The volume of micropores and the Dubinin—Radushkevich equation

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The substantiation and the area of applicability of the Dubinin—Radushkevich equation for determination of the micropore volume in microporous systems from experimental data on adsorption isotherms were examined. It was shown that the micropore volumes found using the standard procedure are overestimated. A more accurate method for determining the mircopore volumes based on the pressure of filling of micropores was proposed.

Key words: adsorption, isotherm, micropore volume, Dubinin—Radushkevich equation, lattice-gas model.

In the classical work by Dubinin and Radushkevich,[1] an equation for determination of the volume of micropores W_0 in active carbons was proposed:

$$W = W_0\exp(-k\varepsilon^2/\gamma^2), \tag{1}$$

where k is a parameter characterizing the system, γ is the affinity coefficient that connects the "adsorption potentials" of the given and standard adsorbates (for benzene, $\gamma = 1$), and $\varepsilon = RT\ln(p_s/p)$ is the "adsorption potential," *i.e.*, the work needed to compress a vapor from equilibrium pressure p to the saturated vapor pressure p_s under isothermal conditions. The p_s values needed for calculations are taken from experimental data obtained for liquid—vapor equilibria at the experimental temperature T. This equation was derived based on the concept of volume filling of micropores and the Polanyi potential theory.[1–5] This equation is still widely used for determining the micropore volumes for various substrates.

It has been mentioned repeatedly[5,6] that the first attempt to substantiate Eq. (1) was undertaken by Radushkevich[4] based on the idea of inhomogeneous adsorption systems and on the search for the density of the distribution function corresponding to Eq. (1) (more recent studies dealing with justification of this equation were surveyed in Refs. 7 and 8). Later, Eq. (1) was extended to polydisperse microporous adsorbents.[9–14] However, in none of the studies cited above, was the role of intermolecular interactions taken into account. These interactions are responsible for the processes of condensation and volume filling of micropores. In this work, we compare the propositions of the theory of volume filling of micropores (TVFM)[1–5] with those of the molecular adsorption theory[7,8,15] for inhomogeneous systems. It was found that Eq. (1) overestimates the micropore volume W_0, because it includes the saturated vapor pressures p_s for normal liquids; to estimate the W_0 more accurately, one needs to know the real equilibrium pressures corresponding to the filling of micropores.

Main statements of TVFM

Substantiation of Eq. (1) is based on the following statements.[4]

1. Each micropore in active carbon is characterized by a particular average value ε. For a planar adsorbent surface, average ε values are equal to zero. Non-zero ε values are due to specific properties of micropores. A porous adsorbent is characterized by some continuous distribution of ε. 2. As the $x = p/p_s$ ratio increases, micropores are sequentially filled with a condensed liquid phase. At a given x, all pores characterized by ε values not smaller than $\varepsilon(x)$ are considered to be filled. However, at low x, adsorption on active sites is neglected: at low coverages, Eq. (1) is not transformed into the Henry equation, which is an asymptotically accurate result in terms of the strict equations of the adsorption theory.[7,8,15,16] 3. The filling and vacation of micropores following an increase and decrease in the pressure are considered to be completely reversible (no capillary condensation occurs).

The problem of determining the density of the distribution function $\Phi(\varepsilon)$, provided that $W = W_0\int\Phi(\varepsilon)d\varepsilon$, is easily solved[4] using the known distribution function (1):

$$\Phi(\varepsilon) = 2k\varepsilon\exp(-k\varepsilon^2). \tag{2}$$

Previously,[4] the function $\Phi(\varepsilon)$ was represented as $\Phi(\varepsilon) = f(\varepsilon)q(\varepsilon)$, where $f(\varepsilon)$ is the normalized density of the distribution function of the "adsorption potential" in unit

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weight of the adsorbent, $q(\varepsilon)$ is the weight of the liquefied gas that fills the micropore volume $v(\varepsilon)$: $q(\varepsilon) = \rho v(\varepsilon)$, ρ is the density of the liquid at the experimental temperature, and $v(\varepsilon)$ is the volume of the micropores possessing the "adsorption potential" ε. To elucidate the dependence $q(\varepsilon)$, the result obtained by DeBour—Custer[17] ($\varepsilon = b/v$) was used; this means that in the middle of a cavity having a regular geometric form, the "adsorption potential" is inversely proportional to the volume of this cavity and depends on its shape. This dependence is taken into account by the coefficient b. In addition, the coefficient b includes molecular constants for the adsorbent and the adsorptive. It follows from Eq. (2)[4] that $f(\varepsilon) = (4k^{3/2}/\pi^{1/2})\varepsilon^2\exp(-k\varepsilon^2)$ is the normalized Maxwell distribution of the "adsorption potentials." This $f(\varepsilon)$ distribution corresponds to a normalized distribution of the micropore volume in the range from v to $v + dv$: $dW_v/d\varepsilon = (4k^{3/2}/\pi^{1/2})b^3v^{-4}\exp(-kb^2/v^2)$. Analysis of this formula in which the parameters k and b correspond to the experimental systems described by Eq. (1) led to the conclusions that the volumes of micropores lie in a narrow range surrounding the maximum value $v_{\max} = b(k/2)^{1/2}$ and that, for example, active carbons can be regarded as virtually monodisperse materials.

Nonhomogeneous adsorption systems

The molecular theory of adsorption in nonhomogeneous systems gives the following equation for the adsorption isotherm[7,8,15] relating the degree of filling of the micropore volume θ to the equilibrium pressure p

$$\theta(p) = \int_{Q_{\min}}^{Q_{\max}} \theta(p;Q)F(Q)\mathrm{d}Q, \quad \int_{Q_{\min}}^{Q_{\max}} F(Q)\mathrm{d}Q = 1, \tag{3}$$

where $\theta(p;Q)$ is the local filling of the adsorption sites with bond energy Q at a given gas pressure p; $F(Q)$ is the normalized density of the probability to find a group of adsorption sites with a bonding energy from Q to $Q + dQ$. (As the upper and lower limits, $Q_{\max} = \infty$ and $Q_{\min} = 0$ are often used.)

Within the framework of the lattice-gas model,[15] Eqs. (3) are applicable to both nonporous and porous sorbents. According to this simple molecular model, the volume of the adsorption space (the multilayer region over the surface or the volume of the pores) is broken up into unit cells (sites) having the size of the sorbate. The lattice model takes into account the following main properties of the condensed phase: the proper volume of the molecule and interparticle interactions. The proper volume of the molecule is taken into account by assuming that a lattice site can contain not more than one molecule of the sorbate, and the interparticle interactions are taken into account by using the parameter of local interaction E (the average energy of interaction between the particles occupying neighboring sites of the lattice). Below we will restrict ourselves to the simplest variant of this theory according to which the pore walls are considered to be homogeneous and the pores themselves are shaped as slits with width H (the width is expressed in the number of monolayers). We will notice only interactions between the closest neighbors. In the general case, the lattice model makes it possible to take into account all the main properties of real adsorption systems, namely, intermolecular interactions, nonhomogeneous pore walls, different characteristic pore sizes, the presence of capillary condensation, *etc.* The sets of equations derived using the cluster approach[15] make it possible to analyze numerically all characteristics of a porous system based on known model potentials of interaction of the adsorbate molecules with the walls and with one another and on a specified porous structure model.

To calculate local coverages, the space in a pore is divided into monoatomic layers parallel to the walls of the slit-like pore. The lattice of sites is characterized by fixed numbers of closest neighbors (z_q is the number of closest neighbors corresponding to the first coordination sphere for a site in a layer q). Let us denote by z_{qk} the number of closest neighbors, located in a layer k, for a site in a layer q; $k = q, q\pm1$; $z_{qq-1} + z_{qq} + z_{qq+1} = z_q = z$. All the sites in the layer q possess identical properties, because the energy of the sorbate—sorbent interaction varies from layer to layer ($1 \le q \le H$) but remains constant within the same layer. Using the known equations,[15] which take into account the energetic inhomogeneity of lattice sites and the interaction between the closest sorbate molecules, it can be shown that the isotherm of multilayer adsorption has the following form:

$$\theta(p) = \sum_{q=1}^{t} f_q\theta_q(p),$$

$$a_q p = \frac{\theta_q}{1-\theta_q}\Lambda_q, \tag{4}$$

where f_q is the fraction of type q sites in the lattice, θ_q is the mole fraction of particles that occupy sites of type q; $a_q = a_q{}^0\exp(\beta Q_q)$ is the local Langmuir constant for a lattice site with the number q and bonding energy Q_q, $a_q{}^0$ is the preexponential factor for the local Langmuir constant, and $\beta = (kT)^{-1}$. The energy of bonding for a site in a layer q was calculated as $Q_q = U(q) + U(H - q + 1)$, where $U(q)$ is the potential of interaction of the adsorbate with the pore wall; $U(q) = U/q^3$ corresponds to the 3—9 Mie potential in which the repulsive branch of the potential is taken into account by the lattice structure, Λ_q is the term taking into account the lateral interactions between the particles located in the neighboring sites. In the quasi-chemical approximation

$$\Lambda_q = \prod_{p=1}^{z_q}(1 + xt_{qp}),$$

where $t_{qp} = 2\theta_p/[\delta_{qp} + b_{qp}]$, $x = \exp(-\beta E) - 1$, $\delta_{qp} = 1 + x(1 - \theta_q - \theta_p)$, $b_{qp} = (\delta^2{}_{qp} + 4x\theta_q\theta_p)^{1/2}$. In the mean-field approximation

$$\Lambda_q = \exp\left(-\beta E \sum_{k=q-1}^{q+1} z_{qk}\theta_k\right).$$

The equilibrium distribution of particles over various types of sites was found by the Newton method from Eqs. (4). The solutions of this set of equations are used below to discuss the influence of the slit size on the behavior of the saturated vapor curve. Note that the quasi-chemical approximation describes the distribution of molecules over the lattice sites more accurately than the mean-field approximation, but our main conclusions do not depend on the particular type of approximation used.

Now we compare statements of the TVFM with those of the theory of nonomogeneous adsorption systems. The main parameter used in the TVFM is "adsorption potential" ε, whereas the molecular theory is based on energy characteristics E and Q. The distribution of volumes in the TVFM follows from the distribution for ε according to the DeBour—Custer relation,[17] whereas in the molecular theory, the pore volume is the initial basis for the construction of a lattice structure. Statements 1 and 2 of the TVFM presented above are entirely equivalent to the so-called "condensation approximation" in the theory of absorption of gases on nonhomogeneous surfaces.[18—20] In this approximation, it is assumed that all adsorption sites with bonding energy Q larger than Q_c are fully occupied, while those whose energy is smaller than Q_c are fully vacant. Thus, adsorption isotherm (3) is markedly simplified

$$\theta(p) = \int_{Q_c(p)}^{Q_{max}} F(Q)dQ, \qquad (5)$$

where $Q_c(p)$ is the inverse function with respect to $p_c(Q)$, and $p_c(Q)$ is the condensation pressure, *i.e.*, the pressure at which all the sites with energy Q_c ranging from zero to unity are rapidly occupied. The form of the $p_c(Q)$ dependence is determined by the function $\theta(p; Q)$. Comparison of Eq. (5) with Eqs. (1) and (2) shows that the density of the distribution function $F(Q)$ is an analog of the function $\Phi(\varepsilon)$ used previously.[4] Therefore, the real distribution function density differs from the Maxwell one, and this changes somewhat the character of the size distribution of pores.

Next, liquefaction of a gas near an adsorbent surface occurs at a lower temperature than that in the bulk phase, due to the effect of the surface forces; therefore, for open surfaces, the condition $\varepsilon = 0$ in the TVFM means that we are speaking of the excessive "adsorption potentials" caused by the influence of the second wall of the pore rather than of a comprehensive energy characteristic like E and Q. As has been noted previously,[8] this discrepancy can be easily eliminated by using the $(\varepsilon - \varepsilon_0)$ value, where ε_0 is the "adsorption potential" for an open surface, instead of the ε value.

Statement 3 of the TVFM is always fulfilled for open surfaces but is violated for porous systems in the presence of capillary condensation (see below).

Allowance for intermolecular interaction

Liquation of a gas is caused by intermolecular interactions. In a bulk phase, the saturated vapor pressure at a fixed temperature (below the critical temperature) can be determined from the gas—liquid coexistence curve. The calculations[21,22] carried out for porous adsorption systems with allowance for intermolecular interactions have shown that the adsorbate—adsorbent potential appreciably changes the form of the gas—liquid phase diagram for the adsorbate. Figure 1 presents schematically the change in the position of the saturated vapor curve in the $p—T$ cross-section of the phase diagram on going from the bulk phase to a slit-like pore of width H (a similar situation has been found for cylindrical pores for which H is the diameter of the pore). The line AB relates to the bulk phase (point A is the triple critical point, and B is the critical point), while the line A^HB^H relates to a pore with size H. The difference becomes more pronounced as the H value decreases. The decrease in the critical temperature (transformation of point B into point B^H) following a decrease in the size of pores is a well-known fact, which has been confirmed by all theoretical methods: Monte Carlo method, molecular dynamics, the lattice-gas model, the scaling approximation, and also by the density functional theory.[21—28] This finding is a consequence of the fact that in narrow

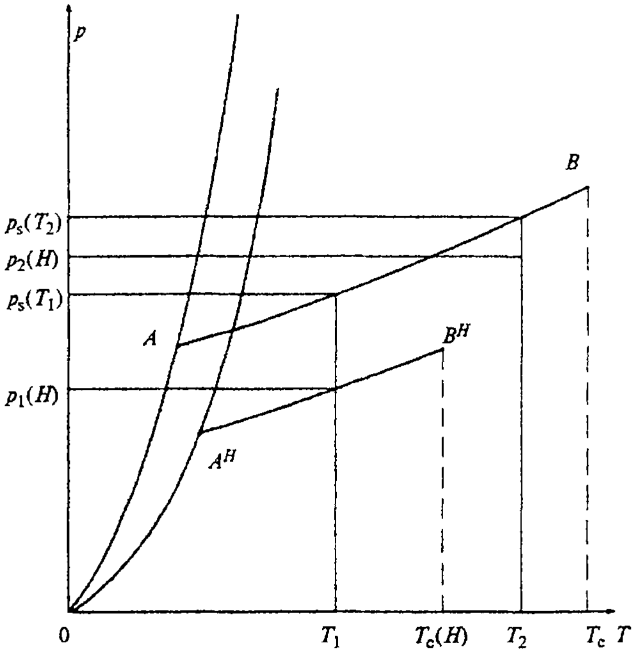

Fig. 1. $p—T$ cross-sections of phase diagrams of the adsorptive in the bulk phase and the adsorbate in a slit-like pore of width H; T_c and $T_c(H)$ are the critical temperatures; $p_s(T)$ is the saturated vapor pressure at temperature T; $p_{1,2}(H)$ is the pressure of filling of the volume of micropores of width H at T_1 and T_2, respectively.

pores, the liquid exists in a state intermediate between the three-dimensional state and a state with a lower dimensionality d ($d = 2$ for monolayer-wide slit-like pores and $d = 1$ for cylindrical pores with $H = \sigma$, where σ is the diameter of the molecule). It is known that upon a decrease in the space dimensionality d, the critical temperature decreases.[15,16] Correspondingly, the vapor pressure in the critical point decreases, and the whole saturated vapor curve shifts downward. The curve for the critical density $\theta_c(H)$ changes in a more complicated manner; in particular, for slit-like pores,[21,28] as the pore size H decreases, the θ_c value changes from 0.5 to values of about 0.7—0.8.

The boundedness of the pore space and the properties of the pore walls influence the critical conditions of condensation over a relatively broad range L, namely, for slit-like pores accommodating up to 25 monolayers. Since the thickness of a monolayer is approximately 3 to 5 Å, the range L covers the whole region of micropores for which $H < 2$ nm according to the Dubinin's classification (this corresponds to only ~6 layers of Ar atoms or 3—4 layers of benzene molecules) and some region of the mesopores. This effect is fundamentally significant for the interpretation of experimental adsorption isotherms for microporous sorbents. For our purposes, variation of the pressure corresponding to completely filled micropores is the most interesting.

It follows from Fig. 1 that depending on the experimental temperature, two situations are possible in narrow pores: $T_1 < T_c(H)$ and $T_2 > T_c(H)$, where $T_c(H)$ is the critical temperature of the adsorbate in a pore of width H. At temperatures T_1, as pressure increases to the $p_1(H)$ value, line A^HB^H is crossed; therefore, condensation of the adsorbate in the pore occurs. If the system was closed, the stratification phase transition would occur in the pores. However, a real experiment occurs in an open system; therefore, a pore is completely filled with the "liquid" adsorbate. The $p_1(H)$ value is an analog of the saturated vapor pressure for a bulk liquid phase. At temperatures T_2, the adsorbate in a pore occurs above the critical state, and the volume filling of a pore is not accompanied by a phase transition. The potential of both walls attracts the adsorbate; hence, micropores are filled more efficiently than an open surface. Let us denote the pressure at which micropores are filled at temperature T_2 by $p_2(H)$. In both cases, filling of micropores ends at a certain pressure $p_{1,2}(H)$, which is smaller than the saturated vapor pressure p_s at the same temperature.

Equation (1) is convenient for practical purposes, because the p_s value is well known from independent (other than adsorption) measurements. For microporous systems, the $p_{1,2}(H)$ value cannot be determined independently from other measurements. Since analysis of the physical nature of the filling of micropores indicates that the micropore sizes found from Eq. (1) are overestimated, to determine this value more accurately, additional measurements should be invoked (for example, X-ray diffraction analysis) or theoretical models should be used. Below we will use a simplified variant of the set of equations (4), in order to estimate qualitatively the $p_{1,2}(H)$ values suitable for practical purposes.

Estimation of the pressures corresponding to the volume filling of micropores

To obtain qualitative estimates for the pressures $p_1(H)$ and $p_2(H)$, we will use an approach developed previously.[29] The use of the condensation approximation and the equation for the spreading pressure in a multilayer system yielded an expression[29] for the pressure at which two-dimensional condensation of molecules occurs within each layer during the layer-by-layer filling of an open surface. This expression can be easily extended to the model of slit-like pores considered here. Then we obtain a relation for the pressure at which the volume filling of the pores occurs

$$a_0p_1(H) = \int_0^1 \ln\Lambda_{\text{pore}}\mathrm{d}\theta_{\text{pore}} - \beta Q_{\text{pore}}, \qquad (6)$$

where Q_{pore} describes the interaction of the adsorbate with the wall of a pore.

According to the results of the previous study,[21] for $T_1 < T_c(H)$, the capillary condensation always occurs when the first monolayer on each side of the pore is completely filled, *i.e.*, $\theta_1 = \theta_H \approx 1$; the remaining $(H - 2)$ layers in a pore with $H > 2$ are considered to be a homogeneous phase with the density θ_{pore}. Then the complete filling of the pore can be represented, instead of Eq. (4), as $\theta = f_1\theta_1 + f_{\text{pore}}\theta_{\text{pore}}$, where $f_1 = 2/(H - 2)$ and $f_2 = 1 - f_1$. For simplicity, the equation for θ_{pore} can be written, for example, in the mean-field approximation: $a_{\text{pore}}p(1 - \theta_{\text{pore}}) = \theta_{\text{pore}}\Lambda_{\text{pore}}$, $\Lambda_{\text{pore}} = \exp(-\beta Ez_{\text{pore}}\theta_{\text{pore}})$; here, the z_{pore} and Q_{pore} values ($a_{\text{pore}} = a_0\exp(\beta Q_{\text{pore}})$) are found by averaging the corresponding z_{qk} and Q_q values over the $(H - 2)$ layers of the pore. This gives $z_{\text{pore}} = [z_{qq}(H - 2) + 2z_{qq+1}(H - 3) + 2z_{qq+1}\theta_1/\theta_{\text{pore}}]/(H - 2) \approx z + 2z_{qq+1}/(H - 2)$, because $\theta_1/\theta_{\text{pore}} \approx 2$ and $Q_{\text{pore}} = 2Q_1\varphi(H)/(H - 2)$, where $\varphi(H) = \sum_{q=2}^{H-1} q^{-3}$ and Q_1 is the heat of adsorption of molecules at low coverages of the monolayer on an open surface. By substituting the above expressions into Eq. (6) and taking into account that $p_s = \exp(-z\beta E/2)$, we obtain the target formula

$$p_1(H) = p_s\exp(-b_1),\ b_1 = \beta[z_{12}E + 2Q_1\varphi(H)]/(H - 2). \qquad (7)$$

As the slit width H increases, the b_1 value decreases, and the pressure at which the pore is filled rapidly (exponentially) approaches the bulk pressure p_s. This model adequately describes the above-mentioned variation of θ_c as a function of H. Then we obtain $\theta_c = (H + 2)/2H$; hence, $\theta_c = 1/2$ for $H \to \infty$ and $\theta_c = 0.75$ and 0.83 for $H = 4$ and 3.

For the second case ($T_2 > T_c(H)$), we will consider the last stage of the layer-by-layer filling of a pore; *i.e.*, the situation when the preceding layers have already been filled. Here we can obtain two estimates (the upper and the lower) for the pressure corresponding to the filling of the last layer. To make the upper estimate, we will assume that in the last layer, two-dimensional condensation occurs. Then Eq. (4) assumes the form

$$a_0\exp(\beta Q_{\mathrm{layer}})p_2^+(H) = \theta_{\mathrm{layer}}\Lambda_{\mathrm{layer}}/(1 - \theta_{\mathrm{layer}}), \quad (8)$$

in which the $\Lambda_{\mathrm{layer}} = \exp(-\beta E z_{\mathrm{layer}}\theta_{\mathrm{layer}})$, $z_{\mathrm{layer}} = z_{11}$, and $Q_{\mathrm{layer}} = [2z_{12}E + Q_1D(H)]$ values were introduced; here $D(H)$ is equal to $[1/(H/2)^3 + 1/(1 + H/2)^3]$ for even H values or to $2/((H + 1)/2)^3$ for odd H. From an equation completely analogous to Eq. (6), we obtain (by replacing the index "pore" by "layer")

$$p_2^+(H)/p_s = \exp\{-b_2^+(H)\},$$

$$b_2^+(H) = \beta[z_{12}EC(H) + Q_1D(H)], \quad (9)$$

where $C(H)$ is equal to 1 for odd H and 1/2 for even H.

The lower estimate of $p_2^-(H)$ can be obtained from Eq. (8) for $\theta_{\mathrm{layer}} \to 1$. Using the known relation[30] and assuming that the probability of finding a vacancy in the dense phase is $1 - \theta_{\mathrm{layer}} \approx \exp(-\beta zE)$, we can write

$$p_2^-(H)/p_s = \exp\{-b_2^-(H)\},$$

$$b_2^-(H) = \beta[zE/2 + Q_1D(H)]. \quad (10)$$

This estimate gives $p_2^-(H) < p_2^+(H)$. Note that if the Frenkel′—Helsey—Hill equation for multilayer adsorption[31] is extended to porous systems and assumes the form $\ln(p(H)/p_s) = -\beta Q_1[q^{-3} + (H - q + 1)^{-3}]$, $1 \le q \le H$, then, due to the confined size of the pores, the right-hand side of the equation takes the minimum value at $q = H/2$ (even H) or at $q = (H + 1)/2$ (odd H); this makes it possible to find the ratio of pressures $p_2^+(H)/p_s = \exp\{-\beta Q_1D(H)\}$ at which the pores are completely filled. (In the case of multilayer adsorption, the right-hand side of the Frenkel′—Helsey—Hill equation contains only q^{-3}; this gives $p(H) \to p_s$ at $q \to \infty$.)

All the estimates made here do not depend on what particular approximation (quasi-chemical or mean-field) has been used. In any case, micropores are filled at pressures lower than the saturated vapor pressure corresponding to the same temperature. The contributions of the interaction of adsorbate molecules with the walls and with one another are manifested differently for temperatures below and above the critical temperature. As follows from the formulation of the models, for H = 3 and 4, $D(H) = \varphi(H)/(H - 2)$; therefore, $b_1 = b_2^+$, and for $H > 4$, we obtain $D(H) < \varphi(H)/(H - 2)$. In this case, at H = const, the contribution from the walls for $p_2(H)$ is smaller than that for $p_1(H)$. The contribution of the lateral interactions to the coefficients $b_{1,2}(H)$ decreases with an increase in H in the presence of capillary condensation or remains equal to 1 or 1/2, depending on the evenness of H, when there is no capillary condensation.

Let us estimate the $b_{1,2}(H)$ coefficients for spherically symmetrical particles. For inert gases and molecules like CH_4, N_2, and O_2, adsorption experiments are carried out at $T \approx 0.5$—$0.7\ T_c$, and for them, $Q_1 \approx 10E$. The best description of the critical bulk data[32] is provided by the lattice structure with $z = 6$. For this structure, $z_{12} = 1$, and in the quasi-chemical approximation, $\beta_cE = 0.81$. Assuming that $\beta E = 1.4$, we find that b_1 varies from 4.9 at $H = 3$ to 1.7 at $H = 6$; similarly, b_2^+ varies from 4.9 to 1.2, and b_2^- varies from 7.7 to 2.8.

Equations (7), (9), and (10), like Eq. (4), relate to monodisperse systems of slit-like pores. Nevertheless, as the first approximation, these results reflect the most general conditions for filling of micropores, because the consideration was based on a characteristic value determining the limiting size of a micropore. Equations (7), (9), and (10) do not allow the run of an isotherm to be followed; they only distinguish the characteristic point on an isotherm corresponding to the filling of micropores. The nonhomogeneous surface of the walls or different sizes of the pores change the run of the isotherm but do not alter the relationship between the pressure at which narrow pores are filled and the width of the pores. Therefore, in determining the volume of micropores from an adsorption isotherm, it makes no difference in what coordinates the experimental data are plotted. The isotherms for microporous systems plotted in the θ—p/p_s coordinates, which contain an extended plateau, are well known.[31] These plots are as convenient for the determination of volumes of micropores as the curves drawn in the coordinates of Eq. (1). It should be noted that the isotherms for systems consisting of, *e.g.*, CCl_4, benzene, cyclohexane (all at 25 °C), or isopentane (0 °C) on ammonium phosphoromolybdate,[33] benzene on carbon from anthracite,[34] propane on 5A zeolite (T = 273; 323 and 398 K),[35] and argon on chabazite (from 138 to 195 K)[36] flatten out at p/p_s from 0.1 to 0.3. These data correspond to b values ranging from 2.3 to 1.1. Since experimental absorption isotherms must be corrected to take into account filling of mesopores, the above b values should be increased. These results are qualitatively consistent with the obtained estimates. Note that in a previous study,[5] a value of the order of $0.2p/p_s$ was introduced as a conventional unit for measuring the number of adsorbed molecules of benzene, but, nevertheless, a value extrapolated at $p = p_s$ was used as the volume of micropores W_0.

Determination of the volume of micropores

In order to use the real pressure corresponding to the filling of micropores with characteristic size H in the calculations in terms of Eq. (1), it is necessary to change the standard method of determination of W_0 according to which the W_0 value is found by the linear extrapola-

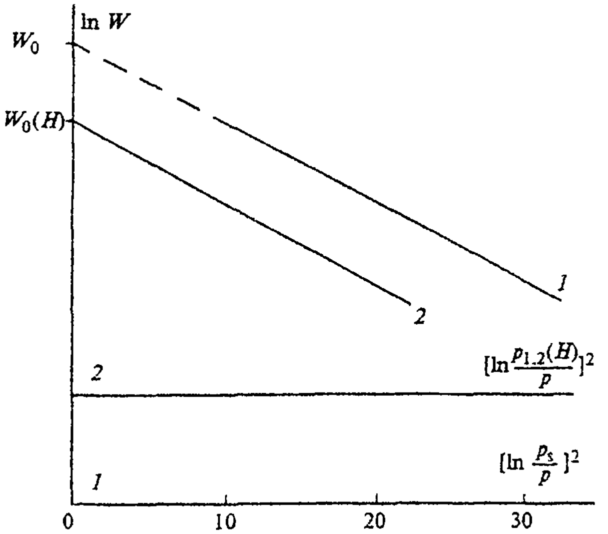

Fig. 2. Adsorption isotherms (*1* and *2*) in the coordinates of Eqs. (1) and (11) with the corresponding abscissa axes *1* and *2* at pressures lower than the $p(H)$ pressure corresponding to the volume filling of micropores of width H; the dashed section of curve *1* corresponds to the standard procedure of determination of the micropore volume W_0.

tion of the dependence of $\ln W$ on $[\varepsilon(x)]^2$ to $x = 1$. In this case, the value of $W_0(H)$ should be matched by the corresponding $p_s(H)$ value. Therefore, instead of Eq. (1), the following equation should be used

$$\ln(W/W_0(H)) = -k(RT/\gamma)^2(\ln[p_{1,2}(H)/p])^2. \qquad (11)$$

The only difference between this equation and Eq. (1) is that p_s has been replaced by $p_{1,2}(H)$. The correlation with the traditional procedure for determination of the volume of micropores is shown in Fig. 2. If the experimental curve is straightened in the coordinates of Eq. (11), its intersection with the ordinate axis determines the volume of micropores $W_0(H)$ with characteristic size H. Note that dependence (11) cannot be continued to higher pressures; hence, the necessity to interpret the deviations of the experimental curve from linear dependence (11) at higher pressures is eliminated. These deviations have been traditionally explained by the presence of micropores characterized by a different parameter k or having a different characteristic size, although the deviations are observed at relatively high coverages. When an experimental curve plotted in the coordinates of Eq. (11) deviates from the linear dependence, this indicates that the microporous system is actually nonhomogeneous. The fact that deviations are observed at relatively high pressures in the coordinates of Eq. (1) but are not observed in the coordinates of Eq. (11) implies that there exists a function of volume distribution other than function (2); this bears no relation to polydispersity of the microporous system. Figure 2 shows that the volume of micropores $W_0(H)$ is smaller than W_0. As H increases, the difference between $W_0(H)$ and W_0 decreases.

If the above-described estimates are applied to $b_{1,2}(H)$, the change in the volumes of micropores depends on the slope of the isotherm straightened in the coordinates of Eq. (1) or (11). For some experimental data (see, for example, Ref. 3), the difference can range from 10 to 50%; this means that the real pressure corresponding to the filling of micropores should be taken into account.

In conclusion, we would like to note that the estimates obtained here provide a correct description of the dependence of the pressure of volume filling of micropores on the size of the adsorbate molecules: as the pressure increases, the number of monolayers H decreases. Therefore, the $b_{1,2}(H)$ values increase, and, consequently, the pressure at which the pore is filled decreases. Consequently, whereas in the case of Eq. (1), the curves should intersect at the same point W_0,[6] in the case where Eq. (11) is used, the isotherms for various substances should end at the same W_0 value but at different pressures $p_{1,2}(H)$.

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