potential.) Then the n_i values and parameters of the distribution function of the first layer are the fitted parameters. From here on, the number of the layer k = 1 will not be marked by indices.

The unknown values $\varepsilon^i{}_{max}$ and $\varepsilon^i{}_{min}$ and other parameters of the distribution functions were determined from the individual adsorption isotherms. Three pressure regions can be distinguished on the experimental iso-

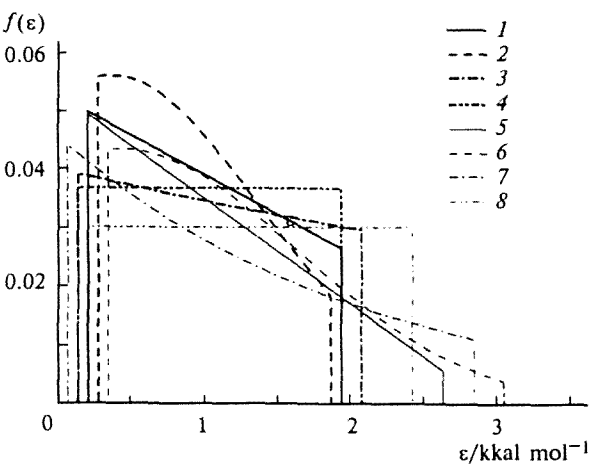

Fig. 1. Functions of distribution over energy of the interaction with anatase for molecules of oxygen (*1—4*) and nitrogen (*5—8*) calculated in terms of the lattice model: trapezoidal (*1*, *5*), Gaussian (*2*, *6*), exponential (*3*, *7*), uniform (*4*, *8*).

Table 2. Parameters of the individual adsorption isotherms of oxygen and nitrogen on anatase

$f(\varepsilon)$	Gas	ε_{max} /kcal mol^{-1}	$\hat{a} \cdot 10^4$ /Torr^{-1}	ε_{min} /kcal mol^{-1}	δ	B	n	%*	%
Exponential	O_2	2.14	6.70	0.12	−0.14	—	2.80	4.30	6.80
($\delta = \gamma$)	N_2	2.90	3.52	0.07	−0.49	—	4.40	5.10	8.00
Gaussian ($\delta = \sigma$)	O_2	1.94	5.08	0.26	1.02	0.007	2.70	4.20	7.60
	N_2	3.13	0.60	0.33	1.22	0.037	4.70	2.30	4.73
Uniform	O_2	2.00	6.03	0.12	—	—	2.70	4.04	7.30
	N_2	2.50	0.64	0.15	—	—	4.40	5.05	6.00
Trapezoidal	O_2	1.96	5.08	0.15	0.38	—	2.40	5.32	8.46
($\delta = f_{max}$)	N_2	2.70	2.53	0.20	0.08	—	4.40	4.60	5.27

therms of both gases: 1) $x \le 0.006$, 2) $0.006 < x \le 0.13$, 3) $0.13 < x \le 0.95$. In the first region, a coverage of the surface θ_i of ~ 1/3 is rapidly attained, and in the second region, the surface monolayer is gradually filled, with no substantial filling of the second layer. In the third region, filling of the second layer and overlying layers occurs. In these regions, the following parameters were successively determined: (1) ε^i_{max}, $\hat{a}^i$; (2) ε^i_{min}, γ_i or b_i, σ_i; and (3) n_i, Z_{kk}. The results of the selection of these parameters are presented in Table 2, and the distribution functions of nitrogen and oxygen, obtained from these data at $x \le 0.13$, are shown in Fig. 1. The accuracy of the description was characterized by the divergence between the calculated and experimental isotherms: $\% = \frac{100\%}{N}\sum_{i=1}^{N}|\theta_i(x)_{exp} - \theta_i(x)_{calc}|$, where N is the number of experimental points used for the selection. The symbol "%*" marks results that refer to the monolayer filling, and "%" denotes results referring to the multilayer filling. We obtained $Z = 2 \pm 0.04$. The parameters found ensure a relatively high accuracy of the agreement between the calculated and experimental isotherms (Fig. 2, *a*, *b*). The uniform function of distribution provides a worse description of the monolayer filling. Figure 1 shows that the exponential and Gaussian distribution functions correlate qualitatively with each other both for nitrogen and for oxygen: the ε^b_{min} and ε^b_{max} values for both functions are close to each other, and both functions virtually monotonically decrease.

This behavior of the distribution functions is in good agreement with the concept of the similarity of molecular properties of these gases. For a more detailed analysis of the distribution functions of the anatase surface, one may additionally consider a trapezoidal function located between the exponential and Gaussian curves and can also estimate the ranges of variation of the parameters of the distribution functions, corresponding to an accuracy of description of ~8 %, which matches the accuracy of the experimental measurements of 5—8 %. The former proposal should provide a noncontradictory solution, compared to the found exponential and Gaussian solutions, and the latter proposal makes it possible to elucidate the parameter sensitivity of various solutions.

The trapezoidal distribution function has the form $f_i(\varepsilon_i) = (E_i - f^i_{max}) - (\varepsilon_i - \varepsilon^i_{min})(E_i - 2f^i_{max})/\Delta\varepsilon_i$, $E_i = 2/\Delta\varepsilon_i$, where $f^i_{max} = f(\varepsilon^i_{max})$. The parameters of this distribution are the following: f^i_{max}, ε^i_{max}, and ε^i_{min}. The parameters found are given in Table 2, and the distribution functions are shown in Fig. 1. All three of these functions (Gaussian, trapezoidal, and exponential) for each gas are in good agreement with each other.

Table 3 presents the ranges for the parameters of four functions of distribution and the n values corre-

Table 3. Ranges for the values of the parameters of individual adsorption isotherms of oxygen and nitrogen on anatase

$f(\varepsilon)$	Gas	$\hat{a} \cdot 10^4$ /Torr^{-1}	ε_{min} /kcal mol^{-1}	δ	B	n
Exponential	O_2	3.10—10.6	0.00—0.20	−0.53÷0.10	—	2.29—15.4
($\delta = \gamma$)	N_2	1.50—4.4	0.00—0.11	−0.84÷−0.39	—	3.44—11.0
Gaussian ($\delta = \sigma$)	O_2	3.70—8.9	0.21—0.34	0.81—82.6	0.00—0.43	2.22—18.9
	N_2	0.34—1.1	0.24—0.43	0.99—1.7	0.00—0.20	3.08—11.3
Uniform	O_2	2.96—10.1	0.00—0.21	—	—	2.17—14.9
	N_2	0.28—1.3	0.00—0.28	—	—	2.93—14.0
Trapezoidal ($\delta = f_{max}$)	O_2	4.30—11.5	0.10—0.29	0.32—0.7	—	1.64—2.5
	N_2	1.10—3.5	0.03—0.24	0.00—0.2	—	3.02—11.0

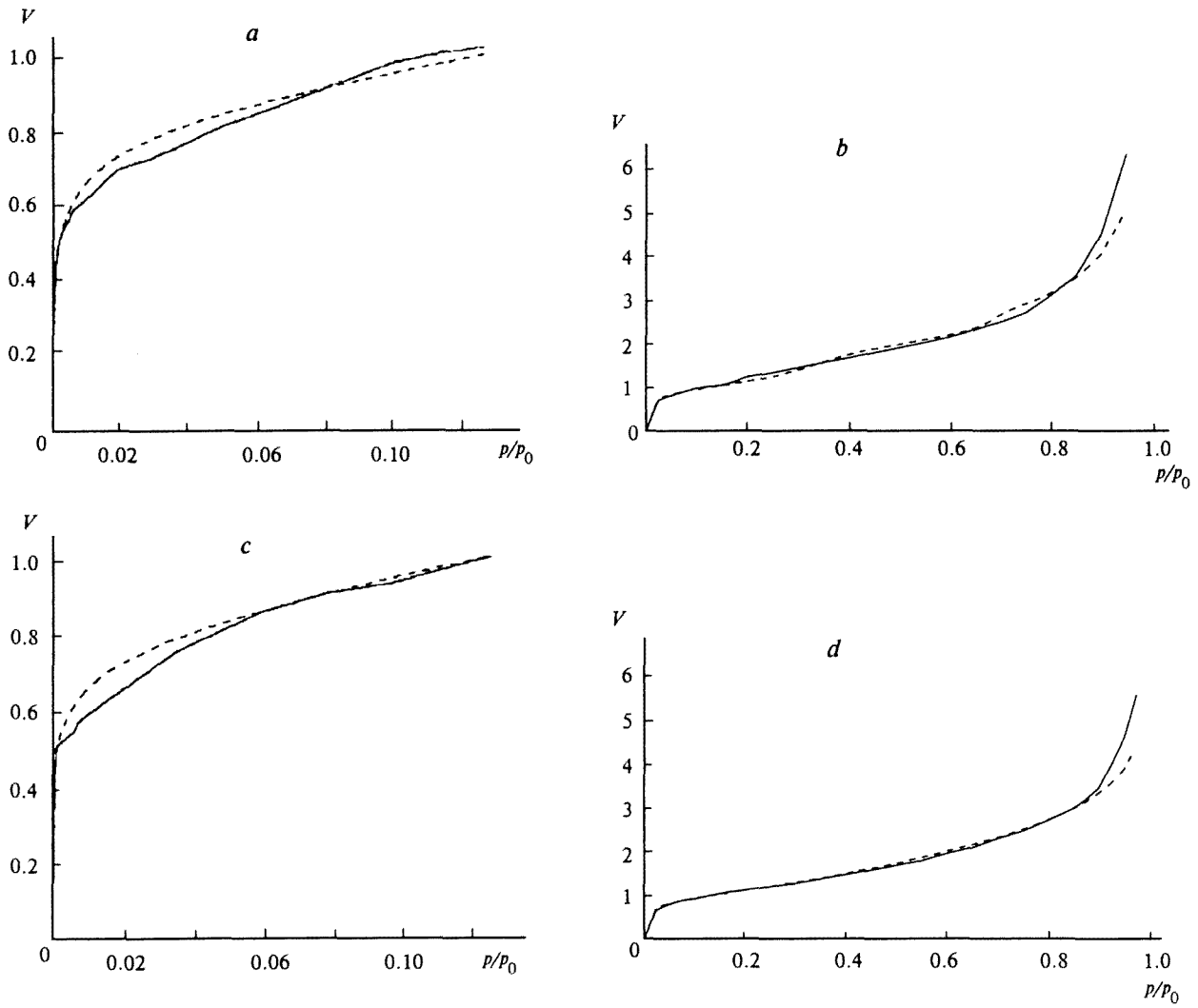

Fig. 2. Individual isotherms for the adsorption of oxygen (*a*, *b*) and nitrogen (*c*, *d*) on anatase for the exponential distribution function ($V = V_{ads}/V_m$, V_{ads} is the adsorbed volume): solid line corresponds to experimental results and dashed line corresponds to calculations. Monolayer filling of the anatase surface (*a*, *c*), multilayer filling (*b*, *d*).

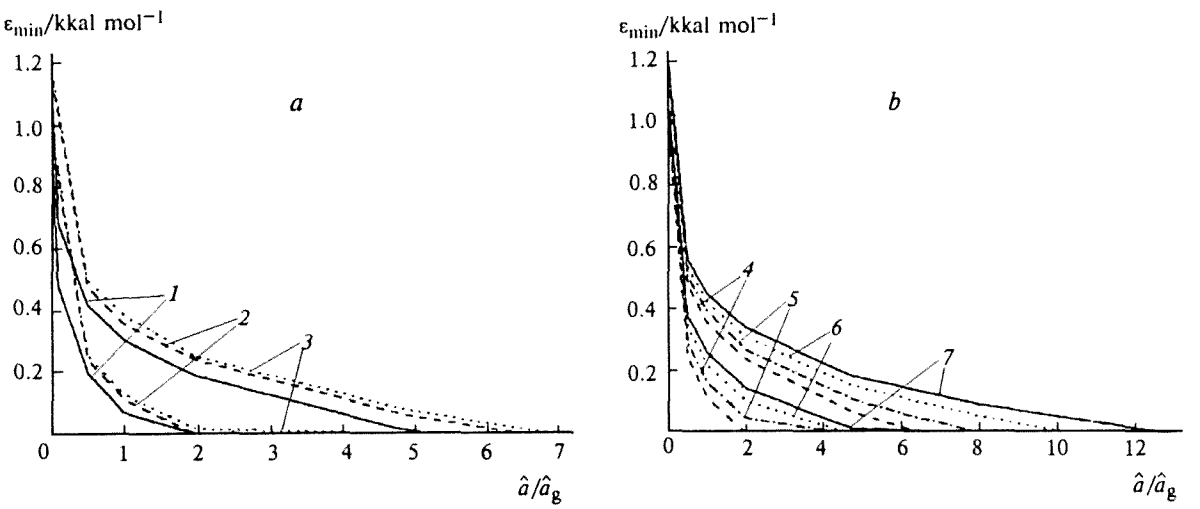

Fig. 3. Dependence of the ε_{min} on the energy parameter $\hat{a}/\hat{a}_g$ for nitrogen; exponential distribution function: *a*. $\gamma = -0.4$; *1*, $n = 3.4$; *2*, $n = 4.4$; *3*, $n = 5.4$; *b*. $n = 4.4$; *4*, $\gamma = -0.4$; *5*, $\gamma = -0.49$; *6*, $\gamma = -0.6$; *7*, $\gamma = -0.7$.

sponding to the above-mentioned level of accuracy of the description of experimental curves. The accuracy for ε^i_{max} is 0.42 kJ mol^{-1}. The values of other parameters vary more markedly. Figure 3 shows the dependences of ε_{min} on $\hat{a}/a_g$ calculated for various values of the n and γ parameters, the isotherm for nitrogen being described using the exponential distribution function within an 8 % accuracy level. These curves indicate that the ranges in which the parameters investigated vary decrease approximately 2—3-fold on their correlated variation. In this situation, instead of the traditionally suggested confidence ellipsoid for the correlated variation of the model parameters, a relatively narrow region confined with curves of the hyperbolic type from above and from below is realized. The large upper value of the parameter n is due to a decrease in the sensitivity of the course of the isotherm to a variation of this parameter. The physical meaning of the assumptions used imply that the values $n < 5.5$ should be taken as the upper limit of this parameter. A similar loss of the parametric sensitivity is observed for the half-width of the Gaussian distribution function for oxygen.

Multilayer adsorption of a mixture

Despite the similarity of the molecular properties of both gases and of the oxygen/anatase and nitrogen/anatase individual isotherms, the description of the adsorption of their mixture is to some extent problematic. In particular, the extension of the BET theory[2] to a gas mixture suggested by Hill[3] proved to be inadequate for the description of the experimental data[1] both when x varies over a wide range at Y_a = const and when Y_a varies at x = const. This is caused by the different behavior of the partial isotherms of oxygen and nitrogen for the first and the fifth compositions of the gas mixture. In the case where the mixture of the first composition is taken, nitrogen is adsorbed predominantly over the whole pressure region, and the partial isotherm of oxygen increases with an increase in the overall pressure. An increase in the fraction of oxygen in the gas changes the ratio between $\theta_a(x)$ and $\theta_b(x)$ at x = const, where $x = p/p_0$, $p = p_a + p_b$, p_i is the partial pressure of the component i, p_0 is the pressure of the saturated vapor of the mixture, and $\theta_i(x)$ is the partial isotherm of the component i. For mixtures with $x < 0.04$, the adsorption of nitrogen predominates, while at $x > 0.04$, the adsorption of oxygen predominates, the $\theta_b(x)$ value remaining virtually constant over a wide range, *viz.*, $0.05 < x < 0.70$, and slightly increasing at $x > 0.70$.

The parameters found for the lateral interaction of oxygen and nitrogen, as well as the distribution functions for their multilayer adsorption on the anatase surface, make it possible to calculate the multilayer isotherms for the adsorption of a mixture, if the functional dependence between the heats of adsorption of nitrogen and oxygen molecules is known. The particular character of the $\varepsilon_k{}^i(\varepsilon_k{}^L)$ dependence can be elucidated only from an analysis of the adsorbate—adsorbent potential energy. In rougher considerations, the adsorption of a mixture of components having similar molecular properties is often calculated using linear relationships between the heats of their adsorption.[13—15] In the present work we used the relationship $\varepsilon^b = \alpha\varepsilon^a + D$, $\alpha = (\varepsilon^b{}_{max} - \varepsilon^b{}_{min})/(\varepsilon^a{}_{max} - \varepsilon^a{}_{min})$, $D = \varepsilon^b{}_{max} - \alpha\varepsilon^a{}_{min}$, where $\varepsilon^i{}_{max}$ and $\varepsilon^i{}_{min}$ are defined in Table 2. The partial isotherms were calculated from Eqs. (6). The overall isotherm is the sum of the partial isotherms for oxygen and nitrogen at a given x. Table 4 presents the deviations of the partial and overall isotherms of multilayer adsorption for various compositions of the gas phase, and the parameters for individual isotherms are given in Table 2. It can be seen from Fig. 4 that the experimental and calculated overall and partial adsorption isotherms for mixtures with Y_a = 0.149 and

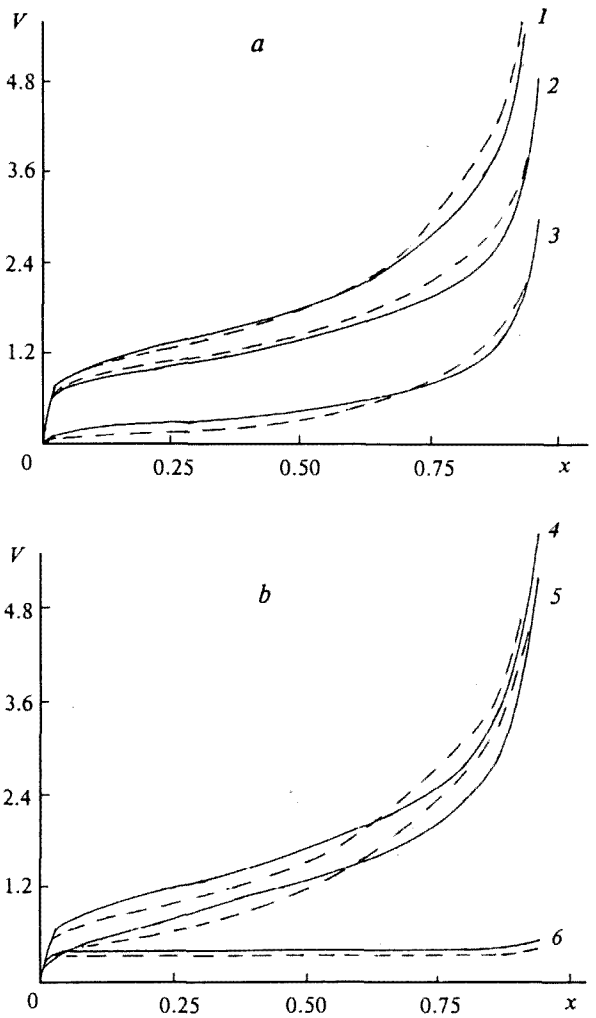

Fig. 4. Adsorption isotherms of a mixture of oxygen and nitrogen on anatase at Y_a = 0.149 (*a*) and 0.853 (*b*). Solid lines correspond to experimental results[1] and dashed lines correspond to calculations ($V = V_{ads}/V_m$, V_{ads} is the adsorbed volume): overall adsorption isotherms (*1*, *4*) and partial isotherms for nitrogen (*2*, *6*) and oxygen (*3*, *5*).

Table 4. Results of the prediction of the description of mixtures: calculated partial and overall isotherms in % of the experimental results[1] for the O_2+N_2/TiO_2 (anatase) system

$f(\varepsilon)$	Component of the system	Composition of the mixture I	II	III	IV	V
Exponential	O_2	22.30	15.20	14.70	12.30	8.51
	N_2	3.78	3.47	8.16	12.00	33.90
	O_2+N_2	6.57	7.66	10.90	10.70	9.72
Gaussian	O_2	18.70	11.50	11.20	10.10	9.99
	N_2	6.62	6.88	14.20	18.70	38.10
	O_2+N_2	6.56	7.69	9.92	10.20	10.30
Uniform	O_2	66.80	87.40	74.80	60.50	48.40
	N_2	16.50	26.20	45.40	61.00	78.60
	O_2+N_2	7.45	13.00	13.30	15.00	11.50
Trapezoidal	O_2	27.40	21.00	19.50	15.40	10.70
	N_2	4.79	7.18	3.55	7.58	34.00
	O_2+N_2	6.37	8.14	11.40	12.30	12.30

0.853 are in good agreement. An analogous correspondence is fulfilled for other gas mixtures. It thus follows that the lattice model describes satisfactorily the multilayer adsorption of a mixture over the whole pressure region by a single set of parameters for various compositions of the gas phase (this set is given in Table 2). The model chosen reflects adequately the character of the variation of partial isotherms at a fixed x and varying Y_a. Table 4 indicates that all the distribution functions provide approximately equally satisfactory agreement for the overall adsorption isotherm (the exponential and the trapezoidal functions provide the best results) and reflect properly the general features of adsorption known for partial isotherms.

The model suggested reflects only the main real properties of an adsorption system. The assumption that various adsorption sites are distributed randomly, a simplified way for allowing for the roughness of the surface, and simple procedures for the description of the adsorbent—adsorbate potential and intermolecular interactions in the mean-field approximation are used in this model. In the general case, each of these factors can lead to a substantial alteration of the isotherms. Therefore, the results obtained should be considered satisfactory. Note the high sensitivity of the results for the partial multilayer isotherms to the parameters $\hat{a}^i$ and ε^i_{min}. These values characterize the equilibrium redistribution of the molecules in the surface layer and in the overlying layers at practically complete filling of the surface layer. They determine the difference between the experimental and calculated isotherms of the multilayer region. This is illustrated by the data of Table 5. Note that an improvement of the description of the oxygen distribution for the fifth composition results in a deterioration of the agreement of the nitrogen distribution for the first composition with the experimental data, and *vice versa*. The character of the variation of the overall isotherm and other general regularities do not change qualitatively,

Table 5. Effect of parameters (ε_{min} and $\hat{a}$ of oxygen) on the partial and overall isotherms of the mixtures in percent of deviation from experimental results[1] for the O_2+N_2/TiO_2 (anatase) system with an exponential function of distribution of the adsorbed molecules of the components over the energy of the interaction with the TiO_2 (anatase) surface

Component	ε_{min} /kcal mol^{-1}	Composition of the mixture I	V	$\hat{a}\cdot10^4$ /Torr^{-1}	Composition of the mixture I	V
O_2	0.2	17.0	10.0	7.45	21.0	8.7
	0	33.0	15.0	4.74	28.0	13.0
N_2	0.2	6.4	40.0	7.45	4.7	37.0
	0	1.4	21.0	4.74	2.0	23.0
O_2+N_2	0.2	6.4	8.0	7.45	6.7	9.0
	0	7.3	15.0	4.74	6.8	13.0

since the variations of the parameters under consideration occurs within the ranges given in Table 3. It should also be emphasized that the overall adsorption isotherm is predicted on the basis of individual isotherms with a satisfactory accuracy, though the partial isotherms may deviate substantially.

* * *

The equations of the lattice model for the multilayer adsorption[4,5] make it possible to take into account the specific features of the molecular nature of the adsorption system under study: the heterogeneity of the adsorbent, the formation of a multilayer film, and intermolecular interactions. Based on the lattice model one can obtain simplified versions of the theory. In the present work this was illustrated in relation to the N_2+O_2/anatase system, for which we considered an approximate variant of the allowance for the roughness of the amorphous surface of the adsorbent. The predicted overall isotherms of multilayer adsorption of this mixture are in satisfactory agreement with experimental results. If reliable data on the individual adsorption isotherms are available, one can predict the partial adsorption isotherms.

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