New method for calculating the adsorption of noble gases on amorphous surfaces

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A new approach to calculating the equilibrium characteristics of the adsorption of noble gases on the amorphous surfaces of adsorbents was developed and applied to the Ar—TiO_2(rutile) system. Intermolecular adsorbate—adsorbate interactions are taken into account for the nearest neighbors in the quasi-chemical approximation. The lattice energy parameters of all interactions of the model are determined from the Lennard—Jones potential (12-6). The formation of amorphous TiO_2(rutile) surface includes completion of the surface layers and partial removal of the surface oxygen ions. The quality of the amorphization procedure was confirmed by the experimentally measured heats and isotherms of adsorption of the system under study.

Key words: adsorption, isotherm, isosteric heat of adsorption; argon—rutile, amorphous surface of TiO_2, adsorbent amorphization procedure; quasi-chemical approximation, lattice gas model.

Amorphous surfaces are characteristic of a sufficiently wide range of sorbents widely used in adsorption processes. Among these are not only numerous structural and chemical modifications of silica (silica gels, aerosils, silochromes, porous glasses, *etc.*),[1] but also, for instance, metal oxides[2] whose three-dimensional crystalline structure has strongly disordered surface layers (first indicated in 1956 [3]). The formation procedure is of paramount importance for the state of the adsorbent surface. Depending on the conditions of the crystal growth and the subsequent stages of annealing and/or treatment in active gaseous or liquid phases, one or another structure of the adsorbent surface can be obtained.

Amorphous surfaces are a special case of inhomogeneous surfaces. The theory of the adsorption of gases on inhomogeneous surfaces has been actively developing recently.[4—7] As a rule, for most versions of this theory, the adsorbed particle (atom, ion, or molecule) is assumed to occupy one adsorption center. However, this is not always the case for amorphous surfaces. Analysis of the potential energy of Ar atoms on an amorphous rutile surface has shown[8] that the distances between the local minima are shorter than the diameter of the Ar atom and that the latter can block several adjacent local minima. An analogous result was obtained[9] for the sorption of Kr atoms and CH_4 and CO_2 molecules in amorphous glassy polymeric matrices based on polycarbonate. Such a situation is characteristic of adsorption of multicenter particles: one particle blocks more than one local minimum. This line of the theory has not been well developed because of the great difficulties in theoretical description of this effect (for details, see Ref. 10), and numerical experiment has been the basic investigation technique in this case.[11]

In general, the problem of calculating the adsorption of gases on amorphous surfaces consists of two parts: the first is to simulate an amorphous surface, while the second is to develop a procedure for calculating the adsorption on the generated surface. The degree of inhomogeneity of the surface layer of the adsorbent (and, hence, its adsorption capability) is strongly dependent on the conditions of its formation. In this connection, the necessity arises of elaborating a procedure for describing the process of the formation of the solid to determine the final state of its surface. The state of the surface of an adsorbent is characterized by distribution functions, which describe its composition (a unary function) and structure (paired and cluster functions).[12,13] These distribution functions are solutions of the problem of simulation of the process of the surface formation. Previously,[14] we obtained for the first time kinetic equations for the processes of formation of crystalline solids. A procedure for generating amorphous surfaces by a random process of displacement of the atoms of a crystal lattice from their equilibrium positions has been proposed by other authors.[15] Adsorption on this surface was calculated by the Monte-Carlo method.

Another numerical procedure has been used to simulate amorphous surfaces:[8] a crystalline support was randomly coated ("sputtered") with atoms to form the surface area of a solid. Adsorption on the generated

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1109—1118, June, 1997.

surface was studied for low coverages. Then, adsorption on the same surface was calculated by the Monte-Carlo method in the whole range of coverages of the monolayer. An additional mechanism of generating the amorphous structure of the rutile surface at the expense of the removal of a portion of oxygen from the crystalline surface layer has also been suggested.[16] Refs. 17—19, in which studies on generating amorphous SiO_2 surfaces were carried out using the molecular dynamics technique, should also be noted.

In this work, a new procedure for generating the near-surface area of an adsorbent and a new method of calculating the isotherms of adsorption of spherically symmetrical particles on amorphous surfaces was suggested to describe the adsorption of noble gases on amorphous surfaces. The physical adsorption of gases is believed to cause no change in the surface properties of the adsorbent. The interaction between the gas and the solid is described by the atom-atom approximation. Calculations of the adsorption characteristics imply knowledge of the atom-atom potentials of the adsorbate—adsorbent and adsorbate—adsorbate interactions. Let us consider, as an example, the adsorption of Ar atoms on the amorphous surface of rutile (TiO_2). Experimental data on the isotherms and heats of adsorption[20a,20b] as well as the estimates of parameters of the atom-atom potentials for this system have been reported in the literature.[16] Previously,[10] a new procedure for calculating the adsorption of spherically symmetrical particles on an amorphous surface based on the model of the lattice gas has been suggested. This procedure was first tested in this work.

To exclude the large number of parameters of the lattice model needed for describing any inhomogeneous surface, these parameters were calculated using the atom-atom potentials of the interaction of Ar atoms with each other and with oxygen and titanium ions. The function of distribution of the adsorption centers over the bonding energies was obtained on the basis of experimental data on the heats of adsorption;[20b] only its limiting values (for the maximum and minimum bonding energies) were used to find the conditions of generation of the amorphous surface and to estimate the "quality" of the Ar—Ti^{4+} and Ar—O^{2-} atom-atom potentials. Calculations of the concentration dependence of the heat and isotherm of adsorption were carried out with no additional fitting parameters.

Model of the system

The model of the system under study consists of: 1) procedure of the formation of the amorphous surface of the adsorbent, 2) the atom-atom potentials used, and 3) the lattice model for calculating the adsorption characteristics.

Procedure of formation of the amorphous structure of an adsorbent. The amorphous structure of an adsorbent is assumed to be rigid and unchanged at all degrees of coverage of the surface. Simulation of an amorphous structure was carried out taking into account the conventional geometric concept of an amorphous three-dimensional structure as a completely random arrangement of atoms in a solid. Unlike Ref. 15, we simulated the surface structure of the adsorbent by building up the unit cells of the crystalline support located at a depth of $R = 1.77$ nm using a randomly generated arrangement of the atoms in the three-dimensional structure of TiO_2. Here R is the maximum of two radii of the potentials of the Ar—O^{2-} and Ar—Ti^{4+} interactions. These potentials are nearly equal to zero at $R > 1.77$ nm, which approximately corresponds to six lattice constants. Using a random number generator, the random vectors of positions of new atoms relative to those of previously "arranged" atoms were obtained. Since the build-up is carried out from the depth toward the surface, random displacements are repeatedly accumulated from layer to layer, and the degree of amorphization of the surface layer reaches its maximum value. This procedure is characterized by parameter δ (%), *i.e.*, the maximum displacement of the atoms from the value of the lattice constant. The parameter δ allows one to prevent complete bond cleavage between the atoms since short-range order exists in an amorphous substance. Previously,[8] the Bernal model, which neglected the cationic sublattice, was used for amorphizing an adsorbent. Our model takes into account both cationic and anionic sublattices, which corresponds to a real amorphous substance containing cations and anions.

The second peculiarity of amorphization of the surface consists in the removal of a certain portion γ (%) of the oxygen ions after random displacement of the atoms in the surface layer of the sorbent (see Ref. 16).

The procedure proposed takes into account two basic properties of an amorphous substance: the presence of short-range order and the absence of long-range order.

Potentials of atom-atom interaction. The potential energy of the system was calculated in the atom-atom approximation using a set of potentials based on the Lennard—Jones (12-6) potential:

$$U_{Ar-i}(r) = 4E_{Ar-i}[(\sigma/r)^{12}{}_{Ar-i} - (\sigma/r)^{6}{}_{Ar-i}],$$

where i are the O^{2-} and Ti^{4+} ions and the Ar atom; E_{Ar-i} is the depth of the potential well; r is the distance between the interacting atoms; σ_{Ar-i} are the parameters of the potentials which are given in Table 1. Three sets of parameters for the O^{2-} ions have been previously[16] considered. The second set was proposed as providing the best qualitative agreement with experiment. In this work, the values of parameters of the Ar—Ti^{4+} and Ar—O^{2-} potentials were varied (see below); the parameters listed in Table 1 were used in the calculations, while those for the Ar—Ar potential were taken from Ref. 16.

The lattice model. The lattice model[5,10] was used for calculating the isotherm and heat of Ar—TiO_2 adsorption in the whole range of the monolayer coverage of the surface. A gas—solid interface can be conceived as a

Table 1. Parameters of the Lennard—Jones potential for the Ar—ion interactions

i	$E_{\mathrm{Ar}-i}/k$ /K	$\sigma_{\mathrm{Ar}-i}$ /nm	Reference
O^{2-}	226.1	0.307	16
O^{2-}	160	0.325	16
O^{2-}	130	0.336	16
Ti^{4+}	76.5	0.241	16
Ar	119.8	0.3405	16
O^{2-}	120	0.325	*
Ti^{4+}	60	0.241	*

* This work.

lattice with a constant number of neighbors ($z = 4$), whose sites are adsorption centers. A site occupies a surface area of about the size of an adsorbate molecule d^2 (d is the diameter of the molecule), and the volume of each site is of order d^3. A site can contain no more than one adsorbate molecule. Each site of the surface fragment under consideration is indexed q, $1 \le q \le N$ (N is the number of sites of a surface fragment) and can be characterized by the energy of bonding of the molecule with the amorphous surface of the adsorbent (Q_q) and the local Henry constant (A_q).

An argon atom located on the amorphous surface is capable of blocking several local minima of the adsorbent—adsorbate potential energy; in this case the known equations[4–7] cannot be used. We proposed a procedure to account for such blocking,[10] which consists in partitioning the surface into n^2 lattice structures (each with lattice constant d) that are shifted relative to each other with an increment of d/n (n is an integer equal to 2, 3, *etc.*). For each structure, the sets of parameters Q_q and A_q are obtained and then the systems of equations are solved for local coverages of sites of different types. These equations, which are similar to those for particles blocking one site[5,7] but take into account the differences in the energies of the lattice sites and the interactions between adjacent adsorbate molecules, can be written as follows:

$$\theta(p) = \sum_{q=1}^{N} f_q\theta_q(p), \quad A_q p = \frac{\theta_q}{1-\theta_q}\prod_{p=1}^{z_q}(1 + xt_{qp}),$$

where

$$\sum_{q=1}^{N} f_q = 1, \quad t_{qp} = \frac{2\theta_p}{b_{qp} + \delta_{qp}},$$

$$\delta_{qp} = 1 + x(1 - \theta_q - \theta_p), \; b_{qp} = (\delta^2{}_{qp} + 4x\theta_q\theta_p)^{1/2}; \quad (1)$$

$x = \exp(-\beta\varepsilon) - 1$ ($\beta = (kT)^{-1}$, k is the Boltzmann constant, T is temperature); z_q is the number of nearest neighbors of site q; p is the gas pressure, which corresponds to the surface coverage θ; θ_q is the probability of covering site q; the index p is the number of the current site adjacent to site q. Lateral interactions are taken into account in the quasi-chemical approximation, which retains the effects of direct correlations between adjacent molecules; ε is the parameter of the lateral interaction (whose physical meaning is the average energy of the interaction of a pair of adsorbed molecules located in adjacent lattice sites).

Equations (1) describe the coverage of individual sites of the surface fragment when $f_q = 1/N$ (the distributed model[5,7]). In the case of macroscopic surface areas, f_q is a discrete function of the distribution of the sites of a non-uniform surface that have local Henry constants A_q, *i.e.*, the fraction of sites of type q.[5,6]

After solving all n^2 systems of equations, the desired isotherm of adsorption $\theta(p)$ is constructed: to each p value there corresponds a θ_k value ($1 \le k \le n^2$) that corresponds to the minimum free energy of the system calculated according to the formulas in Ref. 21. The isosteric heat of adsorption was determined from the standard equation:

$$Q_{\mathrm{is}} = -(\mathrm{d}\ln p/\mathrm{d}\beta)_{\theta=\mathrm{const}}.$$

The lattice parameters. The parameters of the lattice model ε, Q_q, and A_q are related to the interaction potentials in a complicated way. The minimum and maximum values of parameter ε can be estimated using the following equations:[9,22]

$$\varepsilon_{\min} = \beta^{-1}\ln(D_{qp}), \; D_{qp} = \int\limits_{V_q}\int\limits_{V_p}\exp[-\beta E_{\mathrm{Ar-Ar}}(r)]\mathrm{d}V_q\mathrm{d}V_p/V_qV_p,$$

$$\varepsilon_{\max} = \int\limits_{V_q}\int\limits_{V_p} E_{\mathrm{Ar-Ar}}(r)\exp[-\beta E_{\mathrm{Ar-Ar}}(r)]\mathrm{d}V_q\mathrm{d}V_p/B,$$

$$B = \int\limits_{V_q}\int\limits_{V_p}\exp[-\beta E_{\mathrm{Ar-Ar}}(r)]\mathrm{d}V_q\mathrm{d}V_p,$$

$$Q_q = \int\limits_{V_q} U(r)\exp[-\beta U(r)]\mathrm{d}V_q/A_q, \; A_q = \int\limits_{V_q}\exp[-\beta U(r)]\mathrm{d}V_q. \quad (2)$$

Expressions for the lattice parameters Q_q and A_q were given in Ref. 22. In Eqs. (2) V_q is the volume (d^3) of the site with index q, which is located above the surface of the adsorbent; $U(r)$ is the potential of the adsorbate—adsorbent interaction, which is obtained by summing all paired contributions $U_{\mathrm{Ar}-i}(r)$ from the atom-atom potentials of the interaction of an Ar atom with the titanium or oxygen ions ($i = Ti^{4+}, O^{2-}$) that are located within a sphere of radius R. Since all atoms of the adsorbent are randomly distributed in three-dimensional space, the volume integrals in Eqs. (2) were calculated numerically because their analytical calculation is impossible.

In the lattice models, the parameters ε, Q_q, and A_q are conventionally believed to be "fitting" parameters, determined from a comparison of calculations with experiment. If expressions (2) are used, these quantities are not independent parameters, since they are determined using the parameters of the atom-atom potential curves that can be found in the literature. In the absence of the latter, the above parameters can be calculated using Eqs. (1) and (2), for instance, by comparing calculated and experimental isotherms of adsorption.

Analysis of the model

Analysis of the potential energy of the adsorption system. Calculations of the potential relief $U(r)$ were carried out with an increment of 0.025 nm. The increment value was chosen with an eye to further averaging of the calculated energies of interactions and obtaining the potential relief network in the optimal computing time. The potential relief network was located above the pre-generated amorphous structure of the adsorbent. The height of the network was determined by the diameter of Ar atoms (d = 0.38 nm). Surface areas of size 10×10, 15×15, and 20×20 diameters of an Ar atom (hereafter fragments) containing N = 100, 225, and 400 sites of the lattice structure were considered. In the case of calculations of the potential relief of the boundary domains of the fragment, a surface area was built up on each side with a strip of a width equal to the radius of interaction R. Local minima of the potential energy of the Ar—TiO_2 interaction were determined by a numerical procedure in the course of the calculation, namely, changes in the signs of the increments of the functions in the vicinity of each point in a three-dimensional space were analyzed, while the values of the minima were additionally refined using a three-dimensional quadratic approximation.[23] The potential relief of an amorphous surface containing 400 sites of the lattice structure is shown in Fig. 1. The parameters of the generation procedure, δ = 22% and γ = 45%, used in plotting this and the other figures are discussed below.

An analysis of the potential reliefs showed that an Ar atom can block up to nine local minima. From 1 to 3 local minima of the potential energy are most often blocked (Table 2). On average, each atom blocks 2—3 local minima, at the same time almost one-tenth of the sites have no local minima. These data point to the convenience of calculating the adsorption characteristics according to the procedure that we described previously:[10] a small number of partitions is necessary to account for blocking several adjacent local minima of $U(r)$, one need only n = 2 or 3 (calculations of the systems of equations for one-center particles are fast).

Table 2. The distribution function of the number of local minima of potential energy $f(m)$ corresponding to one lattice site (m is the number of local minima in the site, N_m is the total number of local minima, $\hat{N}_m$ is the average per one lattice site)

m	$f(m)$		
	10×10	15×15	20×20
0	0.12	0.15	0.11
1	0.15	0.24	0.20
2	0.24	0.20	0.26
3	0.23	0.21	0.18
4	0.13	0.11	0.12
5	0.09	0.05	0.08
6	0.01	0.02	0.03
7	0.02	0.01	0.01
8	0.01	$<10^{-5}$	0.0025
9	—	—	0.0025
N_m	257	492	968
$\hat{N}_m$	2.57	2.19	2.42

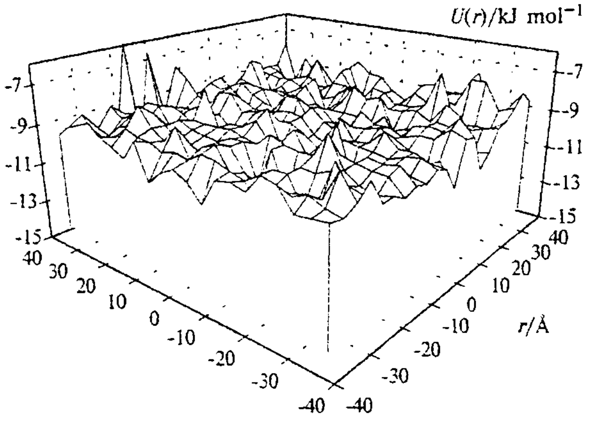

Fig. 1. Potential relief of an amorphous surface (δ = 22%, γ = 45%, volume is 7.6×7.6×0.38 nm^3).

As was mentioned above,[12,13] to characterize the properties of the obtained potential surfaces, one must introduce distribution functions: a unary function for describing the composition and an additional function (at least binary) for describing the structure of the adsorbent surface. The distribution function $f(Q)$ (or $f(\ln A)$), which characterizes the fraction of the surface sites with bonding energy between Q and Q + dQ (and analogously for $\ln A$), is convenient to use for analyzing the inhomogeneity of the surface composition. (Calculations of the distribution functions were performed with an accuracy of ±0.5 kJ mol^{-1}.) The logarithmic scale is used for A because it varies by 5—6 orders of magnitude. A comparison of the distribution functions $f(Q)$ and $f(\ln A)$ (Fig. 2, a, b) showed that their variation is correlated. The differences between them are due to different values of the preexponentials of the local Henry constants $A_0 = A(Q)\exp(-\beta Q_{\text{eff}})$, which can differ from each other by more than 2 orders of magnitude (their distribution is shown in Fig. 2, c). The mean A_0 value for the given system is equal to $2.35 \cdot 10^{-7}$ Torr^{-1}. The results of the calculations are evidence for the fact that the conventional assumption that the value of the preexponential of the local Henry constants is constant is a strong simplification.

To describe the structure and energetics of the generated surface, let us define the two-dimensional distribution function $f(\Delta U,R)$, characterizing the distribution of the local minima of the potential energy over both the differences in the values of the ΔU minima and the

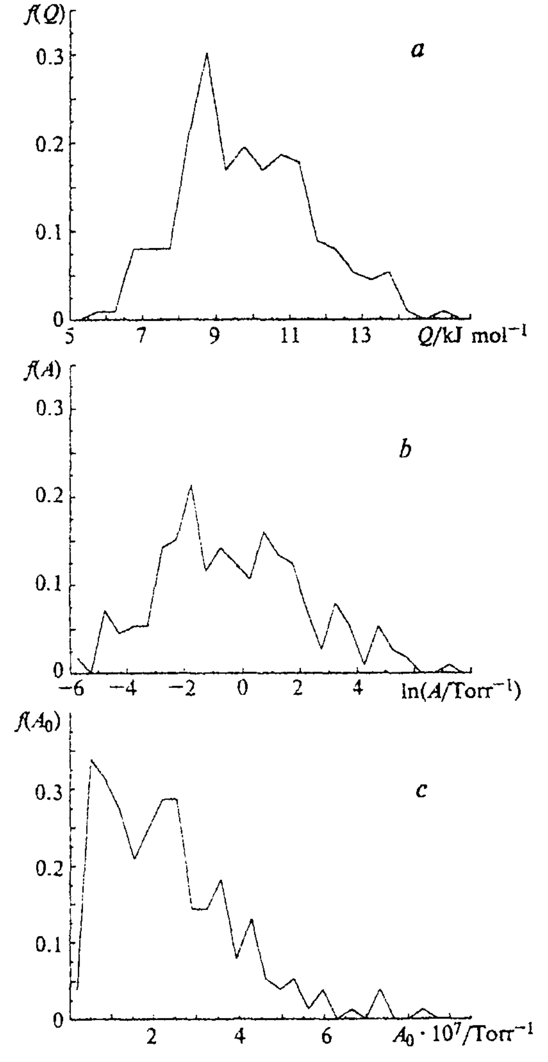

Fig. 2. The distribution functions of the adsorption centers (15×15, δ = 22%, γ = 45%) over the bonding energies $f(Q)$ (*a*), the Henry constants $f(\ln A)$ (*b*), and the preexponentials of the Henry constants $f(A_0)$ (*c*).

distances R between them ($f(\Delta U,R)$, is the portion of the minima that simultaneously fall both into a certain interval of increments $\delta\Delta U$ and in the interval ΔR; the $\delta\Delta U$ and ΔR values of 0.5 kJ mol^{-1} and 0.05 nm, respectively, were used in the calculations). This distribution function is a generalization of well-known binary distribution functions of the distances between the atoms of an amorphous substance, since it additionally accounts for the differences in the values of the local minima. The profiles of this two-dimensional distribution function for different cross-sections along the ΔU coordinate are presented in Fig. 3.

The analysis of the function indicates that the portion of the minima that fall into the same intervals of R values decreases as the differences in the ΔU energies increase. This conclusion is of particular importance for short ($R < d$) distances. The area under the radial distribution curve characterizes the size of a site of the lattice structure. Figure 4 shows these areas for the radial distribution curves presented in Fig. 3. The probability of uniting several local minima that strongly differ in bonding energies into one site is low. Therefore, joining several nearest local minima into one adsorption center and going to lattice parameters that are averaged over the site volume is justified, since the energy properties of these nearest local minima are not much different. This conclusion is different from the results reported previously in Ref. 8, in which adjacent local minima might have large ΔU values. This distinction is due to the models of the solid used. Previously,[8] only the anionic sublattice has been considered. Our model takes into account both ionic sublattices of rutile.

At long distances, the cross-sections of the function $f(\Delta U,R)$ at ΔU = const have shapes analogous to those of the radial distribution curves for amorphous solids: a "chaotic" shape of the curve fluctuating about a certain average value, which increases as R increases (see Fig. 3, *a*, *b*, fragments of size 15×15 and 20×20, hereafter denoted as fragments). However, as can be seen in Fig. 3, *c*, *d*, the rate of increase in the average value decreases as ΔU increases. The curves for the fragment of size 10×10 (see Fig. 3) differ still further from the standard behavior of radial distribution curves of amorphous solids. To appreciate the reason for this difference, one must compare three-dimensional images of these functions. The complete distribution function $f(\Delta U,R)$ for the fragment of size 20×20 is shown in Fig. 5. At long distances (R = const), the function behaves nonmonotonically as ΔU increases: three maxima are observed, the greatest of which corresponds to $\Delta U \approx$ 8.25 kJ mol^{-1}. However, its value is smaller than that of the function $f(\Delta U,R$ = const) at small ΔU. In the case of the fragment of size 10×10 and at large R values, this maximum has an appreciably larger value than the values of the function $f(\Delta U,R$ = const) at small ΔU (due to association of the three above maxima into one). This fact indicates that the fragment of size 10×10 is too small to use for separating the obtained maxima in the case of large R and ΔU values. The function $f(\Delta U,R)$ for the 15×15 fragment is similar to that for the 20×20 fragment. The indicated distinctions in the complete functions $f(\Delta U,R)$ are associated only with the dimensions of the fragments. Fragments smaller than 15×15 seem to be too small to use for describing the properties of amorphous surfaces.

The above introduced two-dimensional functions make it possible to describe the structure and energetics of the considered areas of amorphous surfaces in some detail. Since these functions reflect the distinctions in the final states of the surface areas depending not only on the interaction potentials used, but also on the "technological" parameters of the process of generating the surface, they can be used for their "identification."

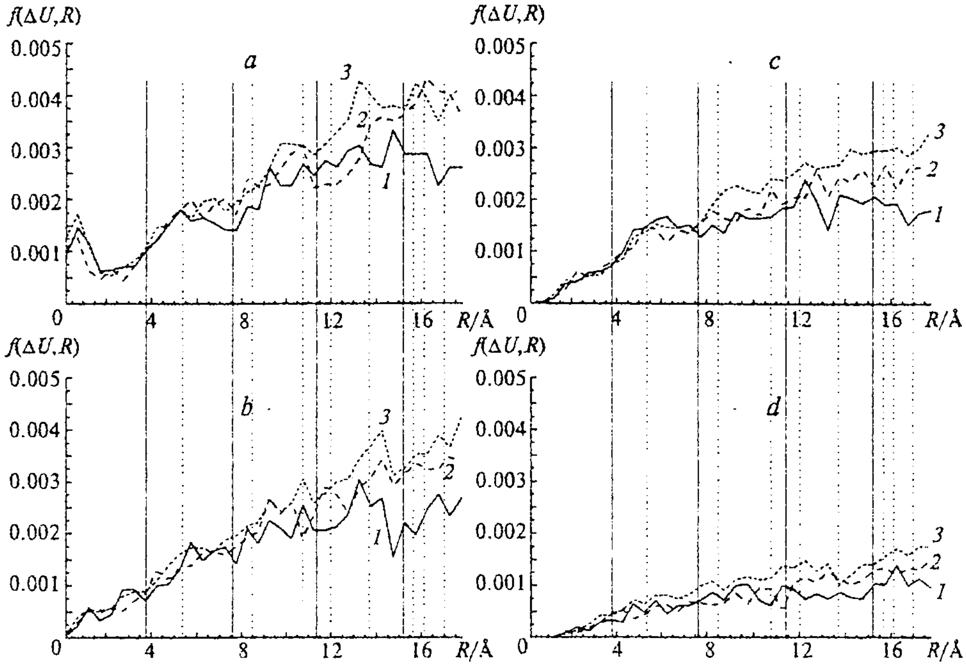

Fig. 3. Cross-sections of two-dimensional distribution function $f(\Delta U,R)$ ($\delta = 22\%$, $\gamma = 45\%$) at ΔU/kJ mol^{-1} = 0.25 (*a*), 1.25 (*b*), 2.25 (*c*), and 4.25 (*d*) (ΔU is the midpoint of the energy interval of the cross-sections under consideration): *1*, a surface fragment of size 10×10; *2*, 15×15; *3*, 20×20. (Vertical dotted lines correspond to the crystal structure of closely packed Ar atoms at $\theta = 1$.)

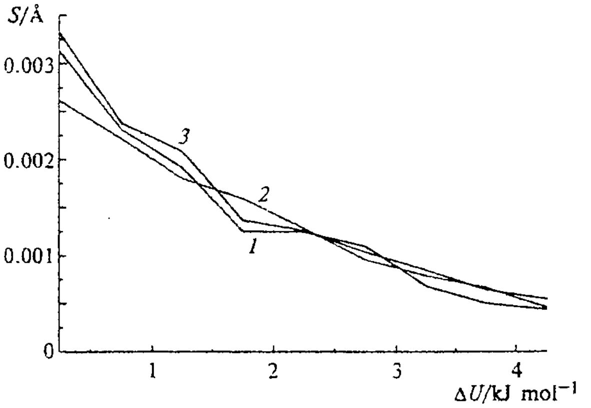

Fig. 4. Dependence of the area S on ΔU at $0 < R \le d$ for the cross-sections shown in Fig. 3: *1*, a surface fragment of size 10×10; *2*, 15×15; *3*, 20×20.

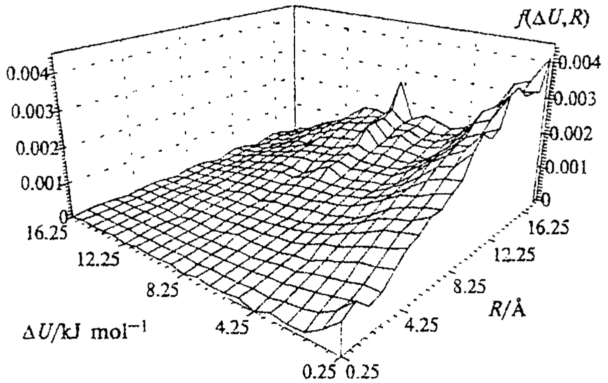

Fig. 5. Two-dimensional distribution function of pairs of local minima $f(\Delta U,R)$ for a surface fragment of size 20×20 ($\delta = 22\%$, $\gamma = 45\%$).

To evaluate the effect of the method of partitioning the adsorbate—adsorbent potential relief into sites, let us compare changes in the Q values for two different techniques for partitioning at $n = 2$ and 3. In the first case, the site volume is partitioned into four equal fractions, and the coordinate system is shifted sequentially from the center of the site to the center of each fraction. Correspondingly, the boundaries of successive sites are determined relative to the shifted center. Four different variants of partitioning and four sets of quantities Q_k and A_k are obtained. The results of such partitions are presented in Fig. 6, *a* as the distribution functions $f_k(Q)$, $1 \le k \le n^2$. The obtained distribution functions are fairly close to each other. The differences in the Q values at the outermost points of the intervals are less than 1 kJ mol^{-1}, while the differences in the intermediate values of the functions do not exceed 20%. Similar behavior is characteristic of the distribution func-

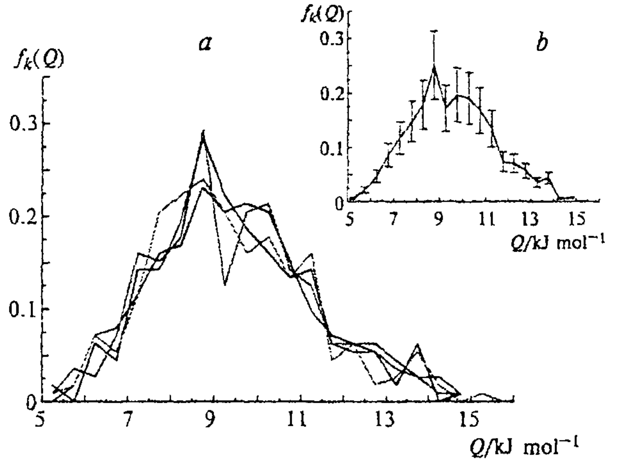

Fig. 6. The distribution function $f_k(Q)$ (δ = 22%, γ = 45%) for $1 \le k \le 4$ (*a*) and the curve averaged over $1 \le k \le 9$ (*b*) (the corridor of maximum deviations for 9 functions $f_k(Q)$ is also shown).

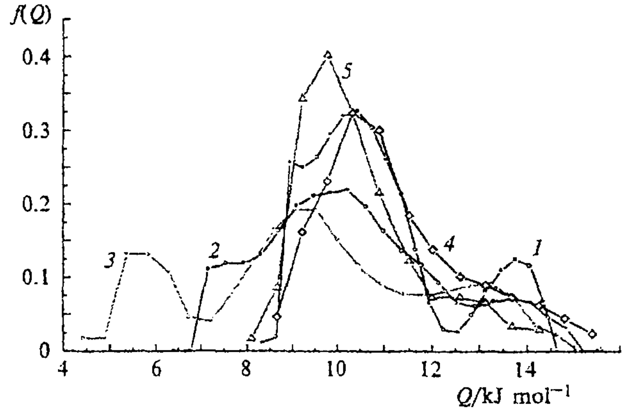

Fig. 7. The distribution functions $f(Q)$ obtained from the inverse problem of the description of the experimental dependence of $Q_{\rm is}(\theta)$ at ε/kJ mol^{-1}: 0 (*1*); 0.4 (*2*); 1.0 (*3*); *4*, experimental, see Ref. 20a; *5*, experimental, see Ref. 24.

tions for ln$A$ and A_0. In the second case, the site volume is partitioned into nine parts. In Fig. 6, *b*, the corridor of maximum deviations (to 25%) for nine functions $f_k(Q)$ is shown. The results of calculations of the isotherms and heats of adsorption corresponding to the different distribution functions for both partitioning techniques differ by no more than 2—4%. This is evidence for a reasonably high degree of amorphization of the adsorbent surface, since the values of the lattice parameters depend only slightly on the method of partitioning and the equilibrium characteristics of adsorption become nearly identical.

Analysis of the distribution functions. The calculated distribution functions (for instance, $f(Q)$) can be compared to the analogous functions obtained by solving the inverse problems of the description of the experimental isotherms or heats of adsorption

$$\theta_{\rm exp} = \int_{Q_{\rm min}}^{Q_{\rm max}} \theta_{\rm loc}(Q) f(Q) {\rm d}Q,$$

where $\theta_{\rm loc}(Q)$ is the local coverage of sites with energy Q. The functions $f(Q)$ for the Ar—rutile system (Fig. 7) were calculated from the published data.[20a,20b] Curves *1—3*, curve *4*, and curve *5* were obtained from the heats of adsorption, the recalculation of the data on the heat of adsorption in the range from 85 to 0 K,[20a] and the isotherm of adsorption (see Ref. 24), respectively. Curves *1*, *4*, and *5* are in fairly good correlation with each other. They correspond to a formal description of experimental data using Eqs. (1) (without additional partition of the sites into small parts) at $\varepsilon = 0$. The Langmuir model, where $A(Q) = A_0\exp(\beta Q_{\rm eff})$ and $Q_{\rm eff}$ is the value of the effective heat of adsorption for a given coverage of the surface θ, was taken as a nucleus of the integral equation $\theta_{\rm loc}(Q)$. Curves *2* and *3* (see Fig. 7) were obtained taking into account the lateral interactions in the quasi-chemical approximation. To obtain curves *1—3*, Eqs. (1) were used in the integral form for macroscopic areas, and functions $f(Q)$ were determined. Taking account of lateral interactions changes the shape of the distribution function and makes it possible to separate the adsorbate—adsorbent interactions Q from the total energy contribution $Q_{\rm eff}$ in its explicit form. (An analogous distribution function is obtained when scanning the potential relief of the surface using the adsorbate atom.) That is why curves *2* and *3* should be taken as the basis for comparing the distribution functions we obtained and the above atom-molecular description.

In the atom-atom approximation, the values of parameter ε are assumed to be independent of the energy of the adsorbate—adsorbent interaction. Curve *2* corresponds to $\varepsilon = \varepsilon_{\rm min}$; the calculated value of parameter ε is equal to 0.4 kJ mol^{-1}. Curve *3* corresponds to $\varepsilon = \varepsilon_{\rm max}$ when ε is approximately equal to the depth of the potential well: $\varepsilon \approx$ 1.0 kJ mol^{-1}. A nearly identical estimate of ε is obtained from the condition $\beta_c\varepsilon = \varepsilon/kT_c = 2\ \ln(z/[z-2])$, which determines the critical temperature in the quasi-chemical approximation for the lattice gas model,[5,25] where $z = 6$ for the three-dimensional gas phase, T_c is the critical temperature of the adsorbate (150.8 K for Ar [26]). Thus, in any case the $Q_{\rm min}$ value must be less than 7 kJ mol^{-1}, whereas neglect of the interatomic interactions gives $Q_{\rm min} > 8$ kJ mol^{-1}. All estimates for $Q_{\rm max}$ agree with each other: $Q_{\rm max} = 15.0 \pm 0.5$ kJ mol^{-1}. The value found for the interval of the differences in the energies of the rutile surface ($Q_{\rm min}-Q_{\rm max}$) was taken as the basis for choosing the conditions of formation of the amorphous surface of rutile and testing the parameters of the potential reported in Ref. 16.

Analysis of the effect of conditions of the formation of the rutile amorphous surface and the potential parameters. The effect of "technological" parameters δ and γ was studied using the second variant of the $Ar-O^{2-}$ potential (see Table 1). The results of model calculations of the atomic potential were compared with curves *2* and *3* at the characteristic points: at Q_{min}, Q_{max}, at the maximum, *etc.* (see Fig. 7, curves *2* and *3*). As an example, the results of calculations of the distribution of the Q_{min} values for different δ and γ are shown in Fig. 8. In the general case, changes in these parameters result in nonmonotonic changes in Q_{min} (and in the Q values at other characteristic points). The calculations in the whole range of changes in the δ and γ values (from 0 to 100%) performed by using the second variant of the $Ar-O^{2-}$ potential do not afford $Q_{min} < 7$ kJ mol^{-1} and in many cases give $Q_{max} > 16$ kJ mol^{-1}. The test for the third variant of the $Ar-O^{2-}$ potential also demonstrated its inadequacy. This served as a reason for refining the parameters of the $Ar-O^{2-}$ and $Ar-Ti^{4+}$ potentials. This situation is likely due to the fact that previously[20a,24] in choosing the parameters of the $Ar-O^{2-}$ and $Ar-Ti^{4+}$ potentials effective distribution functions with $\varepsilon = 0$ were used.

To reduce the number of independent parameters, they were chosen to fit the condition $E_{Ar-Ti}/E_{Ar-O} = 0.5$, which approximately corresponds to the second variant for the $Ar-O^{2-}$ potential (see above). Variation of parameters E_{Ar-O}, δ, and γ made it possible to determine the three-dimensional neighborhood of the point with coordinates $E_{Ar-O} = 120$ K, $\delta = 22\%$, and $\gamma = 45\%$, for which the energy interval for $f(Q)$ lies in the 5.75—15.25 kJ mol^{-1} range. An increase in parameter δ to 25—30% results in a decrease in Q_{min} to 4.75 kJ mol^{-1} and in an increase in Q_{max} to 16.25—18.25 kJ mol^{-1}. As was mentioned above, $f(Q)$ is affected by "technological" parameters and the parameters of the potentials in a complex nonlinear way. Thus, the identical Q_{min} value of 4.75 kJ mol^{-1} is obtained at $\delta = \gamma = 10\%$ and $E_{Ar-O} = 90$ K; however, in this case $Q_{max} = 9.25$ kJ mol^{-1}. At the same time, the evident condition is fulfilled that an increase in the degree of amorphization results in a decrease in Q_{min} and an increase in Q_{max} in a certain local range of the parameter values of the model. One more "technological" factor should also be noted: when the surface oxygen ions are removed randomly the $Q_{min} - Q_{max}$ interval is 1—2 kJ mol^{-1} broader than when they are removed according to their distance from adjacent Ti^{4+} ions. We used the first variant in our calculations.

By and large, the potentials of interparticle interactions and the reasons for using the atom-atom approximation should be determined by quantum-mechanical methods; however, this problem is still unsolved even for such a relatively simple system as $Ar-TiO_2$(rutile). It should be also noted that the available information is inadequate: even measurements of the isotherms and heats of adsorption for the specific crystal faces of rutile in the above system are unavailable.

The distribution functions of the energies and of the logarithms of the local Henry constants finally adopted for the different size fragments are shown in Figs. 2 and 9. These distribution functions were used for calculating the thermodynamic characteristics of adsorption in the Ar—rutile system.

Calculation of isotherms and heats of adsorption. The obtained distribution functions are closest in their shape to curve *2* (Fig. 10) ($\varepsilon = 0.4$ kJ mol^{-1}). The calculations of isotherms and heats of adsorption were carried out without additional fitting parameters. A comparison of the experimental and theoretical curves for fragments differing in size are shown in Fig. 10. A small fragment does not reflect the behavior of the curve of the heat of adsorption at low coverages of the mono-

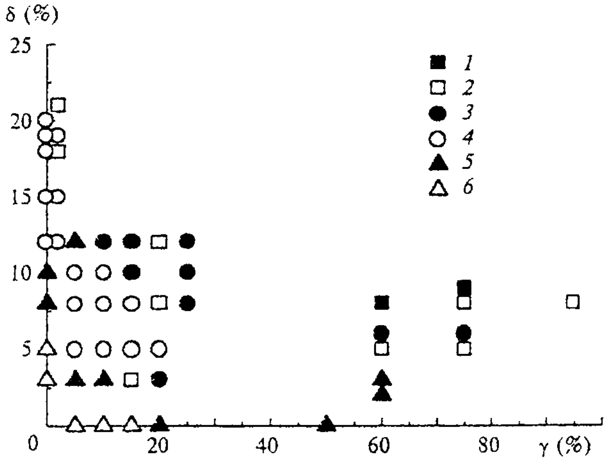

Fig. 8. Scheme of distribution of the Q_{min} values for various δ and γ; Q_{min}/kJ mol^{-1} = 7.75 (*1*), 8.75 (*2*), 9.25(*3*), 9.75 (*4*), 10.25 (*5*), and 10.75 (*6*). The "technological" states of the adsorbing TiO_2 surface.

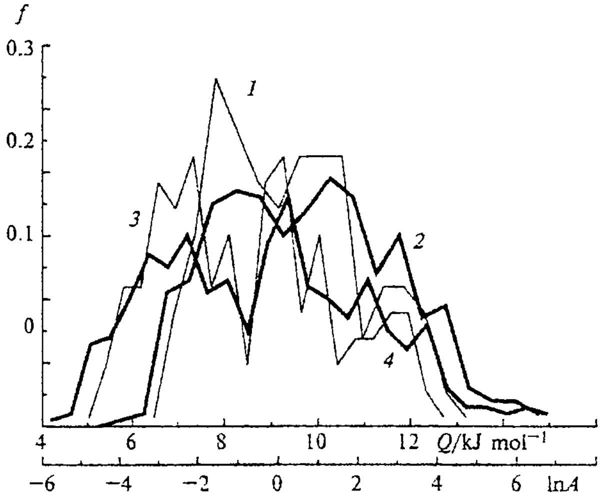

Fig. 9. The distribution functions of $f(Q)$ (*1*, *2*) and those of $f(\ln A)$ (*3*, *4*) at ($\delta = 22\%$, $\gamma = 45\%$) for surface fragments of size: *1*, *3*, 10×10; *2*, *4*, 20×20.

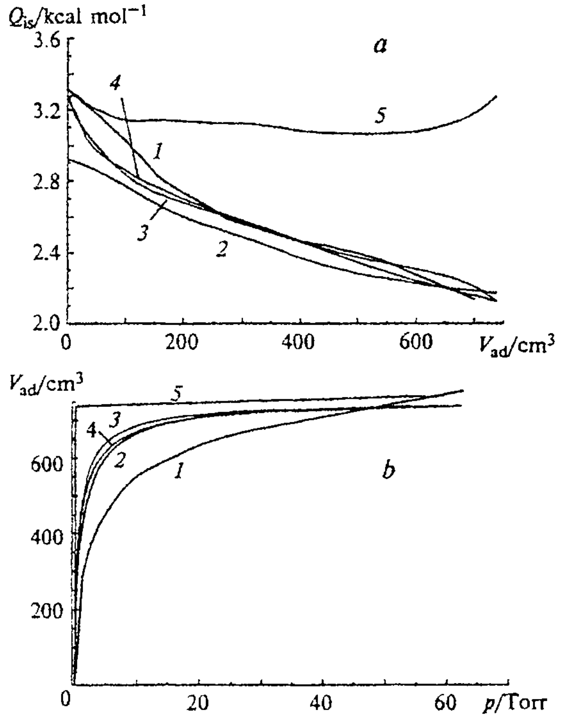

Fig. 10. Concentration dependences of the isosteric heat of adsorption $Q_{is}(V_{ad})$ (*a*) and those of the $V_{ad}(p)$ isotherm (*b*); V_{ad} is the adsorbate volume (V_{ad} = 755 cm^3 is the monolayer capacity).[20b] The parameters of the generated amorphous surface are δ = 22% and γ = 45%. *1*, Experiment, see Refs. 20a and 20b; calculations for surface fragments of size: 10×10 (*2*), 15×15 (*3*), 20×20 (*4*), and 15×15 at ε = 1 kJ mol^{-1} (*5*).

layer; the calculation and experiment are in qualitative agreement at intermediate and high coverages. Increasing the size of the fragment substantially improves the agreement between the calculation and experiment. It is likely that a fragment larger than 15×15 satisfactorily reflects the basic properties of amorphous adsorbents. The mean deviation between calculated and experimental values is ±3%. The differences observed at low coverages are due to the differences in the distribution functions. The similarity of both curves in the case of monolayer coverage is due to the predominance of the contribution of lateral interactions ($z\varepsilon$) over that of differences between Q_{min} for the atom-molecular distribution function and the $f(Q)$ obtained experimentally.

For comparison, a curve with ε = 1 kJ mol^{-1} is shown in Fig. 10; it shows no qualitative agreement with the experimental curve, since the atom-molecular distribution function $f(Q)$ and the corresponding experimental function drastically differ in the low-energy region.

The analogous conclusion should be drawn from the comparison of the calculated and experimental isotherms of adsorption. For them, the mean deviation is ±10%. This large deviation is explained by the fact that the above data for T = 85 K were obtained by calculation. (It was noted in the literature[20b] that in the case of low coverage of a surface (equal to 0—370 cm^3), the pressure in the system is too low to be measured by a mercury manometer.) Data on the pressure in this interval of coverage were obtained[20a] at 120 K and recalculated for T = 85 K using the Clausius—Clapeyron equation from the known temperature dependence of the isosteric heat of adsorption.[20b] The use of the parameter ε = 1 kJ mol^{-1} decreases the agreement between calculation and experiment (as in the case of the heat of adsorption).

* * *

The proposed procedure for calculating the characteristics of spherically symmetrical particles, adsorbed on an amorphous surface and blocking several local minima of the potential energy of adsorbent—adsorbate interaction within one local volume of the order d^3 is efficient in the framework of the quasi-one-center lattice model,[10] since a small number of partitions of the site area into small parts is required. To perform reliable calculations of the adsorption characteristics, the fragment of the amorphous surface should contain no less than 15×15 sites of the lattice structure.

The proposed procedure for generating the structure of the near-surface layers of the adsorbent by completing it above the three-dimensional crystal lattice ensures the formation of an amorphous surface and makes it possible to theoretically calculate the functions of the distribution of the bonding energies of the adsorption centers of the amorphous surface.

A newly introduced two-dimensional distribution function, $f(\Delta U,R)$, which determines the fraction of pairs of local minima of the potential energy separated by distance R and differing by ΔU, makes it possible to characterize the adsorption properties of the surfaces of amorphous adsorbents in detail and can be used to "identify" them.

Taking into account the short-range order in the amorphous structure of TiO_2 (rutile) by simulating the structure of the anionic and cationic sublattices results in close values of energies for most of the adjacent local minima. A series of adjacent minima with strongly differing energies is much less probable than in the case when only an anionic sublattice is considered.

The values of the preexponentials of the local Henry constants on amorphous surfaces can vary by more than two orders of magnitude. The assumption that A_0 has a constant value is a rough approximation. The functions of distribution over the bonding energies $f(Q)$ and those over the local Henry constants $f(\ln A)$ qualitatively correlate with each other but are not identical.

Allowance for the lateral interactions is of paramount importance for determining the functions of distribution over energies $f(Q)$ (or $f(\ln A)$) from experimental data. Neglect of this factor results in qualitatively erroneous values for the low-energy regions of these functions.

The atom-atom potentials of the Ar—TiO_2(rutile) system need further refinement. The available experimental data are inadequate. Direct measurements of the isotherms and heats of adsorption at 85 K at low coverages are required first, including those on the specific crystal faces of rutile.

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Received August 8, 1996;
in revised form December 17, 1996