Adsorption phenomena at high pressures and temperatures
4.* Isotherms of excess and absolute adsorption of Kr on NaA zeolite

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The problem of conversion of an isotherm of excess adsorption measured experimentally into values of the total amount of the adsorbate (absolute adsorption) has been formulated. Five isotherms of excess adsorption of krypton on NaA zeolite were measured (at 334—500 K) at equilibrium pressures of ~160 MPa. The corresponding isotherms of the total amount were calculated and the temperature dependences of the parameters of an equation describing the isotherms of excess adsorption were identified. It was shown that at high temperatures and pressures, krypton atoms diffuse into the β-cavities of the NaA zeolite.

Key words: excess adsorption, isotherms.

One of urgent tasks of the modern science of adsorption is development of a theory that would allow one to convert the excess adsorption measured experimentally to the values of the total amount of an adsorbate in an adsorbent, *i.e.*, to absolute adsorption. Knowing the values of absolute adsorption, one can interpret the results of any physical experiment devoted to the properties of an adsorbate or to the verification of any molecular statistical model of adsorption phenomena. In this connection, of interest are experimental studies of adsorption dealing with an extension of the range of equilibrium gas pressures (densities) to the region in which the approximate equality $\Gamma \approx a$ between the values of excess and absolute adsorption no longer holds (*i.e.*, to the region where $p \gg 0.1$ MPa) and also dealing with the determination of the adsorption volume corresponding to the given adsorptive.

In this work we present the results of our systematic studies carried out along this line. We studied the excess adsorption of krypton on the NaA zeolite at pressures of up to 160 MPa. Each isotherm of excess adsorption $\Gamma = f(\rho)_T$ is matched by an isotherm of absolute adsorption (the total amount) $a = F(\rho)_T$, the Γ and a values corresponding to the same density (ρ) of an equilibrium gas and being related to each other by the universal relationship

$$a = \Gamma + W\rho, \qquad (1)$$

where W is the volume of the adsorption space, which, in the general case, does not coincide with the geometric volume of the adsorbent pores. Correct methods for recalculating the excess adsorption measured experimentally to the absolute adsorption have been reported and analyzed previously.[1]

The NaA zeolite was chosen as the adsorbent, because the validity of the methods suggested for determining the adsorption volume can be verified only in the case of crystalline sorbents. In particular, for the NaA zeolite, the value of the density of the porous solid is known; it has been found on the basis of X-ray diffraction measurements of the unit cell parameters and chemical composition. This approach can serve as an alternative nonadsorptional method for determining the absolute adsorption.

Experimental

All measurements were carried out by the combined gravivolumetric method that we developed. We used the experimental equipment described in detail previously,[2] except that there was one essential distinction: equilibrium pressures in the range between 0.1 to 200 MPa were measured using a new high-pressure gravimetric manometer that we developed, consisting of a titanium (the BT9 alloy) autoclave suspended from a laboratory analytical balance (the autoclave volume was 13.157 cm^3 and the absolute sensitivity of the balance was $0.5 \cdot 10^{-4}$ g). The autoclave was connected to a vessel in which pressure was measured by a thin steel capillary coiled into a helix of large diameter. The autoclave and the balance were arranged in an air thermostat, the temperature being maintained in the 300±0.1 K range. Thus, the density of krypton in the autoclave was measured with high accuracy (the error did not exceed 1 %).

Since the temperature of krypton and of the adsorbent differs in the general case from that of the autoclave of the manometer, the density of krypton in the equilibrium state can be determined by either of two methods, one of which includes the preliminary determination of the $\rho = f(p)_T$ function (for example, using a dead-weight pressure-gage tester), and the other includes the construction of a multiconstant equation of state for krypton, $F(p,\rho,T)$, which makes it possible to calculate the true density of

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the equilibrium gas with good accuracy (the error not exceeding 1 %). For practical reasons, we chose the second method. The multiconstant equation for krypton[3] was used at pressures of up to p = 110 MPa. For higher pressures, the constants of the equation were corrected in such a way that the deviations of the calculated values of p, V, and T from the data reported previously[4] did not exceed 1 %.

Results and Discussion

Calibration of the apparatus. The substantial extension of the range of equilibrium pressures (densities) of gases to higher values naturally leads to more stringent requirements upon the choice of the method for calibrating the apparatus; this actually means more precise determination of the position of the separating surface, with respect to which the excess adsorption is calculated. In view of the fact that one of the main tasks of our study was to develop a method for recalculating the experimentally determined adsorption to the value of the total amount of the adsorbate, we should calibrate the instruments in such a way that the so-called "dead volume" (V_d) of the adsorption tube will be equal to the volume accessible at a given temperature to centers of the molecules of the gas used, *i.e.*,

$$V_d = V_f + W, \tag{2}$$

where V_f is the part of the free volume of the tube in which the action of the adsorption field is insignificant. The calibration amounted to the determination of the overall amount of the adsorptive in the system provided that the excess adsorption is practically equal to zero. For the calibration of tubes of relatively large volumes without an adsorbent with the aid of the p,V,T-parameters of a gas, various gases can be used; however in this case, one must neglect primarily the adsorption on the walls of the vessel, *i.e.*, the increase in the density of the gas on the walls (ρ_a) with respect to its density in the bulk of the tube (ρ_g). This results in the V value found being greater than the true volume of the tube. Besides, the size of the gas molecules is not taken into account,[5] *i.e.*, the volume inaccessible to the centers of molecules is neglected.

$$V_{un} = r_{eff}S, \tag{3}$$

where r_{eff} is the effective radius of the molecule of the gas used for calibration, and S is the inner surface of the vessel. This results in an underestimation of the V value being determined. The true volume of the tube is equal to the sum of the accessible and inaccessible volumes, their ratio depending on the size of the molecules of the gas for calibration. When the tube contains an adsorbent, the sizes of the pores of which are commensurable with the sizes of the molecules, the calibration of the volume of the tube with various gases is impossible due to the substantial adsorption of the gas by the adsorbent (*i.e.*, $\rho_a \gg \rho_g$), which leads to a considerable overestimation of the V value being determined. Therefore, helium is used as the gas for calibration in adsorption studies, because it is virtually not adsorbed at low pressures and relatively high temperatures (*i.e.*, for He, $\rho_a \approx \rho_g$). However, this generally accepted method seems insufficiently correct, since our direct experiments on adsorption on zeolites[6] showed that, with the modern level of experimental instrumentation, the value of excess adsorption of He at room temperature cannot be neglected; in addition, for calibration with helium, the problem associated with the difference in the sizes of He atoms and molecules of an adsorptive has not been solved.

In our experiment, the mass (m) of the gas supplied to the tube with the adsorbent partially enters the free volume of the tube (m_f) and partially is adsorbed in α- and β-cavities of the zeolite (m_α and m_β, respectively) and at the outer surface of the zeolite crystals (m_s), *i.e.*,

$$m = m_f + m_\alpha + m_\beta + m_s. \tag{4}$$

The results obtained by us previously[2] indicate that a noticeable diffusion of nitrogen molecules into β-cavities of the zeolite occurs only at $T \geq 408$ K. Therefore we believe that at T = 334, 337, and 408 K, the Kr atoms, which are much larger than the N atoms, are adsorbed only in α-cavities of the NaA zeolite, while at higher temperatures, diffusion of the molecules into β-cavities should also be expected. The adsorption of krypton at the outer surface of the zeolite crystals at these temperatures and with the surface area being not very high can be neglected, *i.e.*,

$$m = m_f + m_\alpha = \rho_g V_f + \rho_\alpha W = \rho_g V_f + \rho_g W + \Gamma, \tag{5}$$

where ρ_α is the average density of the adsorbate in the α-cavities, and Γ is the excess adsorption according to Gibbs. By dividing all the terms of Eq. (5) by ρ_g we obtain

$$m/\rho_g = V = V_f + W\rho_\alpha/\rho_g = V_f + W + \Gamma/\rho_g. \tag{6}$$

In the region of relatively high gas pressures, $\rho_\alpha \to \rho_g$ or, what is the same, $\Gamma/\rho_\alpha \to 0$, since it is known that with an increase in pressure, the excess adsorption Γ passes through a maximum, then decreases, and drops to zero, whereas the density ρ_g simultaneously increases. One may expect that in this pressure region, the curve of the m/ρ_g—p dependence should contain a rather extensive horizontal section (Fig. 1), where

$$m/\rho_g = V = V_f + W = V_d = \text{const.} \tag{7}$$

It can be seen from Eq. (7) that the approach considered above results in the calibration of the adsorption instrumentation, *i.e.*, in the determination of V_d with the same adsorptive used in the study. This method has a further important advantage, associated with the fact that in this case, calibration is a part of the measurement of the adsorption isotherm, rather than an additional procedure. It is seen from Fig. 1 that the volume V for the Kr—NaA system in the high-pressure region does not

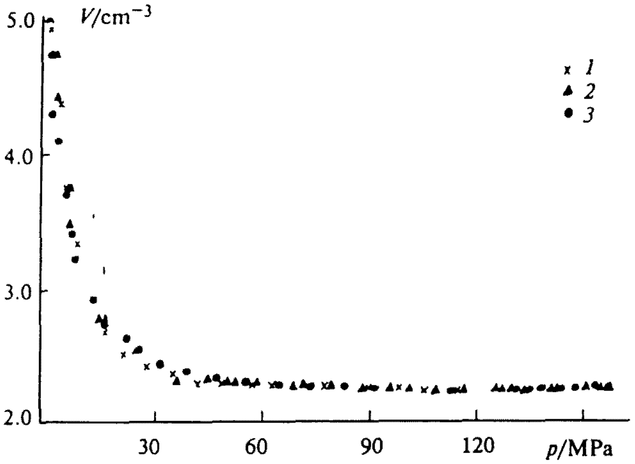

Fig. 1. Dependence of the volume $V = m/\rho_g$ on pressure and temperature for the Kr—NaA system at T/K = 334 (*1*), 373 (*2*), and 408 (*3*).

depend on the temperature (for 334, 373, and 408 K) and that the V_d(Kr) value is equal to 2.162±0.005 cm^3. At higher temperatures (448 and 500 K), V_d(Kr) = 2.194±0.006 cm^3. The $V_d(N_2)$ value was found in a similar way to be 2.27±0.01 cm^3 for T = 305, 334, and 373 K; and V_d(Ar) = 2.185±0.003 cm^3 for T = 334 and 373 K. The $V(N_2)$, V(Kr), and V(Ar) volumes were determined in the pressure range between 125 and 160 MPa, in which deviations of V from a constant value were random. The V_f value was determined directly from the mass and the density of degassed CCl_4, which was let into the tube with the zeolite (the CCl_4 molecules could not diffuse into the pores of the zeolite, because they are too large); this gave V_f = 1.833 cm^3. By determining the difference between the V_d and V_f values and dividing it by the mass of the sample (m_A = 1.9241 g), we calculated the volumes of the adsorption space: W(Kr) = 0.171±0.008 cm^3 g^{-1}, W(Ar) = 0.185±0.005 cm^3 g^{-1}, and $W(N_2)$ = 0.23±0.01 cm^3 g^{-1}. For T = 448 and 500 K, W(Kr) = 0.188 cm^3 g^{-1} was found; however, one cannot claim that at the high temperatures employed, the equilibrium is reliably achieved.

The sequence $W(\mathrm{Kr}) < W(\mathrm{Ar}) < W(\mathrm{N_2})$ correlates with that for the sizes of atoms of these gases: $r_{\mathrm{Kr}} < r_{\mathrm{Ar}} < r_{\mathrm{N_2}}$ (see Ref. 7). Previously[8] the uptake at saturation of the pores of the NaX zeolite has been determined by adsorption measurements at low temperatures. On the assumption that the density of the adsorbate corresponds to the density of the equilibrium phase in the bulk, the volume of the pores of this adsorbent was calculated to be 0.3 (Ar), 0.27 (Kr), and 0.25 (Xe) cm^3 g^{-1}, which correlates with the variation of the effective diameters of the molecules: Ar (0.3465 nm) < Kr (0.3610 nm) < Xe (0.4055 nm) (from the results of measurements of the viscosities of the gases[5]). It is seen from the data presented above that the volume of the adsorbent pores W being determined, and, hence, the volume V_d should depend on the effective sizes of molecules of the gas used for calibration.

After determining the "dead volume" of the NaA—Kr system at T = 334, 373, and 408 K (V_d = 2.162 cm^3), we calculated the experimental isotherms of excess adsorption measured over a wide range of pressures (0.5—160 MPa) and for all temperatures including 448 and 500 K. Figure 2 shows a typical isotherm of excess adsorption $\Gamma = f(\rho)_T$ for T = 334 K as an example. This isotherm contains the following characteristic points: a maximum with the coordinates ρ_{max} and Γ_{max} and a point with the coordinates ρ_B and Γ_B at which the excess adsorption is equal to zero (we suggest that this second point be referred to as the Bering[9] point). The physical sense of the negative values of excess adsorption requires special investigation. The adsorption excess as the difference between the total amount of a substance in the adsorption space and its amount in the equilibrium gas phase obeys a complex dependence on the pressure (density) of the bulk gas phase. Apparently, the isotherm of excess adsorption measured over a wide range of pressures reflects the effect of the adsorbent on the adsorbate more clearly than any other characteristic of the adsorption process. At low pressures in the equilibrium gas phase, this value increases and reaches a maximum, at which the energy of attraction between the adsorbate molecules themselves and between the molecules of the gas and the adsorbent is counterbalanced by the energy of repulsion between the adsorbate molecules. As pressure increases, the excess adsorption decreases to zero. At this point, the average density of the adsorbate becomes equal to the density of the equilibrium gas phase, *i.e.*, actually, the adsorbent has no effect on the adsorptive.

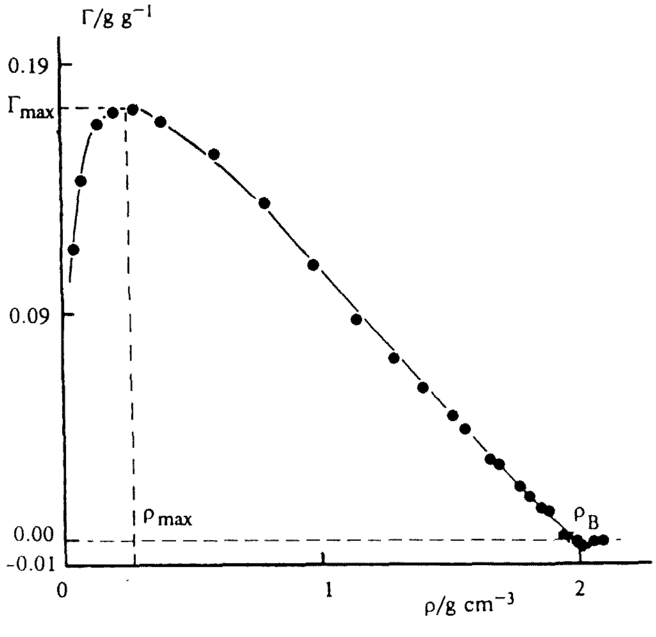

Fig. 2. Isotherm of excess adsorption of krypton on NaA zeolite at T = 334 K in the "adsorption—gas density" coordinates.

When we measured the family of the isotherms of excess adsorption, we attempted to solve the problem of describing them analytically. It should be noted that equations describing adsorption isotherms for gases measured over wide pressure ranges are quite scarce in the scientific literature, and, furthermore, they do not reflect experimental results very well. To describe analytically the isotherm of excess adsorption Γ as a function of the density of the equilibrium gas phase, we used the following equation[10]:

$$\Gamma(\rho) = \Gamma_{\max} \cdot \exp\left[-(RT/E)^2 \cdot \ln^2 \frac{\rho_{\max}(\rho_B - \rho)}{\rho(\rho_B - \rho_{\max})}\right] \qquad (8)$$

Here the $\rho_{\max}$ and $\Gamma_{\max}$ parameters are coordinates of the point of the isotherm maximum; ρ_B is the density of the gas at which the excess adsorption Γ is equal to zero; E is energy parameter; and ρ is the density of the equilibrium gas phase. The temperature dependences of the parameters of Eq. (8) are adequately described by the following relationships:

$$\Gamma^T_{\max} = \Gamma^{T_0}_{\max} \cdot \exp\left[-\alpha(T - T_0)\right], \qquad (9)$$

$$\rho^T_{\max} = \rho^{T_0}_{\max} \cdot \exp\left[\beta(T - T_0) / (TT)\right], \qquad (10)$$

$$\rho^T_B = \rho^{T_0}_B \cdot \exp\left[g(T - T_0) / (TT_0)\right], \qquad (11)$$

$$E^T = E^{T_0} \cdot \exp\left[æ(T - T_0) / (TT_0)\right], \qquad (12)$$

where α, β, γ, and æ are the corresponding temperature coefficients, and T_0 is the temperature chosen as the reference temperature (334 K).

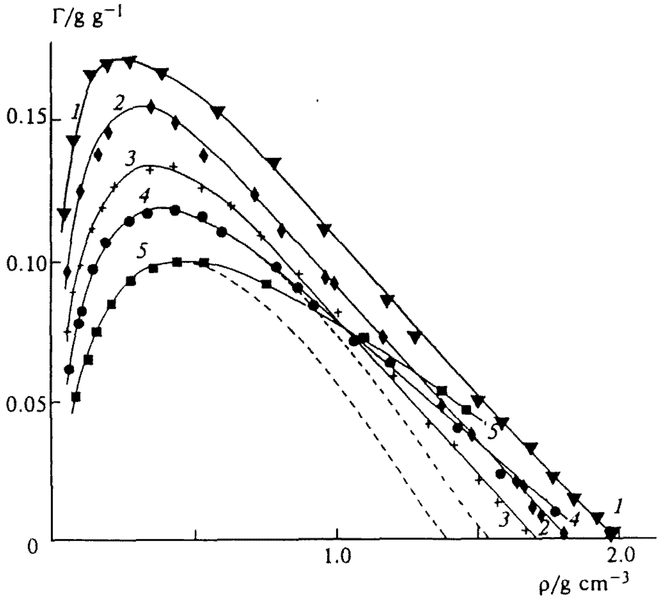

Fig. 3. Family of isotherms of excess adsorption of krypton on NaA zeolite. The curves were obtained by calculation from Eq. (8) for T/K = 334 (*1*), 373 (*2*), 408 (*3*), 448 (*4*), and 500 (*5*); the dots are experimental results; the dashed lines are based on calculation from Eq. (8) at the corresponding temperatures, taking into account adsorption only in the α-cavities.

Figure 3 shows a family of five experimentally obtained isotherms of excess adsorption of krypton on the NaA zeolite obtained at 334, 373, 408, 448, and 500 K (V_d = 2.162 cm^3). It is seen from Fig. 3 that all the isotherms provide a correct qualitative reflection of the temperature dependence of adsorption up to the equilibrium density of the gas phase, $\rho \approx 0.45$ g cm^{-3} (22.5 MPa), *i.e.*, the higher the temperature, the smaller the Γ value. At higher densities of the gas phase, this temperature dependence of Γ is retained only for the isotherms measured at T = 334, 373, and 408 K down to $\Gamma \approx 0$, which corresponds to pressures in the equilibrium gas phase of 130—160 MPa. At T = 448 and 500 K, the course of the isotherms is disturbed and the Γ values become so great that these curves intersect the isotherms obtained for lower temperatures. The increase in the adsorption at T = 448 and 500 K is due to the diffusion of molecules of krypton in the β-cavities of the zeolite, which has also been shown during the calibration. The continuous curves in Fig. 3 were drawn according to Eq. (8) using the parameters obtained from the experimental adsorption isotherms. It is seen from Fig. 3 that Eq. (8) describes well the experimental isotherms of excess adsorption over the whole range of pressures (densities) of the equilibrium gas phase. We suggested that calculations would make it possible to separate two processes of adsorption, *viz.*, adsorption in the α- and β-cavities of the zeolite. For this purpose, the coefficients $\alpha = 3.361 \cdot 10^{-3}$, $\beta = 5697$, $\gamma = 244.1$, and æ = 217.0 were found from the isotherms for T = 334, 373, and 408 K. By substituting these coefficients in Eqs. (9)—(12) we determined these parameters for T = 448 and 500 K, and used the values obtained to calculate the corresponding isotherms, which describe (like the isotherms measured at T = 334, 373, and 408 K) the adsorption of krypton only in the α-cavities of the NaA zeolite. The differences between the ordinates of the initial (experimental) and "corrected" isotherms correspond to the amounts adsorbed in the β-cavities of the zeolite. The parameters of Eq. (8) for all temperatures are listed in Table 1.

Table 1. Parameters of Eq. (8)

T/K	$\Gamma_{\max}$ /g g^{-1}	$\rho_{\max}$ /g cm^{-3}	ρ_B /g cm^{-3}	E /J mol^{-1}
334	0.1712	0.251	1.985	7765
373	0.1545	0.300	1.827	8469
408	0.1335	0.342	1.700	8736
448*	0.1184	0.387	1.560	9248
500*	0.0994	0.442	1.399	9725

*The parameters were calculated from Eqs. (8)—(12).

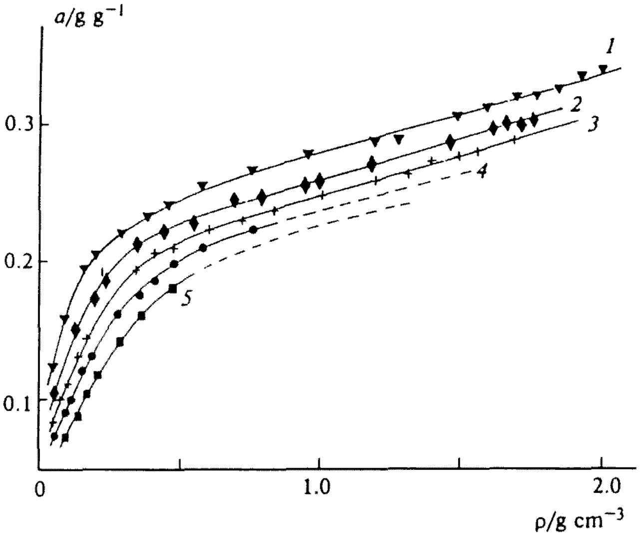

Fig. 4. Family of isotherms of absolute adsorption of krypton on NaA zeolite. The curves were obtained by calculation for T/K = 334 (*1*), 373 (*2*), 408 (*3*), 448 (*4*), and 500 (*5*), and the dots are experimental results.

To construct an isotherm of absolute adsorption, one should merely add the product of the constant parameter W(Kr) and the current value of the density of an equilibrium gas ρ, *i.e.*, the $W\rho$ value to each ordinate of the experimental adsorption isotherm. The calculations of the isotherms of the total content of the adsorbate were carried out using the W(Kr) = 0.171 cm^3 g^{-1} value calculated by us. The adsorption volume of a zeolite can also be determined by an alternative method, if the mass of the evacuated adsorbent, its density, and the volume of the empty tube are known.[11] This method gave a W value of 0.167 cm^3 g^{-1}, which is somewhat lower than that obtained in our experiment. Figure 4 presents five isotherms of the total content of the adsorbate (absolute adsorption) for T = 334, 373, 408, 448, and 500 K and isotherms calculated from Eq. (8) (continuous lines) using the temperature dependences of the parameters (see Eqs. (9)—(12)). The isotherms for T = 448 and 500 K describe the adsorption only in the α-cavities of the NaA zeolite, *i.e.*, the initial isotherms (see Fig. 3) have been corrected by the value of the adsorption in the β-cavities of the zeolite. It can be seen from Fig. 4 that the experimental values are adequately described by Eq. (8), and, hence, the accuracy of the prediction is quite satisfactory.

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