New method for the determination of adsorption space volume for sorbents with an arbitrary porous structure from excess gas adsorption isotherm measurements

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A new method for the determination of adsorption space volume has been proposed, which is applicable to adsorbents with an arbitrary porous structure, including nonporous adsorbents with open surfaces. The method is based on the use of an experimental excess adsorption isotherm measured over a wide range of pressures in the equilibrium gaseous phase (as a rule up to 100—150 MPa) and the absolute adsorption isotherm equation with unspecified parameters in the most general form, given by statistical physics. The method has been tested for a number of adsorption systems, and it has been found that the result was always unambiguous, correct, and stable in the sense of input data.

Key words: adsorption, adsorption volume, excess adsorption, adsorption isotherm equation.

Over recent years, the range of parameters measured to characterize adsorption equilibria in studies on physical adsorption could be extended significantly.[1—4] In particular, measurable equilibrium pressures of the adsorbed gases reach values as high as 200 MPa. As a rule, the gas density in this state is close to that of a liquid adsorptive at a conventional boiling point. Under these conditions, the excess adsorption and absolute adsorption (total content) are described by different isotherms (Fig. 1). With an adsorption experiment only the excess quantity can be determined directly, whereas all molecular statistical models are based on the concept of the total content. This contradiction hampers the development of adsorption science. The basic difficulty in resolving this contradiction stems from the need to find a method for determining the adsorption volume W suitable for all adsorbents irrespective of their nature and porous structure that would relate the absolute and excess quantities of adsorption functionally. By definition,

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

where Γ and a are the excess adsorption and absolute adsorption, respectively, and ρ is the density of the equilibrium gas phase in an adsorption experiment. However, the following question should be answered first: can the sought volume W exist generally and in systems with nonporous adsorbents specifically? The analysis and solution of this problem have been reported earlier.[5,6] In these works, a physically justified boundary of the region of inhomogeneity was drawn near the surface of a solid adsorbent. The authors of these works consider the adsorption space (volume) as the region near the surface of a solid in which the van der Waals forces of the potential field of the solid are capable of effecting substantial[5] variations in the density of the adsorbed gas

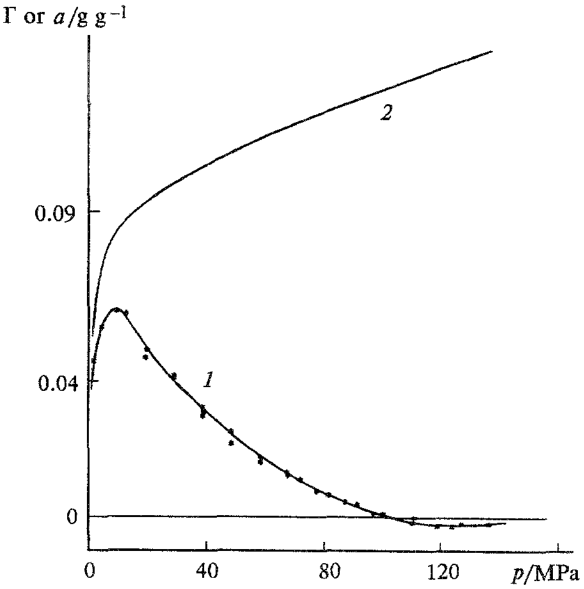

Fig. 1. Isotherms of the excess (*1*) and absolute (*2*) uptakes of N_2 in NaA zeolite at 334 K. Isotherm (*2*) was calculated using the values of the adsorption volume W found with Eq. (5).

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at any point of the region. It can be, therefore, inferred that the volume of the adsorption space does not necessarily coincide with the geometric volume of the pores in a solid.

All quantities included in Eq. (1) have accordingly a strong physical meaning and can be found using one method or another. The aim of the present work is to suggest a physically justified and correct method for calculating the adsorption volume W using an available isitherm of the excess adsorption obtained from an experiment. The suggested method is based on the assumptions and proposals that follow.

An experimental isotherm of the excess adsorption $\Gamma(f)$ as a function of fugacity f of the equilibrium gas phase is available and the corresponding measurements were conducted over a reasonably wide range of pressures.

All possible types of the isotherm of the total content $a(f)$ can be described by an equation of the form[7]

$$a(f) = k_0 \frac{k_1 f + 2k_2 f^2 + \ldots + nk_n f^n + \ldots}{1 + k_1 f + k_2 f^2 + \ldots + k_n f^n + \ldots} \quad (2)$$

The number of coefficients (terms) in Eq. (2) is not restricted. The last proposal is based on the fact that Eq. (2) can be derived with a minimum of rational assumptions from the most general thermal equation of adsorption that is given by statistical physics,[8]

$$N = [\partial \ln \Sigma / \partial \ln f]_T, \quad (3)$$

where Σ is the statistical sum of the great canonic ensemble of the adsorption system, and N is the number of molecules adsorbed.

The dependence of the density of the equilibrium gas phase on fugacity $\rho(f)$ can be treated as a special case of the dependence of the mean density of an adsorbate from fugacity. It would appear reasonable that this dependence can also be described by an equation of type (2), while other values of the coefficients should be used (Eq. (4)).

$$\rho(f) = \bar{k}_0 \frac{\bar{k}_1 f + 2\bar{k}_2 f^2 + \ldots + n\bar{k}_n f^n + \ldots}{1 + \bar{k}_1 f + \bar{k}_2 f^2 + \ldots + n\bar{k}_n f^n + \ldots} \quad (4)$$

The latter assumption refers to the value of the adsorption volume that is generally a function of temperature and equilibrium fugacity $W = W(T, f)$. Under the isothermal conditions, the adsorption volume W can vary, firstly, due to the adsorption deformation experienced by an adsorbent and, secondly, owing to the fact that the extent of the inhomogeneous region near the surface of a solid varies in response to the variations in the density of the equilibrium gas phase. The impact of these both factors is however negligibly small. For instance, since the highest relative volume deformation does not exceed the value of ~10^{-4} for aluminosilicate and carbon sorbents, the fluctuations in the adsorption volume induced by deformation should not exceed the one per cent level.[9,10] The effect of density (pressure) of the phase occupying the pore volume on the extent of the inhomogeneous region can be discernible only if this dencity approaches that of the bulk liquid. However, this effect is to some extent counterbalanced by the effect of adsorption deformation, because both effects have opposite signs at high equilibrium pressures. The quantity W depends in a complex manner on temperature. On the one hand, the thermal expansion (compression) changes the surface area and pore volume, although, due to a small expansion factor for solids (~10^{-6}), the value of ΔW would not be greater than 1 % even over a substantially broad range of temperatures (500 K). On the other hand, the extent of the region of inhomogeneity on the solid-gas phase interface (z_0) has the most pronounced temperature dependence adequately described by the relation $z_0 \sim T^{-1/3}$. Accordingly, the adsorption volume W should show a negligible temperature dependence and that is usually obseved. Consequently, under the isothermal conditions, W can be treated as a constant to a quite good approximation.

Method for calculating adsorption volume *W*

At the first step of calculation, the dependence of the density of the equilibrium gaseous phase on its fugacity $\rho(f)$ is approximated by Eq. (4). For the calculations, use was made of the experimental reference data or the values of ρ and f derived from equations of state for real gases over the relevant range of pressures. Further, the conventional calculation procedure was applied to find the coefficients k_0, k_1, k_2, k_3, *etc.* As a rule, the number of coefficients needed is not greater than 3—4, whereas an increase in their number virtually does not change the corresponding sum of the squared deviations.

To calculate the isotherm of the excess adsorption, the following function with unknown coefficients can be written:

$$\Gamma = k_0 \frac{k_1 f + \ldots + nk_n f^n}{1 + k_1 f + \ldots + k_n f^n} - W\bar{k}_0 \frac{\bar{k}_1 f + \ldots + n\bar{k}_n f^n}{1 + \bar{k}_1 f + \ldots + \bar{k}_n f^n} \quad , \quad (5)$$

where $\bar{k}_0$, $\bar{k}_1, \ldots, \bar{k}_n$ are the known coefficients obtained from the preliminary calculations. Further, the unknown coefficients k_0, $k_1, \ldots, k_n$, W can be found by the mean square method

$$Y = \sum_{i=1}^{n} \left[\frac{\Gamma_{ei} - \Gamma}{\Delta\Gamma_{ei}} \right]^2 = \min \; , \quad (6)$$

where Γ_{ei} and $\Delta\Gamma_{ei}$ are the values of the experimentally determined excess adsorption and its relative error at point i, respectively; Γ is the value of the excess adsorption at point i, calculated from Eq. (5); and n is the total number of experimental points. The only condition of general nature, that should be satisfied by the three continuous functions in Eq. (5), is their linear inde-

Table 1. Adsorption volumes W calculated from Eq.(5)

System	T/K	Coefficients in Eq. (5)		$W = k_0/\bar{k}_0$
N_2—NaA	305	$\bar{k}_0 = 0.2491$ $\bar{k}_1 = 4.0803 \cdot 10^{-2}$ $\bar{k}_2 = 1.28628 \cdot 10^{-3}$ $\bar{k}_3 = 4.9013 \cdot 10^{-6}$	$k_0 = 0.052311$ $k_1 = 1.7860$ $k_2 = 3.32877 \cdot 10^{-1}$ $k_3 = 7.2452 \cdot 10^{-4}$	0.210
N_2—NaA	334	$\bar{k}_0 = 0.2504$ $\bar{k}_1 = 3.8619 \cdot 10^{-2}$ $\bar{k}_2 = 9.1279 \cdot 10^{-3}$ $\bar{k}_3 = 2.6000 \cdot 10^{-6}$	$k_0 = 0.057091$ $k_1 = 0.17160$ $k_2 = 5.87085$ $k_3 = 4.57338 \cdot 10^{-4}$	0.228
Kr—NaA	334	$\bar{k}_0 = 1.000$ $\bar{k}_1 = 1.629 \cdot 10^{-3}$ $\bar{k}_2 = 2.145 \cdot 10^{-5}$	$k_0 = 0.1860$ $k_1 = 8.127 \cdot 10^{-2}$ $k_2 = 5.314 \cdot 10^{-4}$	0.186
Kr—NaA	373	$\bar{k}_0 = 1.001$ $\bar{k}_1 = 2.472 \cdot 10^{-2}$ $\bar{k}_2 = 1.028 \cdot 10^{-3}$	$k_0 = 0.191$ $k_1 = 2.780 \cdot 10^{-1}$ $k_2 = 1.441 \cdot 10^{-2}$	0.191
Kr—NaA	408	$\bar{k}_0 = 1.027$ $\bar{k}_1 = 2.430 \cdot 10^{-3}$ $\bar{k}_2 = 6.893 \cdot 10^{-6}$	$k_0 = 0.1980$ $k_1 = 3.194 \cdot 10^{-2}$ $k_2 = 9.346 \cdot 10^{-5}$	0.193

pendence. This condition is actually met since the Vronsky determinator has a nonzero value.

The number of the selected coefficients for the first term in the right-hand side of Eq. (5) should be the same as in the relation for $\rho(f)$. From the condition $f \to \infty$ it follows that $\Gamma \to 0$, $a \to k_0 n$, and $\rho \to \bar{k}_0 n$, therefore $k_0 = W\bar{k}_0$ and this reduces the number of the selected coefficients by unity. To facilitate computerizing, it is advisable to use the corresponding values of k_i as the initial values for $\bar{k}_i$.

The procedure outlined above was applied to the systems that we have investigated experimentally: zeolite NaA—krypton, (T = 334, 373 and 408 K) and zeolite NaA—nitrogen (T = 305 and 344 K). The resulting values of the adsorption volume W made it possible to compute the corresponding isotherms of the absolute adsorption. To be positive that the calculations were

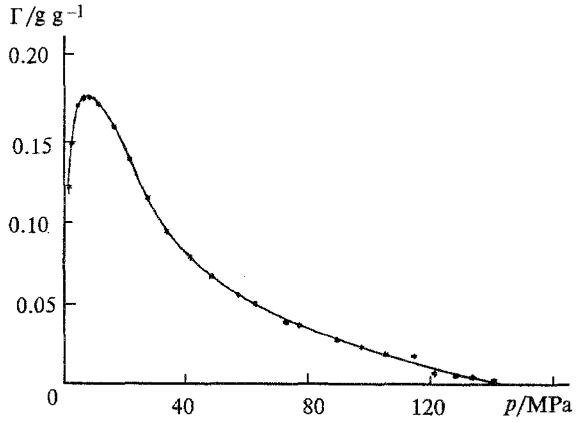

Fig. 3. Isotherm of the excess adsorption of Kr in NaA zeolite at 334 K.

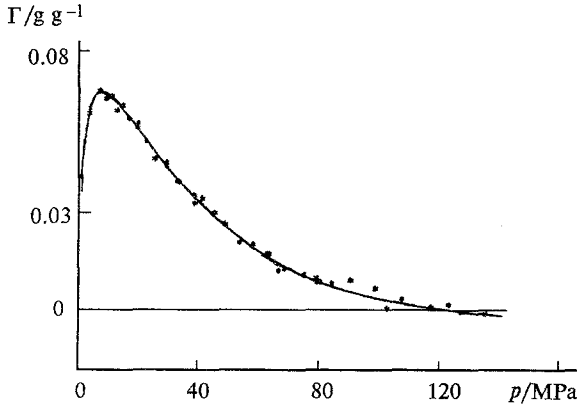

Fig. 2. Isotherm of the excess adsorption of N_2 in NaA zeolite at 305 K.

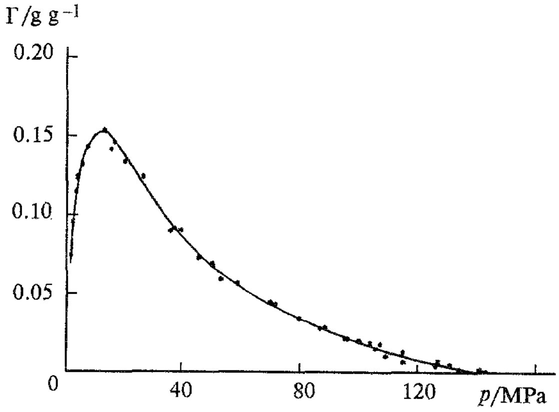

Fig. 4. Isotherm of the excess adsorption of Kr in NaA zeolite at 373 K.

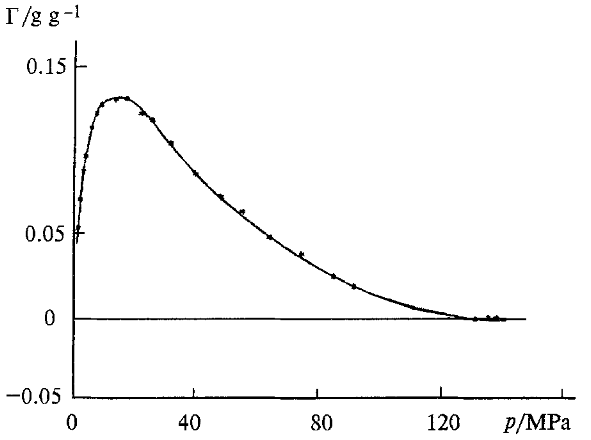

Fig. 5. Isotherm of the excess adsorption of Kr in NaA zeolite at 408 K.

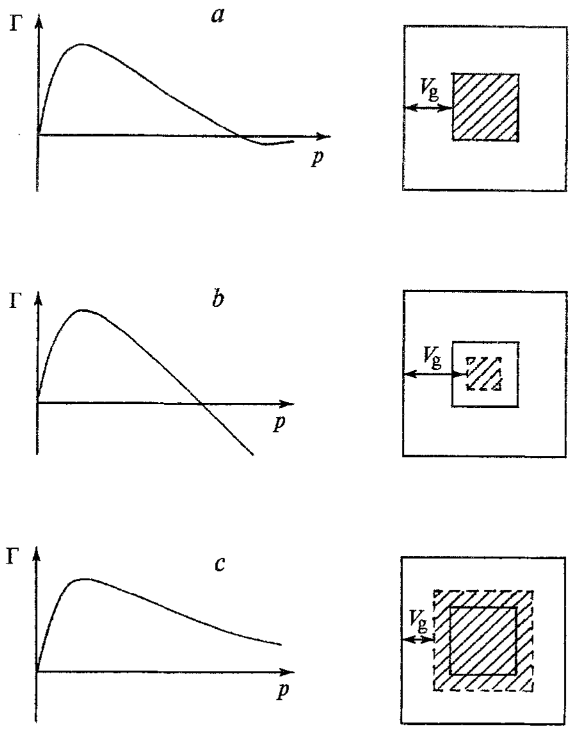

Fig. 6. Schematic representations of the excess adsorption isotherms at correct (*a*), overestimated (*b*), and underestimated (*c*) values of the accessible volume V_g of the adsorption system.

properely made, the computed curves were compared with the isotherms determined from an experiment. With the zeolite systems chosen, the knowledge of the adsorption volume *W* for calculating the value of the absolute adsorption is unnecessary. The results of calculations are listed in Table 1 and depicted in Fig. 1 through 5.

Figure 6, *a* shows a schematic representation of the typical isotherm of the excess adsorption that is similar to those observed in an experiment. Its characteristic features are a positive maximum with the position changing in the range of the equilibrium pressures 5—20 MPa according to the temperature and the nature of the pair adsorbent-adsorbate, a zero value of the excess at pressure 80—120 MPa, and an insignificant in magnitude negative excess occuring at the minimum of the slope at higher pressures. Finally, as the pressure of the equilibrium gaseous phase increases indefinitely the quantity of the adsorbed material approaches asymptotically zero. A small negative excess amounting to ~1 % of the highest positive excess and appearing at high densities of the adsorbate is related as a rule, to the effect of the closely packed adsorbate in the adsorption space. The latter can be represented as the grouping of the energetically different and numerous interstitial spaces of a very small volume with the size comparable with the atomic dimensions. At the same time, there is a number of the experimentally investigated systems[3] such as neon and krypton on the active coal GAC-250 that examplify the negative excess values exceeding in the absolute magnitude positive excess quantities at a maximum by a factor of 2.5 (Fig. 6, *b*). This does not mean, of course, that the density of the gaseous phase can exceed at some point the mean density of the adsorbate. The effect arises due to overestimation of the volume V_g accessible to the adsorptive molecules in the course of calibration of an adsorption unit. In any case, the calibration serves to establish actually the position of the Gibbs boundary and it is through calibration procedure that a definite position of this surface can be chosen. And, finally, Fig. 6, *c* gives an example illustrating underestimation of the accessible volume due to the procedure and specific conditions of calibration.

It should be particularly emphasized that any choice of boundary is justified and has the same validity from the standpoint of thermodinamics. However, if there is a need to leave the frameworks of the purely phenomenological approach to solve the problems related to the state and structure of the adsorbate, to the adsorption mechanism and to other similar questions, then it is important to know how the boundary surface should be chosen which would actually help to distinguish the regions unaccessible and accessible to the adsorptive molecules. Only in this case the isotherm of the excess adsorption can be described by the curve with the characteristic contour shown in Fig. 6, *a* and it is to this isotherm that the above method of determining the volume of the adsorption space *W* refers. In order to minimize the error encountered in choosing the Gibbs boundary surface, it is necessary to calibrate the adsorption unit with the same gas, the adsorption of which would be investigated, to mantain the same temperature as in measuring the adsorption isotherms, and finally to remain in the range of the equilibrium pressures that involes the region of the excess adsorption at high pressures.

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