Adsorption phenomena at high pressures and temperatures.
3.* Determination of the effective diameter of molecules and their orientation toward the adsorption surface on the basis of adsorption data

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Equilibrium adsorption isotherms for Ar, Kr, and N_2 on crystalline NaA zeolite were measured in the pressure range of 0.1—160 MPa and temperature range of 305—448 K. The method for determining the inaccessible volume of the adsorption system (free volume + micropore volume) and the micropore volume of a sorbent with the use of such adsorbates as monoatomic Ar and Kr and diatomic N_2 was applied. The effective radii of N_2 and O_2 molecules were calculated from the dependence of micropore volume of the zeolite on the radius of the monoatomic gas used. On the basis of this result, one can determine the orientation of the molecules of nitrogen and oxygen in the pores of the zeolite, caused by sorption forces. The use of Ar and Kr as the adsorbates allows one to determine the total surface area of the zeolite, which was found to be equal to 1458 m^2/g.

Key words: adsorption, radius of a molecule, adsorbent, surface, pore volume.

Potential energy of the interaction of spherical molecules $\phi(r)$ is described well by the Lennard—Jones equation:

$$\phi(r) = 4\varepsilon\,[(\sigma/r)^{12} - (\sigma/r)^6]. \qquad (1)$$

The σ constant, *i.e.*, the effective diameter of the molecule, can be determined by measuring the values of viscosity or diffusivity of gases or by calculating the second virial coefficient.[2] These methods for determining the σ value are simple enough and can be used for both monoatomic and multiatomic molecules. However, in the case of multiatomic molecules, these methods do not take into account the peculiarities of molecular structure. For example, the σ value for the N_2 molecule obtained on the basis of viscosity is equal to 0.3681 nm,[2] whereas the diatomic dumbbell-like N_2 molecule should have a second parameter σ_N that is significantly less than σ. These methods are unsuitable in principle for estimating the σ parameters of adsorbed molecules. In this case, an adsorbent should unambiguously affect the orientation of multiatomic molecules relative to its surface. The NMR technique can be used for molecules whose nuclei possess a magnetic moment.[3] In this work, we attempted to use adsorption measurements of gases at high pressures up to ~160 MPa for determining the σ values. The adsorption of monoatomic (Ar and Kr) and diatomic (N_2) gases on NaA zeolite was studied. In NaA zeolite, cavities of two types, α and β, occur, but adsorbed molecules diffuse into β-cavities only at elevated tempetatures.

Experimental

A schematic diagram of the high-pressure adsorption setup is shown in Fig. 1.

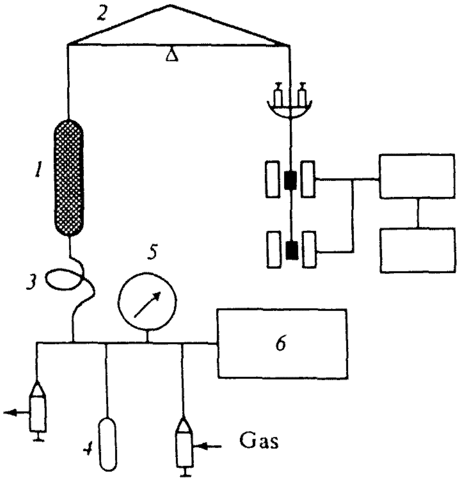

Fig. 1. Schematic diagram of the adsorption setup. *1*, ampule with a sample, *2*, beam balance, *3*, capillary spring, *4*, ballast space, *5*, Bourdon manometer, *6*, gravimetric manometer, *7*, electronic unit for the balance control.

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* For Part 2 see Ref. 1.

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Metallic ampule *1* with a zeolite (1.9241 g) is suspended to a beam balance *2* (VRL-200). Gas is supplied into the ampule *1* through a metal capillary *3* coiled into a spring. The second end of the capillary is connected to a steel cylinder *4* (of 300 cm^3 volume). Total sensitivity of such a gravimetric setup is $5\cdot10^{-4}$ g. The pressure in the setup was determined with the Bourdon manometer *5* (Q ~1600 кg/cm^2, class 1) and with a gravimetric manometer *6* developed by us, which was joined up in parallel; its principle of operation and sensitivity are similar to those of a gravimetric setup. Combined volume of the suspended ampule and capillary is equal to 13.157±0.002 cm^3. The volume of the ampule with the capillary was estimated by the weight and density of degassed CCl_4 which was supplied into the ampule through the capillary. The temperature of the thermostat for the manometer was maintained constant (300±0.1 K).

The pressure in the system was determined on the basis of *P, V, T* data for the gases under study using the density of the weighed gas according to works.[4,5] More detailed description of the setup is presented in work.[6] The large volume of the ampule and relatively high sensitivity of the gravimetric manometer allow one to determine the low pressure of gases under study with an accuracy up to 2 %. In the range of middle and high pressures, the error of determination of the ρ values with the gravimetric manometer is significantly less and the error of the determination of the pressure in the system does not exceed 1 %. Calculation of the pressure and ρ_g for other temperatures with the aid of the multiconstant equation for these gases is described in work[7] in more detail.

Results and Discussion

For the determination of relatively large volumes of vessels without adsorbents on the basis of *P,V,T*-data, one can use various gases but it is necessary to neglect the adsorption on the walls of the vessel, *i.e.*, an increase in the density of the gas (ρ_a) on the walls as compared to that in the volume of the vessel (ρ_g). This results in an increase in the volume being estimated as compared to the real volume of the vessel. In addition, the volume inaccessible to the centers of gas molecules is not taken into account ("wall-layer effect"). This volume is equal to

$$V_H = r_{eff}\cdot S, \qquad (2)$$

where $r_{eff} = \sigma/2$ is the effective radius of the molecule of the gas for calibration and *S* is the inner surface of the vessel. In this case, the sizes of the gas molecules are not taken into account and this results in a lower estimated volume. When the adsorbent, whose pore sizes are commensurable with the sizes of the molecules, is in the vessel, the calibration of the vessel volume by different gases is impossible because of high gas adsorption on the adsorbent, *i.e.*, $\rho_a \gg \rho_g$, and this results in great overstating of the volume of the vessel. Therefore, in adsorption studies helium is used as the gas for calibration, because it is practically not adsorbed at low pressures and fairly high temperatures ($\rho_a \approx \rho_g$). However, upon calibration with He, some fraction of the vessel volume remains inaccessible to the centers of the gas molecules. Owing to diffusion of He into the zeolite pores, the volume of the ampule containing NaA zeolite, when calibrated with He, would be equal to

$$V(\mathrm{He}) = V_{free} + W(\mathrm{He}), \qquad (3)$$

where V_{free} is the volume of the ampule unoccupied by zeolite crystals and $W(\mathrm{He})$ is the pore volume of the zeolite accessible to the centers of He atoms. If the calibration was carried out with Xe, we would obtain $V(\mathrm{Xe}) = V_{free}$ because of the large size of the gas molecules, which cannot penetrate the pores of the zeolite. Thus, in the work,[6] the volume V_{free} of the ampule with zeolite was determined with CCl_4 as 1.833 cm^3. In the work,[8] the limiting filling of the pores of the NaX zeolite was determined by adsorption measurements at low temperatures, and the calculated pore volume of this zeolite, equal to 0.3 for Ar, 0.27 for Kr, and 0.25 $cm^3\ g^{-1}$ for Xe, was obtained under the assumption that the density of the adsorbate corresponds to the density of the volume phase. This is in line with the regularity of change in the effective diameters: Ar (0.3465) < Kr (0.361) < Xe (0.4055 nm), which were obtained on the basis of the viscosity of the gases.[1] It is obvious that the pore volume of the adsorbent under study *W* and consequently the volume of the ampule should depend on the effective size σ of the molecules of the gas used for calibration: the greater the σ of a molecule, the lesser is the accessible pore volume (*W*) of the zeolite. In this case, the real crystallographic pore volume of the zeolite is equal to

$$W_{cryst} = W(N_2) + S\cdot\sigma(N_2)/2 = W(\mathrm{Kr}) + S\cdot\sigma(\mathrm{Kr})/2 = = W(\mathrm{Ar}) + S\cdot\sigma(\mathrm{Ar})/2, \qquad (4)$$

where *S* is the total surface area of the zeolite, and $S\cdot\sigma(i)/2$ is the inaccessible volume (*W*) for the centers of the molecules of a corresponding gas.

In our experiment, the weight *m* of the gas entering the ampule with the adsorbent (Fig. 1) partially falls into a free volume (m_{free}) and partially is adsorbed in α- and β-cavities of the zeolite (m_a and m_b) and at the outer surface of the zeolite crystals (m_s):

$$m = m_{free} + m_a + m_b + m_s. \qquad (5)$$

At temperatures 305, 334, and 373 K, nitrogen does not penetrate to β-cavities of the zeolite.[6] Similar phenomenon was also observed for Kr at 334, 373, and 408 K [9] and for Ar at 334 and 373 K. The adsorption at the outer surface of the crystals of the zeolite, m_s, is small at relatively high temperatures, and it can be neglected. Therefore, we shall further consider the adsorption of gases only in the α-cavities of the zeolite:

$$m_a = \rho_a W_a = \rho_g W_a + \Gamma_a, \qquad (6)$$

where ρ_a is the average density of the gas adsorbed in the α-cavities of the zeolite, ρ_g is the density of the equilibrium gas phase, W_a is the volume of the α-cavities of the zeolite, and Γ_a is the excess adsorption according to Gibbs. Substituting (6) into (5) and dividing all members by ρ_g, we obtain

$$m/\rho_g = V = V_{\mathrm{free}} + W_a \cdot \rho_a/\rho_g = V_{\mathrm{free}} + W_a + \Gamma_a/\rho_g. \quad (7)$$

In the range of high enough pressures of the gas, $\rho_a \to \rho_g$ and, according to equation (7), $\Gamma_a/\rho_g \to 0$. At the same time, it is known that with a rise in pressure, the Γ_a value passes through a maximum, then decreases and drops to zero, while ρ_g increases with increasing a pressure. One should expect that in this pressure range, fairly long horizontal segment should be observed on the curve of the m/ρ_g—P dependence (Fig. 2), where

$$m/\rho_g = V_{\mathrm{free}} + W_a = \mathrm{const.} \quad (8)$$

Equation (7) shows that if the volumes of vessels are calibrated by the gas which is then used in the adsorption measurements, the adsorption on the vessel walls is excluded upon calibrating and "the wall-layer effect" is also taken into account. Such a calibration procedure has the advantage of carrying out in the course of measuring the adsorption isotherms.

Figure 2 presents the adsorption isotherms measured by us in the m/ρ_g—P coordinates for N_2, Kr, and Ar at different temperatures. The horizontal segments are seen in the figure which are characterized by the values: $V(N_2)$ = 2.27±0.01 cm^3, V(Kr) = 2.162±0.005 cm^3, V(Ar) = 2.185±0.003 cm^3. The $V(N_2)$, V(Kr), and V(Ar) volumes were determined in the pressure range of 135—160 MPa and temperature range of 305—448 K, where the deviations of V from the constant were random.

By subtracting V_{free} = 1.833 cm^3 from the V value, determined from the horizontal segment of the isotherm, and dividing by the weight of the sample, 1.9241 g, we obtain the values of the specific pore volume W, which is accessible for the centers of the molecules of the corresponding gas: $W(N_2)$ = 0.23±0.01 cm^3 g^{-1}, W(Kr) = 0.171±0.008 cm^3 g^{-1}, W(Ar) = 0.185±0.005 cm^3 g^{-1}. The sequence $W(N_2) > W(\mathrm{Ar}) > W(\mathrm{Kr})$ was obtained for the NaX—Ar and NaX—Kr adsorption systems. In the case of monoatomic gases, σ_{Kr} = 0.361 nm and σ_{Ar} = 0.3418 nm, *i.e.*, $\sigma_{\mathrm{Kr}} > \sigma_{\mathrm{Ar}}$ and the accessible volumes for the centers of the gas molecules $W(\mathrm{Kr}) < W(\mathrm{Ar})$, but for the diatomic molecule N_2 (σ = 0.3749 nm), one could expect, according to equation (4), that $W(N_2)$ is less than W(Kr) and W(Ar). However, the $W(N_2)$ value proved to be substantially higher than W(Ar). This difference is possibly due to that $\sigma(N_2)$ was obtained from the measurements of the viscosity or diffusion when the diatomic nitrogen molecule manifested itself as a sphere. In our case, the surface of the zeolite can orientate the nitrogen molecule by two atoms with respect to it (Fig. 3), so the effective radius of the nitrogen molecule is equal to σ of the nitrogen atom. Hence, according to equation (4), the accessible volume W should be greater. Since Ar, Kr, and N_2 are not adsorbed in the pores of the NaA zeolite at low temperatures, there are no available data in the literature on the pore volumes estimated by these gases. However, the limiting value of the adsorption of oxygen on the NaA zeolite has been measured at 90.2 K.[10] We found that the pore volume W of the NaA zeolite determined by oxygen is equal to 0.235 cm^3 g^{-1} under assumption that the density of the adsorbate is equal to that of a liquid and $\sigma(O_2)$ = 0.3541 nm.[10] As the σ value of the oxygen molecule is less than that of nitrogen molecule, this result confirms the correctness of the approach based on the use of equation (4). The true crystallographic volume of the α-cavities of the NaA zeolite can be taken as constant, and the content of the cavities per gram of the zeolite ($N = 3.58 \cdot 10^{20}$ g^{-1}) depends on its chemical composition.[8] The large α-cavity is a truncated cubooctahedron, and if one takes a cube as the model of the α-cavity (Fig. 3), its linear size will be equal to

$$L = \sqrt[3]{W(\mathrm{Ar})/N} + \sigma(\mathrm{Ar}) = \sqrt[3]{W(\mathrm{Kr})/N} + \sigma(\mathrm{Kr}) = \sqrt[3]{W(N_2)/N} + \sigma(N_2). \quad (9)$$

We chose especially gases with molecules of spheric symmetry (Ar and Kr) as the adsorbates, because with their aid one can verify the correctness of the approach described and then estimate the σ values for the diatomic N_2 and O_2 $_{\mathrm{molec}}$ules. By substituting into equation (9) the experimental values of W(Ar) and W(Kr), the known values of N and σ(Ar) being taken from the data on the viscosity (Table 1), we obtain σ(Kr) = 0.3626 nm, which agrees well with the σ(Kr) that was also obtained on the basis of the viscosity of the gas (Table 1). The values of σ for atoms of nitrogen and oxygen can be determined in a similar way with equation (9), and they are equal to 0.2814 and 0.2752 nm, respectively, *i.e.*, far less than σ for molecules of nitro-

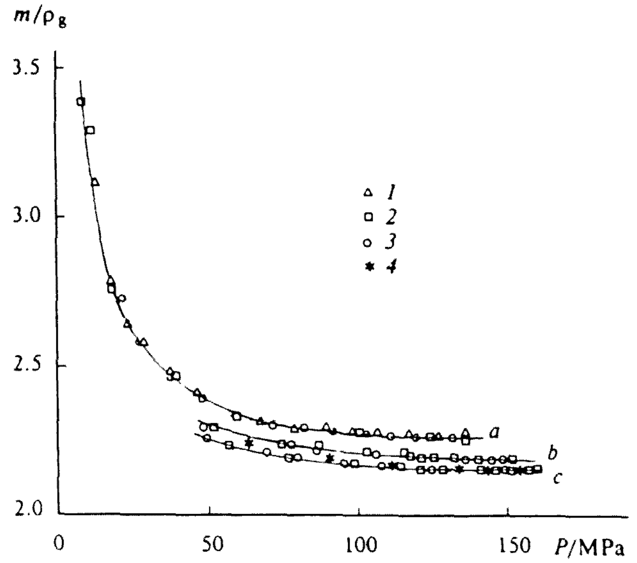

Fig. 2. Dependence of m/ρ_g on pressure at 305(*1*), 334(*2*), 373(*3*), and 448 K (*4*). *a*, nitrogen, *b*, argon, *c*, krypton.

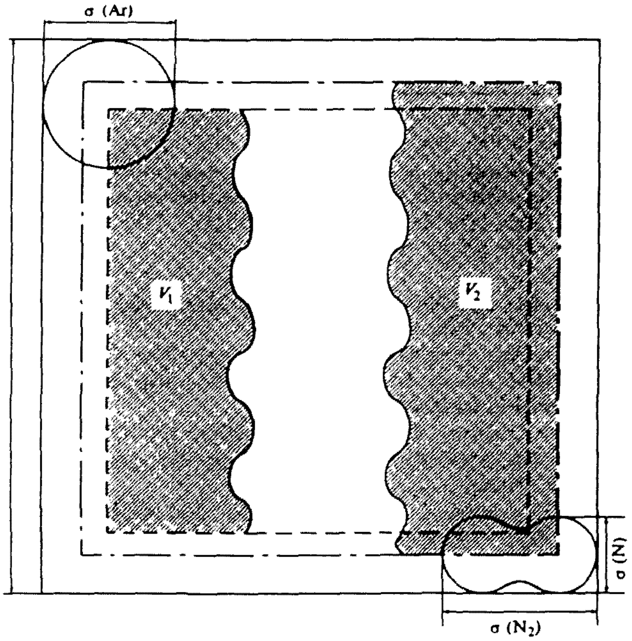

Fig. 3. Cubic model of the zeolite pore. L is linear size of the zeolite pore; V_1 is volume of the pore accessible to the centers of Ar molecules; V_2 is volume of the pore accessible to the centers of N_2 molecules.

gen and oxygen. Because the σ values of atoms of nitrogen and oxygen are unknown, we compared them with the ionic radii of N^{3-} ($\sigma/2 = 0.148$ nm) and O^{2-} ($\sigma/2 = 0.136$ nm),[11] as well as with the σ/2 value of atoms of nitrogen and oxygen obtained on the basis of the model in which the covalent radii of the atoms of nitrogen and oxygen are equal to 0.071 nm and 0.066 nm, respectively,[12] and $\sigma(N_2) = 0.3749$ nm, $\sigma(O_2) = 0.3541$ nm. This calculation resulted in σ/2 values of 0.1164 nm for the nitrogen atom and 0.111 nm for the oxygen atom. Our result is closer to the ionic radii of nitrogen and oxygen (see Table 1).

The linear size of the crystallographic cavity for the chosen model $L = 1.143$ nm and the linear size of α-cavity of the truncated cubooctahedron of the NaA zeolite is equal to 1.14 nm.[8] If one use a sphere as the model of a cavity for determination of the σ value of the molecules, then its radius can be expressed as follows:

Table 1. Effective sizes of molecules, atoms, and ions (σ/nm)

σ	From viscosity measurements (nm)	From adsorption data (nm)*
$\sigma(Ar)$	0.3418[2]	0.3402
$\sigma(Kr)$	0.361[2]	0.3626
$\sigma(N_2)$	0.3749[2]	
$\sigma(O_2)$	0.3541[2]	
$\sigma/2(N^{3-})$	0.148[11]	
$\sigma/2(O^{2-})$	0.136[11]	
$\sigma/2(N)$	0.1164 (Model)	0.1409
$\sigma/2(O)$	0.111 (Model)	0.1376

* Data of this work.

$$L = \sqrt[3]{W(\mathrm{Ar})3/4\pi N} + \sigma(\mathrm{Ar})/2 = \sqrt[3]{W(\mathrm{Kr})3/4\pi N} + \sigma(\mathrm{Kr})/2 = \sqrt[3]{W(\mathrm{N_2})3/4\pi N} + \sigma(\mathrm{N_2})/2 \cdot \qquad (10)$$

According to equation (10), the σ values of the molecules coincide with the values determined according to equation (9), and the linear size of the cavity $2R = 1.33$ nm. Apparently, a model of a cube is closer for the truncated cubooctahedron than the model of a sphere.

One can approach to determining the σ values of the molecules by another way: by using the σ values of spherically symmetric Ar and Kr atoms and the experimental values of W(Ar) and W(Kr), one can obtain the value of the surface area of the zeolite (see equation (4)) which is equal to

$$S = [W(\mathrm{Ar}) - W(\mathrm{Kr})]/(\sigma_{\mathrm{Kr}}/2 - \sigma_{\mathrm{Ar}}/2) = 1458\ \mathrm{m^2/g}. \qquad (11)$$

In the work,[13] the values of surface area of the CaA and NaX zeolites were calculated on the basis of the known crystalline structure. The calculated values were compared with the experimental data. The specific surface areas are equal to 1640 and 1400 $m^2\ g^{-1}$, respectively. This data are in a good agreement with our result.

If the surface area of the adsorbent, the accessible pore volumes W(Ar), $W(N_2)$, and $W(O_2)$ are known, one can determine the σ/2 values for the atoms of nitrogen and oxygen which are equal to 0.1409 nm and 0.1376 nm, respectively. The σ values obtained confirm the suggestion on the orientation of the adsorbed molecules of nitrogen and oxygen by two atoms toward the surface of the zeolite due to adsorption forces (Fig. 3). Unfortunately, we do not know the direction and the value of the electric field near the surface of the zeolite which are necessary to take into account the polarizability of the molecules. However, a good coincidence of the σ(Kr) value obtained by us with the data on the viscosity of gases gives evidence that this correction would be negligible.

The described method for determining the surface area of porous substances can be used for determining the surface area of various highly dispersed materials. In addition, there is no need to use crystalline zeolites as the adsorbents for determining the σ values of molecules by the second method, but rather adsorbents of any type can be used, because methods for determination of W on the basis of the excess adsorption value have been developed.[14]

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