APPLICATION OF SCALING THEORY
TO DESCRIPTION OF ADSORPTION HYSTERESIS
IN OPEN SLIT-LIKE MICROPORES

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To describe the adsorption hysteresis in open slit-like micropores, the theory based on the scaling concept for the variation of the relative pressure of adsorbate in the bulk phase at the adsorption and desorption branches of the hysteresis loop is proposed. The equations obtained from this theory are applied to some adsorption systems leading to a reasonable agreement between the calculated values and experimental data.

INTRODUCTION

Solids, in general, possess a wide variety of pore sizes: from macropores, mesopores and micropores to the 'pores' which correspond to the gaps between the compactions of junctions or dislocations, as well as to the point defects. Therefore, there exists the spectrum of pore sizes.

According to the IUPAC classification, the pores with characteristic size below 2 nm are considered as the micropores; the range of 2 to 50 nm is ascribed to the mesopores, and the macropores possess the characteristic size above 50 nm [1]. It should be stressed, however, that this distinction between various pore classes is rather ill-definite because the adsorption properties of a pore depends both on its geometry and relevant intermolecular interactions.

For the definiteness, the open slit-like micropores are considered here. It is known that in the ensemble of these pores, the adsorption hysteresis mechanism is defined as the first-order phase transition, which is characteristic for the medium values of relative pressure of an adsorbate in the bulk phase. In the low pressure range, the adsorption hysteresis is governed by chemical and diffusion traps [2]. However, the processes which occur in the pores of a nanoporous body due to its interaction with gas (vapour), should be related to the characteristic pore size rather than to the relative adsorbate pressure in the bulk phase. In particular, the capillary evaporation process is described by the modified Kelvin equation if the characteristic pore size is higher than five Van der Waals molecular diameters of adsorbed molecules.

Hereinafter the adsorption hysteresis process is considered, which takes place within the pore size range where the capillary evaporation occurs. It is in this very case where main problems arise. It is known that for the pores with the width of a few molecular diameters the Kelvin equation is deficient. This is caused by several reasons: the deviations of the surface tension and the condensate molar volume from their 'normal' values, the fact that in the pores of such volume the concept of the meniscus is quite ambiguous [3]. The attempts to account for the influence of the pore size on the surface tension and the molar volume values in the framework of macroscopic thermodynamics are unlikely to be adequate for the pores which sizes do not exceed several (up to 10) molecular diameters. In the systems which involve relative small number of molecules, all properties exhibit significant fluctuations. In principle, rigorous treatment of the behaviour of adsorbate in thin capillaries is possible in the framework of the small systems thermodynamics [4]; however, the authors are unaware about any particular results in this field.

It is also important to emphasize here that the validity of the Kelvin equation was verified experimentally only for the surfaces with moderate positive curvature (the droplets about

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1 μm in diameter); the negative curvature case remains non-analysed [3]. Therefore, while the approach to the calculation of the adsorption properties in small mesopores based on the Kelvin equation seems to be attractive, it should be kept in mind that the results could probably be deficient [1]. In the present situation there is a lack of methods applicable for the calculations of adsorption properties based on the small systems thermodynamics while the macroscopic thermodynamics fails for the systems considered here. Therefore, the scaling-based models become increasingly popular; note e.g. the calculation of phase transition temperature in the pore [5].

In the present study, the attempt is made to derive the equation for the desorption branch of the hysteresis loop using the scaling approach.

THEORY

The equation for the desorption branch of the hysteresis loop based on the macroscopic thermodynamics will be used for the sake of comparison; therefore, we recapitulate here our results reported earlier in [2]. This equation for the model of the open slit-like pore reads:

$$-\ln x_d = A - B + C ,$$ (1)

$$A = \frac{\eta \gamma V_l}{RT\sigma}\left(\frac{a_m}{b^\alpha}\right)\frac{1}{\left(-\ln x_a\right)^{-\alpha} - \left(-\ln x_d\right)^{-\alpha}} ,$$ (2)

$$B = \left(\frac{\alpha}{\alpha-1}\right)\frac{\left(-\ln x_a\right)^{1-\alpha} - \left(-\ln x_d\right)^{1-\alpha}}{\left(-\ln x_a\right)^\alpha - \left(-\ln x_d\right)^\alpha} ,$$ (3)

$$C = \frac{b^\alpha}{a_m}\frac{\chi p^2 V_l}{RT} .$$ (4)

Here γ is the surface tension, V_l is the condensate molar volume, σ is the Van der Waals diameter of the adsorbate molecule, a_m is the amount adsorbed in the monolayer, η is the pores connectivity coefficient, p is the pressure; b and α are the parameters involved in the Frenkel-Halsey-Hill (FHH) equation [1]:

$$a = a_m\left(\frac{b}{-\ln x_a}\right)^\alpha .$$ (5)

a is the adsorbed amount, x_a and x_d are the relative adsorbate pressures in the bulk phase at the adsorption and desorption branches of the hysteresis loop, respectively. It was shown in [2]

that, in the practical calculations within the first approximation, the contribution of the C term could be neglected. Therefore, the pore connectivity coefficient η could be calculated from Eqs. (1)−(3) as:

$$\eta = \frac{RT}{\gamma V_l}\left(-\ln x_d M + N\right) ,$$ (6)

where $M = [(-\ln x_a)^{-\alpha} - [(-\ln x_d)^{-\alpha}]$, $N = [(-\ln x_a)^{1-\alpha} - [(-\ln x_d)^{1-\alpha}]$. Equation (6) rigorously describes the dependence of the pores connectivity coefficient on the governing parameters of the adsorption system. Once the behaviour of the pores connectivity coefficient is determined from Eq. (6), the practical calculations of the η dependence on the width of the core (the space inside the pore except for the layer adsorbed on the pore wall) could be made using simpler approximations.

The scaling dependence commonly used to describe the variation of the pores connectivity coefficient with the characteristic size of the core was proposed in [6]:

$$\eta = \varphi^{2/3}\left(\frac{d_{min}}{d}\right)^\alpha ,$$ (7)

where φ is the porosity of the sample, d and d_{min} are the pore width and the minimum width of the pore relevant to the pore size range within which the hysteresis is considered, respectively.

As was noted above, among the equations which describe the dependence of the pressure in the phases on the surface curvature for the liquid/vapour systems, the Kelvin equation is the most known one. However, other functional dependencies could also be considered. The equation, which relates the saturation pressure with the surface curvature, can be derived from the simultaneous solution of the Laplace and Poynting equations. For the phase transformations in the slit-like pore this equation reads [7]:

$$p_V = p_0 + \frac{V_L}{V_V - V_L}\cdot\frac{\gamma}{w_c} ,$$ (8)

where w_c is the core width, p_V and p_0 are the saturation pressures above the curved and plane surface, respectively, V_L and V_V are the molar volumes of liquid and vapour, respectively.

It should be noted here that Eq. (8) is valid in its present form only within some assumptions.

In particular, the integration of the Poynting equation assumes the independence of the molar volumes of phases on pressure while the Laplace equation is valid only for very small surface curvatures [8]. In what follows, Eq. (8) will be used to derive the scaling relations which describe the phase transformations in the super-microporous slit-like capillaries.

As the results obtained from the scaling approach should be compared with those derived from the Kelvin equation, its applicability should be assessed with regard to the decreasing pore size. For the dependence of surface tension on the curvature, the equation valid for spherical interface is [7]:

$$\ln \frac{\gamma(r)}{\gamma_\infty} = \int_\infty^r \frac{\frac{2\delta}{r^2}\left[1 + \frac{\delta}{r} + \frac{1}{3}\left(\frac{\delta}{r}\right)^2\right]}{1 + \frac{2\delta}{r}\left[1 + \frac{\delta}{r} + \frac{1}{3}\left(\frac{\delta}{r}\right)^2\right]} \, dr \, , \qquad (9)$$

where r and γ_∞ are the radius of the dividing surface and the surface tension at $r \to \infty$, respectively, $\delta = r' - r$, r' is the radius of the equimolar dividing surface. The general analytical quadrature of Eq. (9) is impossible; also to analyse this equation the assumption that the δ value is constant was made, see [8]. While the estimation of δ value is quite cumbersome, the calculations based on statistical mechanical methods and lattice gas models (as summarised in [8]) yield the reasonable approximation $\delta \approx 3.3$ nm. It should be noted that this value is by its order of magnitude comparable with the Van der Waals diameter σ of the molecules of most interesting adsorbates. Therefore, an approximation valid for the purposes of practical calculation – to replace the dimensionless variable δ/r by $\sigma/(2r)$ – seems to be reasonable. The numerical solution of Eq. (9) assuming $\delta = \text{const}$ was obtained (see [8]) to tabulate the functional dependence:

$$\frac{\gamma(r)}{\gamma_\infty} = f\left(\frac{\sigma}{2r}\right) \qquad (10)$$

for which we propose here the analytical approximation:

$$\frac{\gamma(r)}{\gamma_\infty} = m\left(\frac{\sigma}{2r}\right)^\beta \qquad (11)$$

with the coefficients $m = 0.3$ and $\beta = -0.53$. The maximum relative deviation between the tabulated values of the dependence (10) and those given by Eq. (11) within the range $0.1 < \sigma/(2r) < 1.0$ does not exceed ± 5.3 %.

For the adsorption hysteresis in open slit-like pore considered here, the relative pressure of the adsorbate in the bulk phase on the hysteresis loop desorption branch x_d should be determined. The governing variable in this case is the core width. However, it is convenient to introduce the relative core width d_c which we define here as the ratio of the core width w_c to the Van der Waals diameter of the adsorbate molecule σ. From Eq. (5) one obtains:

$$d_c = w_c/\sigma = b^\alpha[(-\ln x_a)^{-\alpha} - (\ln x_d)^{-\alpha}] \, . \qquad (12)$$

Consider now Eq. (11) which is essentially the scaling dependence in which β should be regarded as the critical index [5]. According to the scaling concept, the replacement of the variable parameter by the analogous variable results only in the change of the proportionality coefficient m while the critical index remains virtually unchanged. Therefore, Eq. (11) for the slit-like pore could be re-written as:

$$\frac{\gamma(d_c)}{\gamma_\infty} = C(d_c)^{0.53} \, . \qquad (13)$$

Introducing the scaling dependencies of the surface tension value into Eq. (8) for the desorption branch of the hysteresis loop, one obtains:

$$x_d = \frac{p_V}{p_0} = 1 - \frac{m_1 V_L \gamma_\infty}{p_0(V_V - V_L)\sigma(d_c)^{1-\beta}} \, , \qquad (14)$$

where m_1 is the proportionality parameter of the scaling dependence which can be estimated from the experimental data processing. Similar equation was derived by A.I. Rusanov [3] in another way. However, Eq. (14) in its present form is inapplicable for the calculation of hysteresis characteristics, because it disregards the size-related effects for the molar volumes of the condensate and vapour. Assuming that these molar volumes also obey the scaling dependence one obtains:

$$\frac{m_1 V_L \gamma_\infty}{p_0(V_V - V_L)\gamma} = Cd_c^n \, , \qquad (15)$$

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where n is the critical index of the scaling dependence which can be estimated from the experimental data. Therefore Eq. (15) finally becomes:

$$x_d = 1 - \frac{CK}{(d_c)^\chi} \, , \qquad (16)$$

where χ, K and C are the parameters defined to comply with Eqs. (13)−(15). As the parameters K and C multiplicatively determine the proportionality coefficient in the scaling equation (16), a single value $C' = C \cdot K$ can be used for the sake of simplicity.

Equation (16) could be reduced to the dimensionless form using the Bond number *Bo* as the governing parameter. For the pores with negligible capillary length the expression:

$$Bo = \frac{\gamma V_L}{RTt\sigma} \qquad (17)$$

was obtained earlier in [9]. Here t is the thickness of the stable adsorbate film which completely fills the pore. Then Eq. (16) reduces to:

$$x_d = 1 - (A \cdot Bo)^\chi \, , \qquad (18)$$

where *A* and χ are the scaling dependence parameters.

RESULTS AND DISCUSSION

Three adsorption systems were considered as the examples: adsorption of water vapour at 303 K on Gluchov Na^{+}-kaolinite [10], on Cherkasy palygorskite sample obtained at the evacuation temperature 533 K [10], and at 298 K on lunar regolith sample No. 64501.228 [11]. So, the adsorbents are referred to as the kaolinite, palygorskite and regolith, respectively.

Figure 1 illustrates the water adsorption isotherm on kaolinite. The fitting of this isotherm by the FHH equation (5) yields the parameters $a_m = 0.98$ mmol/g, $b = 1.82$, $\alpha = 0.87$; with these values the maximum deviation within the range $0.2 \leq x \leq 0.75$ between the experimental data and values calculated from Eq. (5) does not exceed $\pm 8.7\%$. From the considerations presented above it could be assumed that at $x > 0.3$ the mutual influence of the pore walls is negligibly small, therefore the core is formed in the inverse process, and the evaporation process obeys the Kelvin equation. Within the relative adsorbate pressure range in the bulk phase $0.3 \leq x \leq 0.75$

the relative pore thickness is varied from 1.41 to 5.5 and, according to Eq. (13), the surface tension value should be essentially different from its value in the bulk phase. As we have no information about the changes in the condensate, one option is to make calculations for the desorption process disregarding the dependence of the thermophysical properties of the condensate on the pore size. We have calculated first the variation of the connectivity coefficient η according to Eq. (6) with the condensate parameters $\gamma = 71.2$ mN/m, $V_l = 18 \cdot 10^{-6}$ m^3/mol, $\sigma = 2.89 \cdot 10^{-10}$ nm [12].
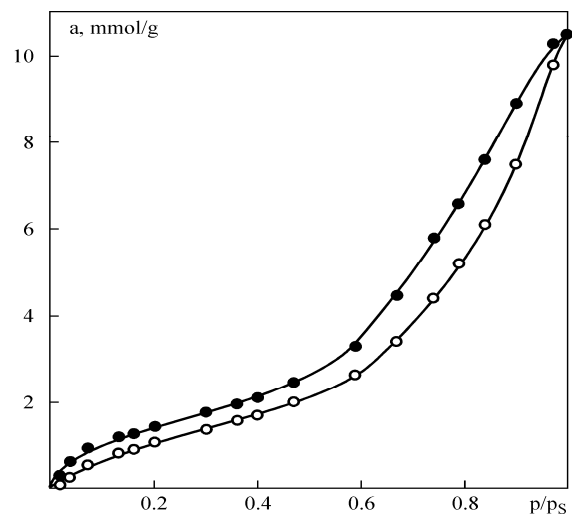

Fig. 1. Isotherm of water vapour adsorption on Gluchov kaolinite: ○ – adsorption, ● – desorption

Figure 2 illustrates the dependence of the connectivity coefficient in the ensemble of pores on the core width. This dependence is approximated by the scaling dependence (7) which for this particular isotherm reads:

$$\eta = \varphi^{2/3} \left(\frac{d_{min}}{d_k} \right)^{0,78} \, , \qquad (19)$$

where $\varphi = 0.65$ is the local value of the sample porosity in the point where the pore size $d_{min} = 0.37$. For these parameters Eq. (19) describes the dependence of η on d_c with maximum relative deviation $\pm 8.5\%$. It could be concluded from Figure 2 that the desorption process in the kaolinite pores, with regard both to the shape of this dependence and to the η values, could be described quite well even if the influence of the pore thickness is disregarded. This fact could be possibly ascribed to the mutual compensation of the effects caused by the

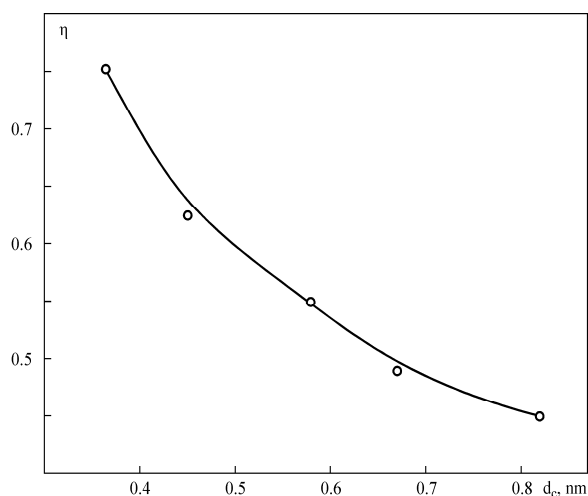variation of surface tension and of molar volume with the variation of the core width.

Fig. 2. Dependence of the connectivity coefficient on the core width for the water vapour adsorption on Gluchov kaolinite
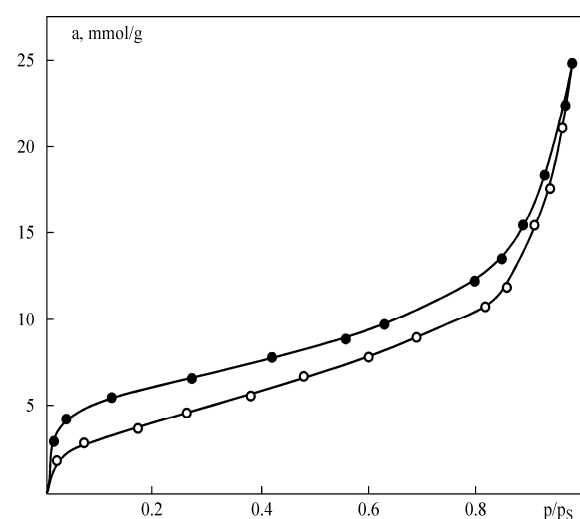

Fig. 3. Isotherm of water vapour adsorption on Cherkasy palygorskite: ○ – adsorption, ● – desorption

For the water adsorption on palygorskite the isotherm is shown in Fig. 3. The fitting of this isotherm by Eq. (5) yields the parameters $a_m = 4.4$ mmol/g, $b = 12.4$, $\alpha = 0.41$; with these values the maximum deviation within the range $0.3 \leq x \leq 0.95$ between the experimental data and values calculated from Eq. (5) does not exceed ± 7.8 %, and the relative pore width is varied from 1.25 to 5.1. The connectivity coefficient values as calculated from Eq. (6) (disregarding the dependence of the surface tension on the pore width) shown in Fig. 4 are seen to be unreasonably low.
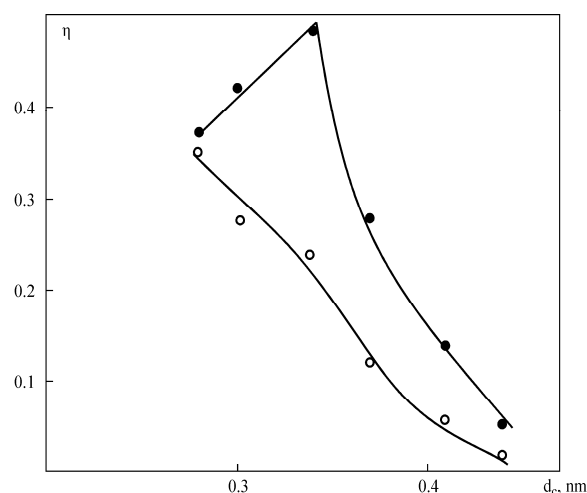

Fig. 4. Dependence of the connectivity coefficient on the core width for the water vapour adsorption on Cherkasy palygorskite: ○ – disregarding the dependence of the surface tension on the pore width, ● – with this dependence taken into account

Next the connectivity coefficient values were calculated with the surface tension dependence on the core width taken into account according to Eq. (13); these results are also plotted in Fig. 4. It is seen that, while the η values become somewhat higher, yet they remain too low. It should be noted also that at the $d_c > 0.3$ the shape of the functional dependence of η on d_c undergoes drastic change, and the connectivity coefficient sharply decreases. This behaviour contradicts Eq. (6) which implies the monotonous dependence of the connectivity coefficient. It could be concluded that for this adsorption system in the pore size range below $d_c = 0.3$ the Kelvin equation is incapable even for the qualitative description of the phase transformation process while in the range above this d_c value such description leads to large errors. Therefore, in this case the scaling approach is preferable.

Consider the application of Eq. (16) for the calculation of the desorption branch of the hysteresis loop for all three adsorption systems analysed here. To do this, the portion of the isotherm in the supermicropore range should be fitted to the dependence:

$$\ln(1 - x_d) = f\left[\ln(d_c)^{-1}\right] . \tag{20}$$

The calculations in this case require the solution (with respect to the sought quantity x_d) of combined Eqs. (12) and (18) for given values b, α, χ, C' and x_a. The resulting transcendent equation was solved by the successive

approximations method using the Mathcad software; maximum deviation of x_d in all cases did not exceed ±9.8 %. The results for all three systems are shown in Fig. 5; the parameter values were: $\chi = 1.82$, $C' = 0.11$ for kaolinite; $\chi = 1.81$, $C' = 0.09$ for palygorskite; and $\chi = 1.80$, $C' = 0.10$ for regolith.
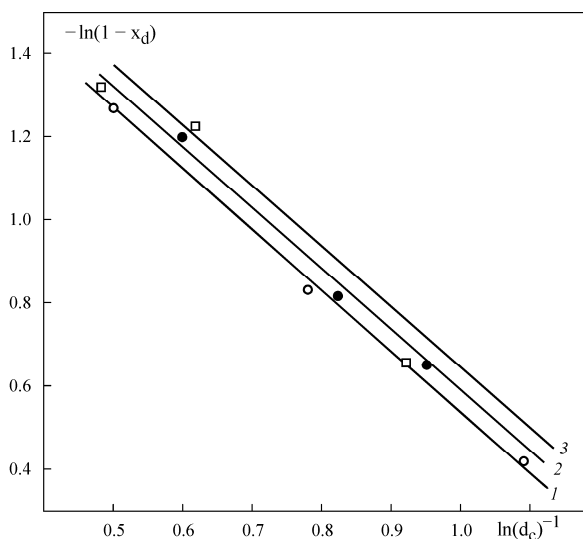

Fig. 5. Water vapour adsorption isotherms plotted in the coordinates of Eq. (18): Gluchov kaolinite *(1)*, Cherkasy palygorskite *(2)*, lunar regolith *(3)*

From the values thus obtained, two essential conclusions could be made. First, the critical index χ values are almost equal for all the systems considered here which is in a perfect agreement with the scaling theory. Second, the parameter C' values for these systems are also rather close: the difference between its values is about 10 %.

However, the averaging involved in the calculations leads to high errors in the determined x_d value. It follows from Eqs. (15) and (16) that the C' value strongly depends on the thermophysical properties of the adsorbate which was the same for all three systems considered here (water). Therefore, to draw more specific conclusions about the C' parameter, the systems involving other adsorbates should be analysed.

Turning now to Eq. (18) it should be noted that the critical index χ is equal (to within the calculations error) to the χ value in Eq. (16). The constant A recalculated via the proportionality coefficients which enter Eq. (6) equals 0.5±0.02. Equation (18) provides a good description of the hysteresis loop in the systems considered here.

CONCLUSIONS

The general equation for the adsorption hysteresis loop in open slit-like micropores based on the scaling concept for the variation of the relative pressure of adsorbate in the bulk phase at the adsorption and desorption branches of the hysteresis loop is proposed. The applicability of this equation is verified for some experimental adsorption systems. It is shown that the critical index χ values are almost equal for all the systems considered here, in agreement with the scaling theory; also the values of proportionality coefficient C' are approximately equal.

The averaging involved in the calculations leads to high errors in the determined values of relative adsorbate pressure on the desorption branch of the hysteresis loop. Also, the C' value strongly depends on the thermophysical properties of the adsorbate, which was the same for all three systems considered here. Therefore, the analysis of the systems with other adsorbates is desirable.

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Застосування теорії скейлінгу для опису адсорбційного гістерезису у відкритих щілиноподібних мікропорах

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Запропоновано теорію адсорбційного гістерезису у відкритих щілиноподібних мікропорах, що базується на теорії масштабної інваріантності, для зміни величин відносного тиску адсорбату в об'ємній фазі на адсорбційній і десорбційній гілках петлі гістерезису. Одержані рівняння перевірені на ряді адсорбційних систем. Показано, що розрахункові і експериментальні дані добре узгоджуються між собою.

Применение теории скейлинга для описания адсорбционного гистерезиса в открытых щелевидных микропорах

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Предложена теория адсорбционного гистерезиса в открытых щелевидных микропорах основанная на принципе масштабной инвариантности, для изменения величины относительного давления адсорбата в объемной фазе на адсорбционной и десорбционной ветвях петли гистерезиса. Полученные уравнения проверены на ряде адсорбционных систем. Показано хорошее соответствие расчетных и экспериментальных данных.