Determination of the adsorption volume and surface of carbon adsorbents with developed mesoporosity

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The isotherms of excess adsorption of CH_4 (at $P = 0.001-160$ MPa), SF_6 (at $P = 0.001-2.4$ MPa), and C_6H_6 (at $P = 0.0001-0.1$ MPa) on carbon adsorbents — microporous carbons CMS and FAS with developed mesoporosity and graphitized soot — were measured in the 298—408 K temperature region. Calculation of the isotherms of absolute adsorption of the total content of these substances requires knowledge of the adsorption volume, which was determined by different methods: by the Dubinin—Radushkevich equation; by the experimental isotherm of excess adsorption and the equation of absolute adsorption; by the method using the intersection of nonlinear isosteres of excess adsorption and isosteres of absolute adsorption; by the comparative plot of values of the excess C_6H_6 adsorption $\Gamma_{FAS}-\Gamma_{soot}$; by the method using the difference of molecular radii of adsorptives and the surface of the specific adsorbent; and by the calculation of the adsorption layer thickness using the FHH equation for mesoporous systems. The results of determination of the adsorption volume for microporous systems of these carbons agree well with each other and with the passport data for the adsorbents. Analysis of the results revealed the peculiarity of the sulfur hexafluoride adsorption related to the formation of associates on the surface of the carbon adsorbents.

Key words: adsorption, carbon adsorbents, sulfur hexafluoride, benzene, methane.

Excess adsorption (Γ) is usually measured in studies of gas and vapor adsorption. Isotherms of excess adsorption of gases obtained in a wide region of changing pressure differ qualitatively from isotherms of total content. The extensive thermodynamic adsorption parameters calculated from experimental data, for example, excess isosteric heats of adsorption, are even transformed into infinity, which does not correspond to the real adsorption process. Nearly all molecular statistical models and the problems of practical application of adsorption are based on the concept of the total content of the adsorbate (a) in the adsorbent. The experimentally obtained excess adsorption is related to the total content adsorption by the known correlation:

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

where ρ_g is the density of the equilibrium gas phase, and W is the adsorption volume.

The adsorption volume does not coincide, as a rule, with the geometric volume of adsorbent pores. However, for microporous adsorbents with pores comparable with sizes of adsorbed molecules, the adsorption field is limited by the geometric volume of the adsorbent pores. In this case, the adsorption volume virtually coincides with the pore volume. Several methods for determination of W were developed in the study of adsorption on microporous adsorbents. In the case of adsorption on a "planar" surface, the adsorption volume is found from the thickness of the adsorption layer and the surface area of the adsorbents. No methods for determination of the adsorption volume are available for micropore-containing adsorbents with a developed surface. In these systems, adsorption in mesopores and micropores cannot be separated. Therefore, only data on the total surface area of these adsorbents and surface area of mesopores are usually present in the literature.

For adsorption of some substances on carbon adsorbents, a phenomenon can be observed when the adsorbate molecules form associates on the adsorbent surface. In this case, the distribution of adsorbate molecule on the adsorbent surface is nonuniform (see, *e.g.*, Ref. 1). Then the calculation of the surface area of adsorbents from the adsorption values gives an incorrect value of the adsorption volume and a substantial deviation of the adsorption isotherms of total content from their true run.

This work is devoted to the determination of the adsorption volume for adsorption systems with carbon adsorbents with different porosities, including adsorbent with developed mesoporosity. Benzene, which usually does not form associates on the surface of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 688—696, April, 2000.

1066-5285/00/4904-0692 $25.00

carbon adsorbents, methane, and sulfur hexafluoride were chosen as adsorptives.

Experimental

Microporous active carbon (CMS trademark, Switzerland), domestic active carbon (FAS trademark), and two types of soots (Table 1) were used as adsorbents. The porous system of the CMS carbon has been well studied.[2,3] According to the theory of volume filling of micropores (TVFM),[4] it possesses the structural-energy characteristics which are presented below (mi and me are micropores and mesopores, respectively, and S_{tot} is the total surface area).

Carbon	E	W_{mi}	W_{me}	$<r>$	S_{me}	S_{tot}
	/kJ mol^{-1}	cm^3 g^{-1}		/nm	m^2 g^{-1}	
CMS	26.19	0.252	—	0.73 (mi)	28	710
FAS	—	0.17±0.05	0.30	23 (me)	—	—

The structural-energy parameters of the domestic FAS carbon are poorly understood. According to the manufacturer's (Elektrostal') certificate data, this carbon contains micropores and mesopores whose parameters are given above. As can be seen from the presented data, the FAS carbon differs from the CMS carbon by a greater volume of micropores. To determine the surface area and adsorption volume of the carbons, we used samples of two soots: graphitized soot with a surface area (S) of 29 m^2 g^{-1} and nongraphitized soot with S = 106 m^2 g^{-1}. The values of the surface area were determined from the benzene adsorption. Sulfur hexafluoride with purity 99.99%, methane (pure grade), and benzene (reagent grade) were used as adsorptives. Experiments were carried out on a high-pressure volume-weighing adsorption setup. The metallic adsorber in the setup was hanged up to an analytical beam balance, and the gas was conveyed to the adsorbent through a thin spiral metallic capillary designed for operation at high pressures. In the setup, the weighing pressure gauge developed by us was switched on in parallel to a Bourdon pressure gauge (depending on the interval of measured equilibrium pressures of 25 or 250 kgf cm^{-2} with an accuracy class of 0.15). The principle of operation and the structure of the weighing gauge are similar to those of a volume-weighing setup with the same absolute sensitivity of 5 · 10^{-4} g. The temperature of the thermostat of the weighing gauge was maintained with an accuracy of ±0.1 K. Due to the relatively large volume of the tube of the weighing gauge (13.157 cm^3), the accuracy of the measured density of adsorptives ρ (g cm^{-3}) at the adsorption equilibrium in the low-pressure region was at most 1% and increased at high pressures. The pressure of methane and sulfur hexafluoride was calculated from the gas density measured by the weighing gauge using the multi-constant equation of state $F = f(P, \rho, T)$.[5,6] In the case when the temperature of the tube with the adsorbent differed from that of the weighing gauge, the density of the adsorptives were calculated by a similar equation. The relatively high sensitivity of the weighing manometer made it possible to measure pressures and densities of gases with an error lower than 1%. Experimental high-pressure adsorption setups have previously been discussed in more detail.[7] Benzene adsorption on the FAS carbon was measured on the second weighing experimental setup including a beam balance with a sensitivity of 10 μg and two gauges that overlap the interval of measured pressures from 0.133 to 1.33 · 10^5 Pa.

Table 1. Calculated values of the adsorption volume (W) and surface area (S) for adsorbents under study

Adsorbent	Method of determination (adsorptive)	S_{me}	S_{tot}	W_{mi}	W_{me}
		m^2 g^{-1}		cm^3 g^{-1}	
Carbon CMS	CP (C_6H_6)	28	—	—	—
	IH (C_6H_6)	—	710	—	—
	2ad (CH_4, SF_6)	—	708	—	—
	BET (SF_6)	—	294	—	—
	Certificate data	—	—	0.25	—
	DR (C_6H_6)	—	—	0.25	—
	EIEA (CH_4)	—	—	0.24	—
	DR (SF_6)	—	—	0.194	
Carbon FAS	CP (C_6H_6)	—	690	—	—
	CP (C_6H_6)	86	—	—	—
	γ'-(C_6H_6)	78	—	—	—
	BET (SF_6)	—	22	—	—
	β (SF_6)	9.9	—	—	—
	Certificate data	—	—	0.17	—
	DR (C_6H_6)	—	—	0.176	—
	CP (C_6H_6)	—	—	0.163	—
	DR (SF_6)	—	—	0.014	—
	Certificate data	—	—	—	0.3
	FHH (SF_6)	—	—	—	0.04
	FHH, DR (SF_6)	—	—	0.054*	—
Graphitized soot	BET (C_6H_6)	—	29	—	—
	BET (SF_6)	—	3.3	—	—

* The value W_{me} + W_{mi} is presented.

The excess adsorption Γ under equilibrium conditions was determined by the equation

$$\Gamma = (m - \rho_g V_{ac})/m_{ads}, \qquad (2)$$

where m is the directly measured weight of an adsorptive in the adsorber, ρ_g is the density of the equilibrium gas phase, V_{ac} is the accessible volume in the adsorber, and m_{ads} is the weight of the adsorbent in the adsorber. As a rule, the accessible volume V_{ac} is found by the calibration of the volume of the adsorber filled with the adsorbent against helium (in the volume method). However, it has previously been shown[8] that the accessible volume is determined by the size of molecules of the calibration gas. A great difference in sizes of molecules of He and adsorptives SF_6 and CH_4 (used as calibration gases) can result in different values of V_{ac} and, according to Eq. (2), the calculated adsorption isotherms differ substantially. In this work, we applied an approach which made it possible to use the really studied adsorptive as the calibration gas. For this purpose, the measured adsorption isotherm was presented in the coordinates m/ρ_g and P (Fig. 1 for the SF_6—CMS system). For this plotting, a horizontal region where $m/\rho_g = V_{ac}$ is observed on the isotherm in the region of increased pressures. If the interval of measured pressures is small and the horizontal region on the isotherm is absent, we find the limit of the approximating function:

$$m/\rho_g = B_0 + B_1/f + B_2/f^2 + \ldots + B_n/f^n, \qquad (3)$$

where f is the fugacity, and $B_0 = V_{ac}$ and B_i are the parameters selected during the processing of experimental data by the Simpson—Newton method. The V_{ac} value for the CH_4—CMS system was determined in the pressure range from 100 to 160 MPa with the horizontal region, and the deviations of the volume values from the mean volume corresponding to the horizontal region on the plot (see Fig. 1) are random.

The experimental isotherms for the systems under study are presented in Figs 2—4.

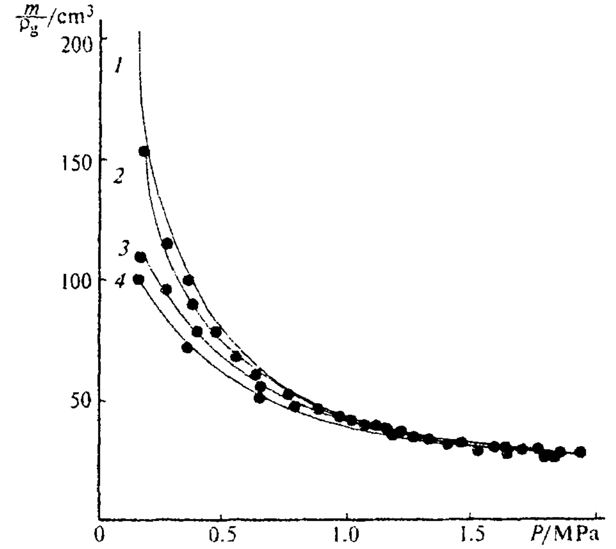

Fig. 1. Plot for determination of V_{ac} for the SF$_6$—CMS system at different temperatures: 327 (*1*), 343 (*2*), 373 (*3*), and 408 K (*4*).

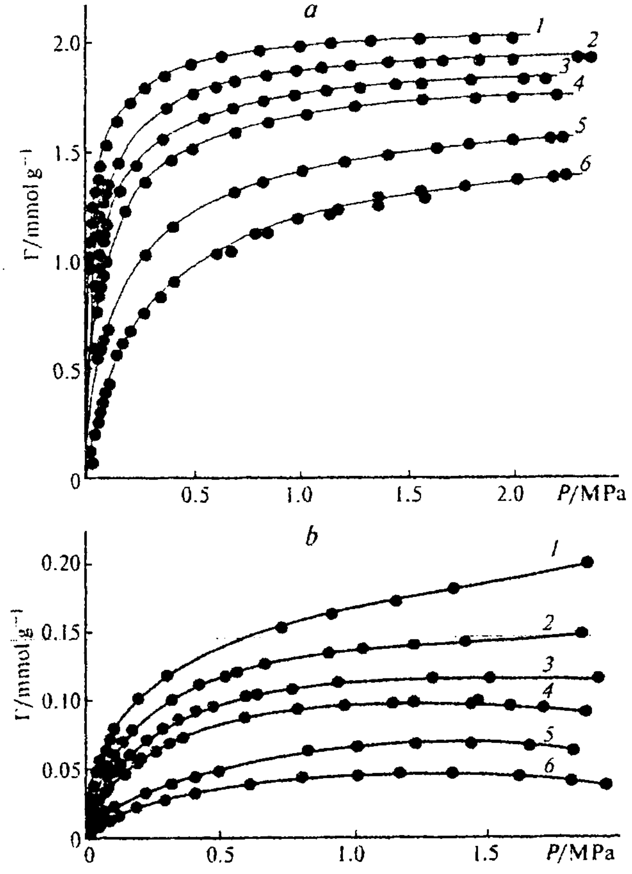

Fig. 2. Isotherms of excess adsorption of SF$_6$ on CMS carbon (*a*) and FAS carbon (*b*) at different temperatures: 298 (*1*), 313 (*2*), 327 (*3*), 343 (*4*), 373 (*5*), and 408 K (*6*).

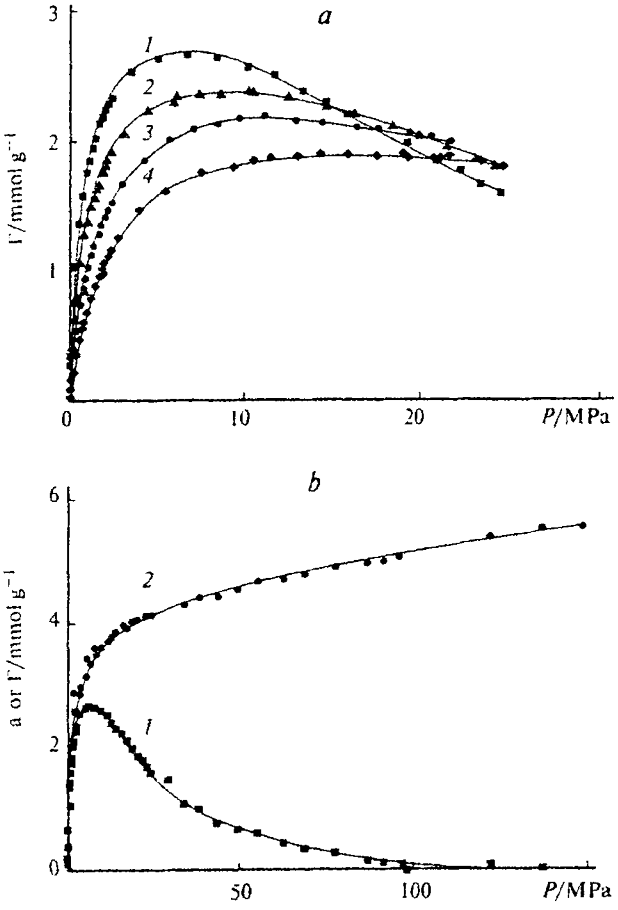

Fig. 3. Isotherms of CH$_4$ adsorption on CMS carbon: *a*, excess adsorption isotherm at different temperatures: 313 (*1*), 343 (*2*), 373 (*3*), and 408 K (*4*); *b*, isotherms of excess (*1*) and total adsorption (*2*) at 313 K.

Results and Discussion

The main task of this work is to determine the adsorption volume of the adsorbent with the mixed porous structure containing micropores and mesopores. To solve this problem, we applied the comparative analysis of adsorption values, surface areas, and adsorption volumes using various methods of processing of experimental data.

Several methods for the determination of *W* were developed to study vapor adsorption on microporous adsorbents, first of all, the TVFM-based method. The limiting adsorption Γ can be determined by the Dubinin—Radushkevich (DR) equation, and *W* can be calculated under the assumption that the adsorbate density is equal to the density of the liquid at certain *P* and *T*. In the study of vapor adsorption, the adsorption volume of carbon micropores can also be determined from the comparative plot (CP).[9] For plotting, one should have two adsorption isotherms of the same substance measured at the same temperature and in the same pressure

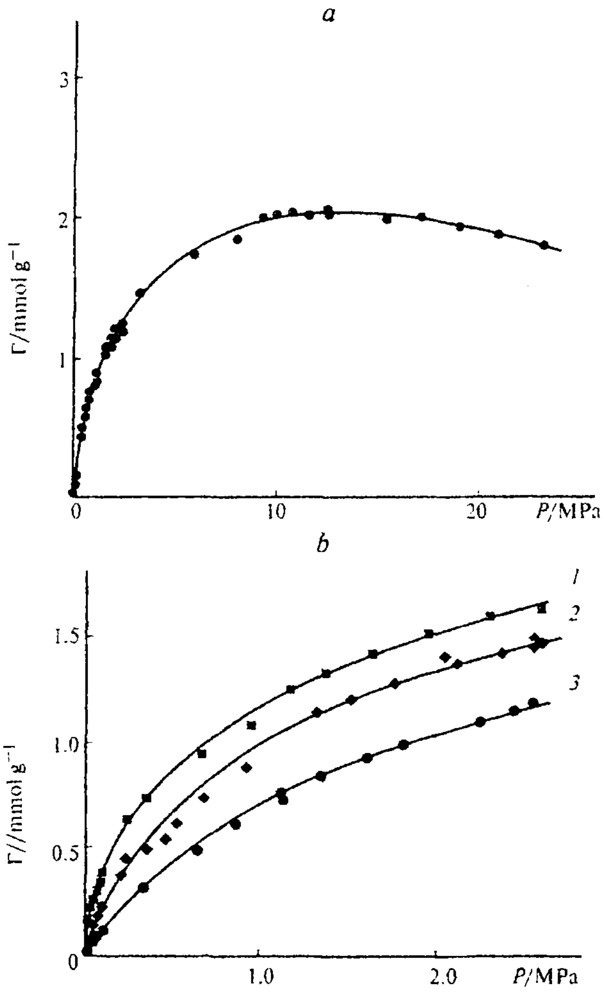

Fig. 4. Isotherm of excess adsorption of CH_4 on FAS at different temperatures: 373 (*a*), 313 (*1*), 343 (*2*), and 408 K (*3*) (*b*).

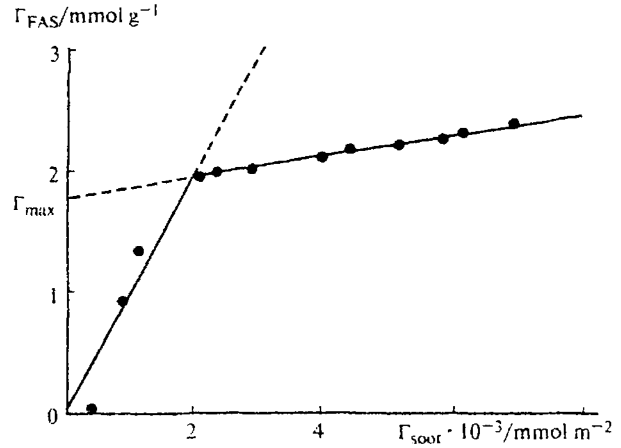

Fig. 5. Comparative plot Γ_{FAS}—Γ_{soot} for benzene at 293 K. Extrapolation to the ordinate for the determination of Γ_{max} is shown by the dotted line, and the experiment is indicated by points.

interval: on soot with a known surface and on the studied sample of the carbon adsorbent. The values of adsorption on the soot at specific absolute or relative pressures of the equilibrium gas phase are plotted on the abscissa in Fig. 5. The adsorption values are found for the same pressures from the adsorption isotherm of the substance on the carbon sorbent sample under study and plotted on the ordinate. The maximum adsorption value Γ_{max} is determined from the intercept on the ordinate that is cut by the straight line passing through the experimental points and extrapolated to the ordinate. The *W* value from CP is calculated as Γ_{max}/ρ_l, where ρ_l is the adsorbate density equal to the liquid density at certain *P* and *T*.

For gas adsorption, we have proposed[10] a method for determination of the adsorption volume *W* based on the use of the experimental isotherm of excess adsorption measured in a wide pressure interval and the equation of the adsorption isotherm of total content (EIEA). This equation was obtained by statistical thermodynamics taking into account that molecules adsorbed in one cavity do not affect those adsorbed in adjacent cavities of the adsorbent[11]:

$$a(f) = \frac{K_1 f + 2K_2 f^2 + \ldots + nK_n f^n + \ldots}{1 + K_1 f + K_2 f^2 + \ldots + K_n f^n + \ldots}. \qquad (4)$$

Here *f* is the volatility of the equilibrium gas phase; and K_1, K_2, ..., K_n are the coefficients of the equation. The coefficients of Eq. (4) and parameter *W* were selected in such a way that the calculated value of excess adsorption Γ_i^{calc} coincides with the measured Γ_i^{exp} value within measuremental error. For this purpose, the functional Φ in correlation (1) should be minimized

$$\Phi = N^{-1}\Sigma[(\Gamma_i^{exp} - \Gamma_i^{calc})/\Delta\Gamma^{exp}]^2 = \min. \qquad (5)$$

Here $\Delta\Gamma^{exp}$ is the experimental error of measurement of Γ, and *N* is the number of points on the experimental adsorption isotherm. This method was applied to Kr (Ar, N_2)—zeolite (monoporous adsorbent)[8] and CH_4—carbon adsorbent[12] systems and showed a good coincidence of the obtained *W* values with the values of the volume determined for the zeolite from the X-ray structural data and for carbon by the DR method.

The method of intersection of isosteres of excess adsorption (IIA) with linear isosteres of total content adsorption is one of the methods for determination of the adsorption volume of micropores.[13] The method is based on the assumption that isosteres of total content adsorption in the studied region of temperature and filling should be linear and the total content adsorption isostere should coincide with the excess adsorption isostere at low adsorption values. The validity of this assumption is confirmed by the extensive experimental data obtained for adsorption on microporous adsorbents.

The initial region of some excess adsorption isoster, which coincides with the total content adsorption isostere $a_1 = \Gamma_1$ = const, is linearly extrapolated to the intersection with another excess adsorption isoster Γ_2 = const. Correlation (1) is valid in the point of intersection of these isosteres. Then $W = (a_1 - \Gamma_2)/\rho_c$, where the density of the gas phase ρ_c is calculated by the equation of state of the gas at the point of intersection of isosteres.

For adsorbents containing micropores, mesopores, and macropores, the adsorption volume does not coincide with the geometric volume of pores, and the determination of the W value is associated with certain difficulties. In this case, we propose to use an approach based on knowledge of the adsorption layer thickness (Z) and surface area of these adsorbents (S).

The Brunauer—Emmett—Teller (BET) method is widely used for the determination of the surface area of adsorbents. The sizes of surface areas (necessary for BET calculations) occupied by molecules of several substances on the surface of various adsorbents have been published previously (see, *e.g.*, Ref. 14).

The method in which two adsorbents (2ad) are used can be another procedure for the determination of the adsorbent surface area. In this case, the size of the adsorptive molecules are taken into account. It is accepted that the true volume of adsorbent pores is equal to the sum of two volumes: the accessible volume of pores for adsorptive molecules W_{ac} and inaccessible volume $W_{inac} = Sr$ (S is the surface area of the whole adsorbent surface, and r is the effective radius of the adsorbate molecule). When the adsorption volumes W are known for two different adsorptives (W_1 and W_2) with the effective radii of the molecules r_1 and r_2, the total adsorbent surface can be determined by the correlation[7]:

$$S_{tot} = (W_1 - W_2)/(r_2 - r_1). \tag{6}$$

The surface area of adsorbents can also be calculated from the immersion heats (IH)[2] measured on a calorimeter. The heat q_h liberated when the studied adsorbent with known specific surface energy ε_h is immersed into the liquid is proportional to the surface area: $S = q_h/\varepsilon_h$.

In the case when it is necessary to determine only the surface area of mesopores, which amounts to a part of the adsorbent surface only, we can use, for example, the γ' method[15] based on the correlation

$$\Gamma = \Gamma_{mi} + \gamma' S, \tag{7}$$

where Γ is the excess adsorption of the standard vapor (benzene) on the carbon sample, Γ_{mi} is the excess vapor adsorption in carbon micropores, and γ' is the excess vapor adsorption calculated per surface area of mesopores S. It was found from analysis of numerous experimental data on benzene adsorption on the carbon adsorbents that the almost complete filling of micropores at 293 K is ceased at P/P_s = 0.40—0.45. Therefore, to determine the mesopore surface by Eq. (7), one should use the experimental isotherm of benzene adsorption on the carbon sample within the interval of relative pressures from 0.45 to 0.75. The empirical formula has been obtained for this pressure interval[15]

$$\gamma' \cdot 10^3 = 15.08/(RT\ln P_s/P)^{0.5645}. \tag{7a}$$

To find the surface area of mesopores S_{me}, the values of Γ as a function of γ' are plotted. The isotherm plotted in these coordinates within the interval of relative pressures of 0.45—0.75 is described by a straight line whose slope is numerically equal to the surface area of mesopores S (m^2 g^{-1}). The surface area of carbon mesopores can also be determined from CP, because the slope of the straight lines passing through the experimental points and extrapolated to the ordinate is equal to the ratio of specific surfaces of two adsorbents: the carbon under study and the soot with known surface area.

Some substances form associates during adsorption on carbon adsorbents, and the distribution of the molecules over the adsorbent surface is nonuniform. In this case, the adsorbent surface areas calculated by the adsorption values of these substances result in an incorrect value of the determined adsorption volume and a substantial deviation of the total content adsorption isotherms from their true run.

The excess isotherms obtained by us for methane adsorption on CMS and FAS carbons are presented in Fig. 2, *a*, *b*. It is seen that the value of excess adsorption of methane on CMS at 313 K measured at a pressure lower than 150 MPa passes through a maximum and decreases to zero at $P > 120$ MPa. The adsorption isotherms of methane on CMS at other temperatures are presented in a more narrow pressure interval. The presence of a maximum on the excess adsorption isotherms is the distinctive feature of adsorption of gases measured in a wide pressure interval (as compared to adsorption of vapors), which is confirmed by the excess adsorption isotherms (see Fig. 3, *a*, *b*).

The determination of the adsorption volume for the FAS—SF$_6$ system under study was impeded by the mixed structure of the pores of the FAS carbon and the specificity of SF$_6$ adsorption, which is not observed for the adsorption of, *e.g.*, methane or benzene on these adsorbents. As can be seen in Figs. 4 and 5, the excess methane adsorption on CMS carbon in the maximum of the isotherm under similar equilibrium conditions (T = 373 K, $P \approx 11$ MPa) is ~2.19 mmol g^{-1} and that on FAS carbon is ~2.07 mmol g^{-1}, which corresponds to the values of adsorption volumes determined with respect to methane for these adsorbents (Table 2, EIEA method). As has been shown previously,[12] the adsorption volumes found with respect to methane and benzene for CMS carbon virtually coincide. The total surface also agrees well with the indicated above values of methane adsorption: for CMS carbon it was 710 m^2 g^{-1} (determined from IH), and for FAS carbon it was equal to 690 m^2 g^{-1} (calculated from CP). A quite different situation is observed by comparison of the results of SF_6 adsorption on the same adsorbents (see Figs. 2 and 3): a sharp difference in the adsorption values. For example, adsorption on CMS in the maximum of the isotherm ($T = 298$ K, $P \approx 2$ MPa) is ~2 mmol g^{-1} and it is only 0.2 mmol g^{-1} on FAS carbon under the same equilibrium conditions.

The value of SF_6 adsorption on CMS carbon is much higher than that on FAS carbon under similar equilibrium conditions (see Table 1). Therefore, it should be expected that the adsorption volume and surface area of this carbon determined with respect to this adsorptive are much higher than those for FAS. This assumption is confirmed by the fact that the volume of micropores of CMS carbon determined at $T = 298$ K by DR for SF_6 is somewhat lower than that for CH_4. However, taking into account the great difference in the effective radii of SF_6 and CH_4 molecules, the calculated adsorption volumes for CMS carbon well agree with each other. This assumption is confirmed by the results of calculations (the total surface area S_{tot} of the CMS carbon determined by the IH and 2ad methods was 710 and 708 $m^2 g^{-1}$, respectively) presented below.

Molecule	W/cm^3 g^{-1}	r/nm
CH_4	0.24	0.21
SF_6	0.194	0.275

For the calculation of the surface area, we used the pore volumes found precisely for these two substances (CH_4 [12] and SF_6) and the difference of the effective radii (r) of their molecules.[16] The surface area of CMS carbon calculated by the formula[8]

$$S_{tot} = [W(CH_4) - W(SF_6)]/[r(SF_6) - r(CH_4)] \qquad (6a)$$

almost coincides with the value obtained by IH.

The adsorption volume of the SF_6—FAS system is summated of the volume of the micropores in which adsorption of SF_6 occurs under the specific equilibrium conditions and the adsorption volume of the mesopores, which is not equal to the geometric volume of the mesopores. In addition to the adsorption volume of the mesoporous structure of FAS carbon, it is also desirable to determine the fraction of the adsorbate which was adsorbed in mesopores. For the adsorption of benzene vapor on FAS carbon at $T = 298$ K and pressures close to P_s, the maximum adsorption value is ~2.4 mmol g^{-1}. This value is close to the adsorption of methane in the maximum of the isotherm and multiply exceeds the adsorption of SF_6 on this adsorbent (see Table 2). It is most likely that the SF_6 molecules due to their greater geometric size cannot adsorb in all micropores of FAS carbon in which methane and benzene molecules adsorb. The small size of pores of FAS carbon is also confirmed by a slow diffusion of methane, which was observed for this carbon in the experiment. Under the assumption that during the adsorption of SF_6 on FAS carbon a great number of micropores do not participate in the adsorption process, we should expect substantial differences in the values of the adsorption volume obtained from the adsorption data for SF_6 and for benzene and methane. This is confirmed by the data presented below (p.d. are certificate data).

Table 2. Parameters of adsorption of CH_4 and SF_6 on CMS and FAS carbons

Carbon	Γ_{max}/mmol g^{-1}		W/cm^3 g^{-1}	
	CH_4	SF_6	CH_4 (EIEA)	SF_6 (DR)
CMS	2.19	2.0	0.24±0.02	0.194
FAS	2.07	0.2	0.20±0.03	0.014

Adsorptive	C_6H_6			CH_4	SF_6
Method	p.d.	DR	CP	EIEA	DR
W_{mi}/cm^3 g^{-1}	0.170	0.176	0.163	0.20±0.03	0.014

It is seen that the volume of micropores by the certificate data almost coincides with the value determined for benzene by the DR method and is close to the adsorption volume W_{mi} found from CP for benzene and methane. Thus, the average volume of pores with respect to these two substances and according to the certificate data is $\langle W \rangle = 0.18 \pm 0.03$ cm^3 g^{-1}. For SF_6 adsorption, the volume of micropores calculated by DR for temperatures of 298 and 313 K is only 0.014 cm^3 g^{-1}. In this case, the fraction of adsorption related to mesopores amounts to a substantial part of the measured adsorption value.

The surface area of mesopores of this carbon determined from CP for benzene (Table 3) is close to that calculated from empirical equation (7a) — γ', whereas the total surface area obtained by BET for SF_6 molecules is only 22 $m^2 g^{-1}$ (including the surface of the micropore fraction indicated above).

The surface area of CMS carbon determined from BET for SF_6 exceeds the surface area of FAS carbon by more than an order of magnitude (see Table 3). This great difference in the S values for two adsorbents can be explained by the behavior of SF_6 during adsorption on these carbons.

A similar situation is observed for the determination of the surface area from benzene and SF_6 for graphi-

Table 3. Surface areas of adsorbents (S/m^2 g^{-1}) determined by various methods

Adsorbent	S_{tot}		S_{me},
	C_6H_6	SF_6	C_6H_6
FAS	690 (CP)	22 (BET)	86 (CP), 78 (γ')
CMS	710 (IH)	294 (BET)	28 (CP)
Graphitized soot	29 (BET)	3.3 (BET)	—

Note. Methods of determination are presented in parentheses.

tized soot (see Table 3), and the S values differ by ~9 times.

As can be seen from the presented data, the S_{tot} values of all studied adsorbents (CMS, FAS, and graphitized soot) calculated by BET for SF_6 are much lower than those determined by different methods using benzene and other adsorptives (see Table 3). Note that the $S(C_6H_6)$ ratios obtained for the same adsorbent strongly differ. For the microporous CMS adsorbent with a low specific surface of mesopores, this ratio is 2.41, and that for graphitized soot is 8.79 (see Table 3). For the adsorption of these substances on FAS carbon, the situation is impeded by the molecular-sieve effect.

The difference in the S values of the carbon adsorbents with respect to benzene and SF_6 can be attributed to the formation of SF_6 associates. When a substance adsorbs on a porous adsorbent, the adsorbate becomes close to an associated state not only due to the interaction of the molecules between each other as on the "planar" surface, but also under the action of the adsorbent. The problem of formation of associates on a "planar" surface (soot) has previously been studied in detail.[1] For study of SF_6 association on the surface of carbon adsorbents, we used data on adsorption on graphitized soot. The formation of associates of the adsorptive molecules on the adsorbent surface is quantitatively characterized[1] by the degree of association (β)

$$\beta = 1 - \theta_{as}/\theta. \qquad (8)$$

Here θ_{as} is the coverage, which represents the ratio of S determined for the adsorbate, whose molecules are capable of association, to the S value calculated with respect to the substance that does not manifest a tendency to association of the molecules on the carbon adsorbents, and θ is the ratio of the number of molecules adsorbed in the experiment at $P \to P_s$ to the calculated number of molecules of the same adsorptive in the compact monolayer. In our case, the degree of SF_6 association on the carbon soot was calculated from the S values for this adsorbent determined from the adsorption of SF_6 and benzene (it is known that benzene does not form associates on carbon adsorbents). According to the published data,[1] $\theta_{as} = S(SF_6)/S(C_6H_6) = 3.33/29 = 0.115$, and $\theta = N_{max}/N_0 = 1.83 \cdot 10^{18}/(4.85 \cdot 10^{18}) = 0.373$ for $T = 298$ K and $P/P_s = 0.9$. Then $\beta = 0.69$, which corresponds to a high degree of association. The β value should be equal to zero when the adsorbate molecules are not associated on the adsorbent surface.

Knowing the surface area of mesopores of FAS carbon determined for benzene (see Table 3), whose surface can be treated as "planar," and using the coverage $\theta_{as} = 0.115$ obtained from the data on the soot for SF_6, we calculated the surface area of mesopores of FAS carbon for sulfur hexafluoride $S_{me}(SF_6) = 86 \cdot 0.115 = 9.9$ m^2 g^{-1}, which comprised a substantial part of the total surface for SF_6, 22 m^2 g^{-1} (see Table 3).

In carbon micropores, the opposite "wall" of the pore, which is absent from the graphitized soot, imposes a restriction on associate formation. This results in an increase in the carbon surface area occupied by the SF_6 molecules. Due to this, the $S(C_6H_6)/S(SF_6)$ ratio for the graphitized soot is much higher than that for the microporous CMS carbon.

In carbon mesopores, the influence of the opposite "wall" on the adsorbed molecule can be neglected due to the relatively long distance between the "walls" and the weak effect of the dispersion forces because they are short-range ($1/r^6$). In this case, to find the adsorption volume of mesopores, we may use the approach based on the determination of the adsorption layer thickness Z and the mesopore surface S_{me}. The adsorption layer thickness can be calculated, *e.g.*, from the equation of the Frenkel'—Halsey—Hill (FHH) isotherm[17]:

$$\ln(f/f_s) = \Delta\varepsilon_1/kT^*(Z_i/Z_1)^{-n};\ Z_i = \Gamma_i/[S(\rho_l - \rho_g)]. \qquad (9)$$

Here Z_i is the distance from the surface of molecules adsorbed in the *i*th layer, Z_1 is the thickness of the first monolayer equal to the effective radius of the adsorptive molecule ($\sigma/2$), $\Delta\varepsilon_1$ is the energy of interaction of adsorbate molecules in the first adsorption layer, k is the Boltzmann constant, n is the exponent, and ρ_l is the density of the liquid.

The disadvantage of this equation is the assumption that the density of the substance in the adsorption layer is unchanged, *i.e.*, the adsorbate—adsorptive interface is distinct. This approach has been developed previously[18] for the transition layer between the adsorbed quasi-liquid film and the equilibrium vapor phase. Nevertheless, the application of the FHH approach to the system, in which the adsorbent contains a large fraction of mesopores along with micropores, makes it possible to calculate the adsorption volume for the mesoporous part of the adsorbent, although with some loss of accuracy. The exponent n in Eq. (9) can serve as a criterion for the applicability of this approach. The exponent n should be equal to three, which is the result of the integration of the term $1/r^6$ of the intermolecular potential, where r is the distance between the adsorbate molecules and atoms of the uniform adsorbent with an ideal "planar" surface. In the case of adsorption on the real surface, the exponent n can differ from three and, for example, for the adsorption of various adsorptives on the soot,[17] n amounts to 2.4—2.9.

In this approach, as can be seen from Eq. (9), the surface area of the mesopores should be known to determine the adsorption layer thickness. To calculate the adsorption layer thickness by FHH, we used $S_{me} = 86$ m^2 g^{-1} (see Table 3).

For the FAS—SF_6 adsorption system, one should determine the adsorption region related to the mesoporous part of the adsorbent, where the exponent n should be close to three. To find the value of the

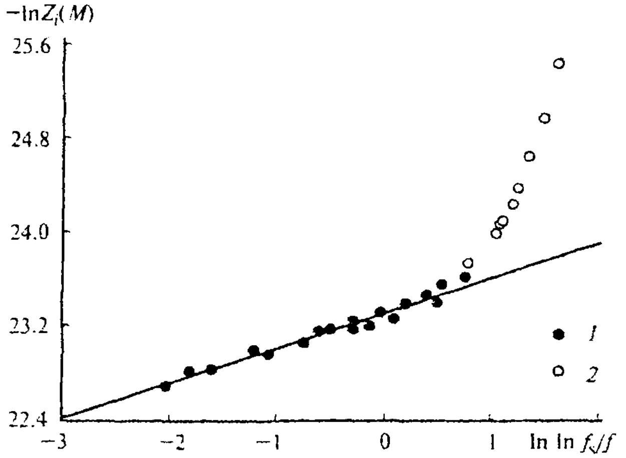

Fig. 6. Determination of the exponent n by Eq. (9a): *1*, points corresponding to Eq. (9a) with an exponent of 3.33 and *2*, other experimental points.

exponent, let us present Eq. (9) in logarithmic coordinates:

$$-\ln Z_i = (1/n)\ln(kT/\Delta\varepsilon_1) + (1/n)\ln\ln(f_s/f);$$

$$Z_i = \Gamma_i/[S(\rho_l - \rho_g)]. \qquad (9a)$$

The excess isotherm of SF_6 adsorption on FAS carbon at $T = 298$ K in the coordinates of Eq. (9a) is presented in Fig. 6. It is seen that the SF_6—FAS system exhibits a region of $\ln\ln(f_s/f)$ values from −2.0 to +0.8 with the exponent $n = 3.33$, whereas for the region $\ln\ln(P_s/P) > 0.8$, the exponent strongly differs from three. This also agrees well with the concept that during adsorption the molecules are adsorbed first (at low values $P \approx f$) on the strongest centers, *i.e.*, in more narrow pores, and then the adsorption occurs in wide pores of the adsorbent (see Fig. 6). For the region where the exponent is equal to 3.33, the layer thickness was determined from Eq. (9) as $Z = 0.44$ nm. The adsorption volume of the mesoporous system of FAS carbon $W_{me} = S \cdot Z = 86 \cdot 10^4 \cdot 0.44 \cdot 10^{-9} = 0.04$ cm^3 g^{-1}, and the total adsorption volume $W = W_{mi} + W_{me} = 0.014 + 0.040 = 0.054$ cm^3 g^{-1}. For the same adsorption system, the W volume calculated by the method developed by us (EIEA) is equal to 0.1±0.04 cm^3 g^{-1}. The same result was obtained by the IIA method (see above).

It is seen from the plot (see Fig. 6) that the adsorption of SF_6 in micropores of FAS carbon ceases at $f_s/f = 11.9$, which corresponds to the break point ($\ln\ln f_s/f = 0.8$). At the break point, the adsorption value is equal to 0.1 mmol g^{-1} at $P = 0.187$ MPa (by the isotherm of SF_6 adsorption in Fig. 2). This value is ~50% of the maximum adsorption, *i.e.*, 0.1 mmol g^{-1} SF_6 are adsorbed in mesopores of FAS carbon ($W_{me} = 0.04$ cm^3 g^{-1}), and the remaining portion (0.104 mmol g^{-1}) is adsorbed in micropores of the carbon ($W_{mi} = 0.014$ cm^3 g^{-1}), which well agrees with the values of the total surface area and the surface of mesopores of FAS carbon, being equal to 22 and 9.9 m^2 g^{-1}, respectively. Based on the values of SF_6 adsorption in micropores and mesopores, we can estimate the average density of adsorbed substances, which is much higher in micropores.

Since the adsorption volume does not coincide, in all cases, with the geometric volume of adsorbent pores, these values can strongly differ for adsorption in mesopores. For example, according to the certificate data for FAS carbon, $W_{me} = 0.30$ cm^3 g^{-1} (by mercury porosimetry, see above), whereas by our calculations, $W_{me} = 0.04$ cm^3 g^{-1}. Adsorption of methane and benzene also occurs in the part of the microporous system of FAS carbon which is inaccessible to SF_6 molecules. By analogy to SF_6 adsorption, it should be expected that the adsorption values of CH_4 and C_6H_6 in mesopores should be ~0.1 mmol g^{-1}, whereas the predominant portion of the substance is sorbed in micropores.

Based on the calculated values of the adsorption volume for the system under study, we plotted the adsorption isotherms of total content. Since the isotherms of excess adsorption and those of total content adsorption for vapor do not qualitatively differ from each other, Fig. 3, *b* presents the isotherm of total content adsorption only for CH_4 on CMS, which, as can be seen in Fig. 3, substantially differs from the excess adsorption isotherm.

In this work, we present the solution of the problem of finding the adsorption volume on adsorbents with different porosities and the problem related to the practical application of the calculation of adsorption processes. Usually it is impossible to separate adsorption on adsorbents in micro-, meso-, and macropores. The application of the methods for determination of adsorption volumes, which have been developed for a "planar" surface, to adsorbents containing both micropores and mesopores makes it possible to solve this problem approximately within the accuracy limit of each method. The calculated values of W and S for all systems under study are presented in Table 1.

FAS carbon with porous structure containing both mesopores and micropores exhibits the molecular-sieve effect, because the latter are narrow, and for each adsorptive, the carbon is as if a "different" adsorbent with a different total surface area and micropore volume.

Also note that we found unusual behavior of SF_6 during adsorption on the carbon adsorbents related to the formation of associates.

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Received March 31, 1999;
in revised form November 29, 1999