

DETERMINATION OF THE SURFACE AREA OF MESOPORES IN
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The surface area of mesopores S_{me} is one of the basic characteristics of adsorbents and catalysts widely used in practice. The estimation of S_{me} is very important for calculating the real parameters of the micropore structure [1]. It is known that adsorption and heterogeneous catalysis are a function of the pore structure of the samples to a significant degree [2, 3]. Different methods have been described for calculating S_{me} . They frequently give ambiguous results. The basic methods of calculation of S_{me} are analyzed in the present article.

Methods of Estimating the Surface Area of Mesopores. Methods (for example, the BET method [3]) based on concepts concerning the formation of a monomolecular adsorption layer are widely used for determining the surface area of samples. The specific surface areas calculated by these methods have no physical meaning for adsorbents containing micropores as well as mesopores [4].

The determination of the specific surface area with a mercury porosimeter is very widespread [3]. Since the contact angle of mercury on the boundary with a solid θ is equal to $\sim 140^\circ$, i.e., it is greater than 90° , excess pressure Δp is required to force the mercury to enter the pores of the solid. The use of depression of mercury for determining the pore size was proposed in [5]. The calculations are performed with the equation

$$r_p = - \frac{2\sigma \cos \theta}{\Delta p} \quad (1)$$

where r_p is the radius of a cylindrical pore; σ is the surface tension of the mercury.

Equation (1) is suitable for use in the case of pores with an arbitrary shape. The concept of the "equivalent radius" is used, $r_{eq} = 2F/\Pi$, where F is the area of the normal section of the pore inlet and Π is the perimeter of the section. S_{me} is calculated with the equation

$$S_{me} = - \frac{1}{\sigma \cos \theta} \int_0^{p_{max}} p dv_p \quad (2)$$

where p and p_{max} are the current and maximum mercury depression pressures; v_p is the volume of the depressed mercury. Strictly speaking, Eq. (2) gives the sum of the surface areas of meso- and macropores, but the surface area of the latter can be neglected [6].

The principles for an improved theory of capillary evaporation based on a more rational equation for the t-curve, which expresses the dependence of the mean statistical thickness of the adsorption layer t on the relative equilibrium pressure p/p_s , are given in [7-10]

$$\ln(p_s/p) = \frac{k}{t^m} \quad (3)$$

where K and m are parameters of the equation. The different variants of this method which permit calculating S_{me} with the desorption branch of the isotherm were examined. The Kelvin equation is used in method I

$$\ln(p/p_s) = -\frac{2}{r} \frac{\sigma v}{RT} \quad (4)$$

where r is the radius of the meniscus of liquid or the cylindrical area between adsorption films; σ and v are the surface tension and molar volume of adsorbate in the liquid state.

Method II, with consideration of the effect of the adsorption field in the mesopores on the thickness of the adsorption layer and curvature of the liquid meniscus according to [7], results in the initial equations

$$\ln(p_s/p) - \frac{K}{t_e^m} - \frac{\sigma v}{RT(r - t_e)} = 0 \quad (5)$$

$$r - t_e = \frac{2\sigma v}{RT \ln(p_s/p)} + \frac{2K}{(r - t_e) \ln(p_s/p)} \times \left[\frac{r^{2-m}}{(1-m)(2-m)} - \frac{rt_e^{1-m}}{1-m} + \frac{t_e^{2-m}}{2-m} \right] \quad (6)$$

where t_e is the average statistical thickness of the adsorption layer in a mesopore of an adsorbent with radius r .

Method III is the further elaboration of method II in which the dependence of the surface tension on the curvature of the liquid meniscus is considered [8]. In this case, the initial equations are

$$\ln(p_s/p) - \frac{K}{t_e^m} - \frac{\sigma_0 v}{RT(r - t_e - \omega)} = 0 \quad (7)$$

$$r - t_e = \frac{2\sigma_0 v}{RT \ln(p_s/p)} + \frac{2K}{(r - t_e) \ln(p_s/p)} \times \left[\frac{r^{2-m}}{(1-m)(2-m)} - \frac{rt_e^{1-m}}{1-m} + \frac{t_e^{2-m}}{2-m} \right] + 4\omega \left[1 - \frac{K}{(r - t_e) \ln(p_s/p)} \frac{r^{1-m} - t_e^{1-m}}{1-m} \right] \quad (8)$$

where σ_0 is the surface tension for the flat surface of the liquid; ω is a parameter of the Tolman equation, equal to 4.64 for benzene at 293 K.

The values of t and r for the entire range of p/p_s examined were calculated with a computer for each method using (3)-(8). The surface area of the mesopores and size distribution are usually determined with the Dubinin approximate method [10], which consists of the following. Desorption is represented as a step process beginning with $p/p_s = 1$. Desorption of an amount of vapor Δa due to evaporation of a capillary-condensed substance and a decrease in the thickness of the adsorption film on the surface of the walls of previously freed pores are the result of the n -th desorption step, which corresponds to a decrease in the relative pressure by $\Delta(p/p_s)$. The desorption value is

$$\Delta V = \Delta a v^* \quad (9)$$

where v^* is the molar volume of the substance in the liquid state. The change in the pore volume ΔV^* corresponding to evaporation of the capillary-condensed substance is expressed as

$$\Delta V^* = \Delta V - \Delta V_c + \Delta V_a \quad (10)$$

where ΔV_c is the change in the adsorption, expressed in volumes of condensed vapor, as a result of a decrease in the thickness of the adsorption layer on the surface of previously evacuated pores as a result of the n -th desorption step with a decrease in the relative pressure by $\Delta(p/p_s)$; ΔV_a is the volume of the adsorption layer of the surface of the pore walls corresponding to the volume ΔV^* .

The increase in the surface of the adsorption film as a result of evaporation of the capillary-condensed substance in the i -th stage of desorption is expressed as

$$\Delta F_i = \frac{2\Delta V_i}{\bar{r}_i - \bar{r}_i} \quad (11)$$

TABLE 1. Parameters of the Pore Structure of Active Carbons

Active carbon	Parameters of the DS equation (effective)			
	$W, \text{cm}^3/\text{g}$	$E_a, \text{kJ/mole}$	x, nm	δ, ma
AC-I	0.461	25.02	0.480	0.0006
AC-II	0.504	22.00	0.545	0.0288
AC-III	0.386	21.80	0.550	0.0031
AC-IV	0.638	20.74	0.578	0.0031
AC-V	0.757	16.90	0.709	0.193
AC-VI	1.00	10.98	1.090	0.420
AC-VII	1.15	9.86	1.217	0.484

TABLE 2. Results of Calculating the Surface Areas of the Mesopores of Active Carbons

Active carbon	$S_{me}, \text{m}^2/\text{g}$				
	poro- sime- try	met- hod	met- hod	met- hod	γ -meth- od
		I	II	III	
AC -I	50	—	—	—	37
AC -II	47	82	61	31	40
AC -III	47	79	58	30	40
AC -IV	44	78	58	30	40
AC -V	92	—	—	—	116
AC -VI	220	425	312	150	192
AC -VII	275	469	347	182	243

where \bar{r}_i and \bar{t}_i are the mean values. The total surface area of the adsorption film corresponding to evacuation of the pores in the $n-1$ preceding stages of desorption can be represented as

$$F = \sum_{i=1}^{n-1} \frac{2\Delta V_i}{\bar{r}_i - \bar{t}_i} \quad (12)$$

Then

$$\Delta V_c = F\Delta t \quad (13)$$

$$\Delta V_a = \bar{t}\Delta F \quad (14)$$

where Δt is the change in the thickness of the adsorption film. As a result, (10) for the change in the volume of the pores freed in the n -th stage of desorption becomes

$$\Delta V_n^* = \Delta V_n + \bar{t}_n \frac{2\Delta V_n}{\bar{r}_n - \bar{t}_n} - \Delta t_n \sum_{i=1}^{n-1} \frac{2\Delta V_i}{\bar{r}_i - \bar{t}_i} \quad (15)$$

The surface area of the mesopores can be calculated with the equation

$$S_{me} = \sum_{i=1}^n \Delta S_i \quad (16)$$

where

$$\Delta S_i = \frac{2\Delta V_n^*}{\bar{r}_n} \quad (17)$$

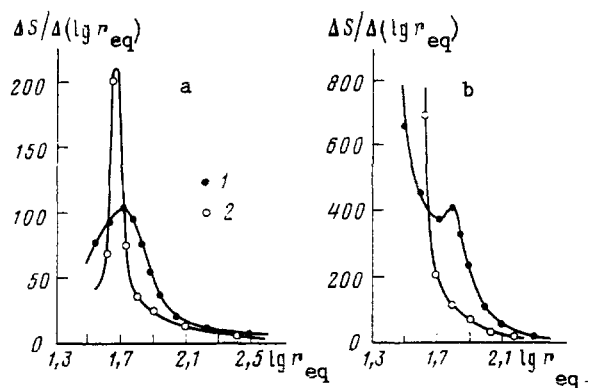


Fig. 1. Mesopore volume distributions of AC-III (a) and AC-VI (b) calculated by mercury porosimetry (1) and method III (2).

Methods based on the use of the dependence of adsorption per unit of adsorbent surface area γ on p/p_s have recently been successfully developed. This particularly concerns the γ method in [11], which is a variety of the t method and is based on the hypothesis that in the region of $p/p_s = 0.45-0.70$, filling of the micropores in carbon adsorbents is almost completed, and capillary condensation has not yet begun. In this region, polymolecular adsorption increases proportionally to the value of γ , which is expressed by the equation

$$\gamma = \frac{9.11}{A^{0.5645}} \cdot 10^{-3} \text{ mmole/m}^2, \quad (18)$$

where

$$A = RT \ln(p_s/p) = 2.438 \ln(p_s/p), \text{ kJ/mole.} \quad (19)$$

Equation (18) expresses the isotherm of adsorption of benzene at 293 K on the surface of the mesopores of carbon adsorbents. The tangent of the slope of the linear experimental isotherm in coordinates of α vs. γ is equal to the surface area of the mesopores in the adsorbent.

The methods described above basically have different physicochemical features, and for this reason, it is interesting to evaluate the possibility of using these methods for calculating the surface area of the mesopores of carbon adsorbents with a different pore structure.

Determination of the Surface Area of Mesopores. Active carbons with a different volume of micropores and type of micropore size distribution for which the isotherms of adsorption of benzene at 293 K were determined in a vacuum setup with a MacBain spring balance were selected as the adsorbents. The parameters of the micropore structure of the adsorbents with the Dubinin-Stockli equation [1] are reported in Table 1. A mercury porosimeter, the theory of capillary evaporation, and the γ method were used for calculating S_{me} . The values of the surface area of the mesopores calculated with these methods are reported in Table 2.

We note that in the γ method, the calculations were performed with the adsorption branch of the experimental isotherm, while they were performed with the desorption branch for $p/p_s = 1.0-0.18$ in methods I-III. The initial data were taken from [9] for the latter methods.

The mercury porosimetric measurements were performed on a P-5 M setup [12] consisting of low- and high-pressure porosimeters. The working ranges of the porosimeters are 0.02-0.12 MPa ($r_{eq} = 40,000-6300$ nm) and 0.12-490 MPa ($r_{eq} = 6300-1.5$ nm). The dilatometer is the basic measuring component of the mercury porosimeter setup. The sample studied was placed in a previously calibrated dilatometer which was connected in series to the low- and then the high-pressure porosimeter [13].

Discussion of the Results of the Studies. The analysis of the data reported in Table 2 shows that three independent methods give the closest results: mercury porosimetry, the γ -method, and method III. Deviations from the average values of S_{me} calculated with these methods are $\leq 30\%$. The data from the first two methods are in especially good agreement, the difference does not exceed 21% (with the exception of AC-IV), and the relative deviation is smaller for the active carbons which have a developed mesopore surface area

(AC-VI, AC-VII). Note that this agreement of the results is obtained for active carbons which significantly differ both with respect to the pore structure and with respect to the starting raw material for their preparation and the method of activation.

The values of S_{me} obtained by mercury porosimetry should probably be considered the most realistic values, although the error of the method increases in the region of pore radii of <4.0-5.0 nm, i.e., near the lower boundary of the mesopores [3]. Of the adsorption methods, the γ method is the most precise and convenient to use. Methods I and II give values of the mesopore surface areas which are significantly larger than the S_{me} obtained by other methods. This can be attributed to the fact that method II and especially method I do not take into consideration the definitely important effects which take place during capillary evaporation: the effect of the adsorption field on the thickness of the adsorption layer and the curvature of the liquid meniscus and the dependence of the surface tension on the curvature of the meniscus. The fact that method III results in slightly lower values of S_{me} is probably due to the unjustifiably large value of the theoretically calculated parameter $\omega = 4.64$. If it decreases to 1.5 [14], the mesopore surface area will coincide with S_{me} calculated with the γ and mercury porosimetry methods.

A comparative estimation of the pore distributions by radii obtained by mercury porosimetry and method III was conducted. The differential curves of the distribution of the mesopore surface area by size for active carbons with narrow (AC-III) and broad (AC-VI) size distributions of the micropore volumes are shown in Fig. 1. The distribution curves obtained by the two methods differ from each other. The causes of this will be examined in subsequent studies.

CONCLUSIONS

1. The use of the existing methods of calculation of the specific mesopore surface area was analyzed on the example of carbon adsorbents with a different pore structure.
2. The calculations with the γ method based on the improved theory of Broekhoff and de Boer with consideration of the effect of the curvature of the liquid meniscus on the surface tension and mercury porosimetry give the closest values of the mesopore surface area for all of the adsorbents studied.

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