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Determination of the adsorption volume of various systems below and above the critical temperature

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A new approach was proposed to determine the adsorption volume of porous adsorbents with allowance for experimental data on the adsorption of substances at temperatures below and above the critical temperature. In the proposed approach, as in the theory of volume filling of micropores, it is assumed that the density of the adsorbate determined at the complete filling is independent of filling. The values of adsorption volumes calculated according to the proposed model are well consistent with the results obtained by other known methods.

Key words: adsorbate, adsorption volume, porous adsorbents, density of adsorbate.

Isotherms of total content are used for both calculation of thermodynamic characteristics of a system under study and practical calculations in adsorption technologies. When adsorption of gases and vapors is studied, values of excess amount adsorbed are measured. Isotherms of excess adsorption of gases obtained in a wide pressure range (up to ~150 MPa) differ qualitatively from total content isotherms. The total content adsorption of gases increases monotonically with the pressure increase, whereas the excess gas adsorption first increases, reaches a maximum, and then decreases down to zero values (Fig. 1). The adsorption volume W_0 should be known for the recalculation of excess isotherms to total content isotherms.

According to the theory of volumetric filling of micropores (TVFM),[1] the micropore volume W_{mi} of porous adsorbents can be determined from the adsorption isotherm of standard vapor of benzene or nitrogen at temperatures below the critical temperature ($T < T_{\mathrm{cr}}$). This method is based on the equation of the Dubinin—Radushkevich (DR) adsorption isotherm and the assumption that the densities of the adsorbate and liquid adsorptive are the same on a given adsorbent. However, only molecular sieve zeolites and some carbon adsorbents, such as polymeric active carbon PAC, are purely microporous adsorbents. The most part of known adsorbents refer to the mixed type: they contain micro-, meso-, and macropores. For practical purposes it is important to use such a method that would allow one to immediately determine the total adsorption volume W_0 of the porous adsorbent, including that of meso- and macropores localized in the near-surface layer. For smooth surfaces and pores different from micropores,

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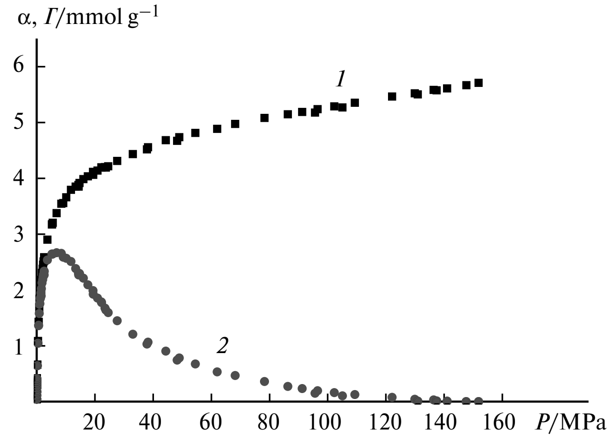

Fig. 1. Adsorption isotherms of methane on the active carbon CMS at 313 K: *1*, adsorption isotherm of total content; and *2*, excess adsorption isotherm.

the adsorption volume W_0 is determined by the volume of the near-surface layer. This volume is equal to the product of the surface area of the smooth surface or the surface of meso- or macropores by the adsorption layer thickness calculated, for example, by the Frenkel—Healsey—Hill adsorption isotherm[2—4]

$$\ln(f_s/f) = b/t^n, \quad (1)$$

where f is volatility, f_s is the volatility on the saturation line, b is constant, t is the thickness of the adsorption layer of the liquid-like adsorbate, and n is the exponent depending on the properties of the adsorbing surface[3] and taking the value $n = 3$.[2,4] The assumption that the densities of the adsorbate and liquid are equal is used in this method of adsorption volume determination, as in the TVFM. We have earlier[5] developed the method for determination of the total adsorption volume for adsorbents with different porosities using experimental data on gas adsorption at temperatures higher than the critical temperature (MDAVG). The method is based on measurements carried out in a wide pressure range, for instance, >40 MPa.[5] However, the range of such high pressures is not always attainable during measurements of adsorption isotherms.

The purpose of the present work is to develop the procedure of determination of the adsorption volume of various adsorbents, including micro-, meso-, and macropores, from experimental data on adsorption of substances under pressures substantially lower than those in the MDAVG method. In the proposed method, one may use values of amount adsorbed for various substances measured at temperature higher and lower than T_{cr}; however, the temperatures should not exceed T_{cr} more than by 100 K. The method is based on the assumption that the adsorbate density ρ_{ad} remains unchanged with an increase in the degree of pore filling.

Theoretical substantiation of the method

It is known that if a liquid is placed in a vessel, its density will be the same over the whole volume. However, if an adsorbed substance exists in a certain pore volume, even for the complete pore filling only the average density of the substance is meaningful, because the adsorbed substance is distributed in the porous space of the adsorbent and also exists on its surface. The question arises as to what density has the adsorbate at pressures of the equilibrium gas phase lower than the saturation vapor pressure P_s?

Using the principles of molecular physics,[6] we can calculate the volume per molecule both in the gas phase at constant P and T and in the liquid phase, because the volumes or densities of the phases are determined by the ratio between the potential energy of mutual attraction of molecules and their kinetic energy. For the liquid one may consider in the first approximation that its density depends on the temperature only. If we can determine the density of the adsorbed substance by any method at the complete filling ρ_{ad}, *i.e.*, at $P = P_s$, then we can calculate the volume corresponding to the volume of one molecule v_{mol} adsorbed under these conditions. Unlike the density of the liquid, the density of the adsorbate at complete filling depends additionally on the energy of interaction of adsorbate molecules and adsorbent atoms. Let us consider that the calculated volume per adsorbed molecule depends on the temperature only and is independent of the equilibrium gas pressure. Then the weight of the adsorbate m_{ad} at temperature T and different pressures P is proportional to the number of molecules N_{mol} occupying the effective volume $W = v_{mol}N_{mol}$. Therefore, the density of the adsorbate ρ_{ad} at $\Delta W \to 0$ remains unchanged at temperature T under any pressure, *i.e.*, $\rho_{ad} = \lim_{\Delta W \to 0}(m_{ad}/W)$.[6] This is the main assumption in our approach. Not the aggregate state of adsorbed molecules is important for this method but the fact that N_{mol} molecules with the total weight m_{ad} exist in the adsorbed state and occupy the volume W in the adsorbent.

After an additional portion of the adsorptive was fed to the adsorber with the constant volume V_a containing the adsorbent with the weight m_{ads} and density ρ_{ads}, the total weight of the adsorptive changes by the value of Δm and the gas phase pressure changes by the value of ΔP at constant temperature T. This change in the weight Δm can conventionally be divided into two components: Δm_{ad} is the change in the weight of the adsorbate and Δm_{gas} is the change in the mass of the gas phase. With an increase in the gas phase pressure in the constant volume V_a, an increase in the volume ΔW occupied by the adsorbate in the adsorbent with the density ρ_{ad} is equal to the decrease in the volume occupied in the adsorption system by the substance with the density ρ_{gas}, *i.e.*, $\Delta W_{ad} = -\Delta W_{gas}$,

$$\Delta m = \Delta m_{ad} + \Delta m_{gas}, \quad (2)$$

$$\Delta m = \rho_{ad}\Delta W + \rho_{gas}(V_a - V_{ads} - \Delta W). \quad (3)$$

It follows from this that

$$\Delta W = [\Delta m - \rho_{gas}(V_a - V_{ads})]/(\rho_{ad} - \rho_{gas}). \quad (4)$$

The volume of the adsorbent framework $V_{ads} = m_{ads}/\rho_{ads}$ is mainly determined by helium picnometry. Equation (4) makes it possible to calculate the effective volume ΔW at a constant temperature for each experimental value of pressure P. The adsorption volume W_0 for the system under study is the highest possible volume of the adsorbate ΔW, which is achieved at the pressure P_s. The density ρ_{ad} differs from the gas phase density. If the saturation vapor pressure is not achieved in the measurement of the adsorption isotherm, the ultimate value of W_0 can be determined by the extrapolation to P_s of the values of ΔW obtained by Eq. (4).

Choice of the adsorbate density at the complete filling. To determine the adsorption volume of various adsorption systems, one should determine the adsorbate density in the temperature range from the boiling point T_b to temperatures considerably exceeding T_{cr} and to choose the method of determination of "P_s", which is an analog of the pressure P_s in the region above the critical temperature. The method is known[7] for the determination of the adsorbate density ρ_{ad} in the temperature range from boiling to the critical point corresponding to the ultimate value of adsorption for other temperatures by the equations

$$\rho_{ad} = \rho_b{}^0\exp[-\alpha(T - T_b)], \quad (5)$$

$$\rho^*_{cr} = \rho_b{}^0\exp[-\alpha(T_{cr} - T_b)], \quad (5a)$$

where $\rho_b{}^0$ is the adsorbate density at the boiling point T_b and pressure P_s, ρ^*_{cr} is the adsorbate density at the critical point T_{cr}, and α is the thermal coefficient of ultimate value of adsorption independent of either P or T.

It can be considered that the adsorbate density at the complete filling is close to the density of the liquid at temperatures both below and above the critical temperature. When oxygen vapor was adsorbed on zeolite NaA (see Ref. 8) at the temperature of liquid nitrogen $T = 77.5$ K and the complete amount adsorbed was $a = 8.1$ mmol g^{-1}, the adsorbate density was $\rho_{ad} = 1.103$ g cm^{-3} and the density of liquid oxygen ρ_{liq} was 1.136 g cm^{-3} at $T_b = 90.18$ K. The density of adsorbed carbon dioxide on zeolite NaX at the complete filling at measurement temperatures $\leq T_{cr}$ is close to the density of the volumetric liquid phase at the boiling point.[9] This is clearly seen in Fig. 2 that shows the temperature dependences of the density of liquid carbon dioxide and carbon dioxide adsorbed on NaX (calculated by the experimental data[9]). The densities of the adsorbed phase and the liquid at the boiling temperature are close, which agrees with the fact that the differential excess entropy of carbon dioxide as adsorbate ($T_{cr} = 304.19$ K) on three ion-exchange forms of montmorrilonite at $T = 303$, 343, and 373 K is close to the entropy of liquid carbon dioxide.[10] Similar ratios of densities were observed even for measuring the adsorption of gases in the region far from the critical temperature.

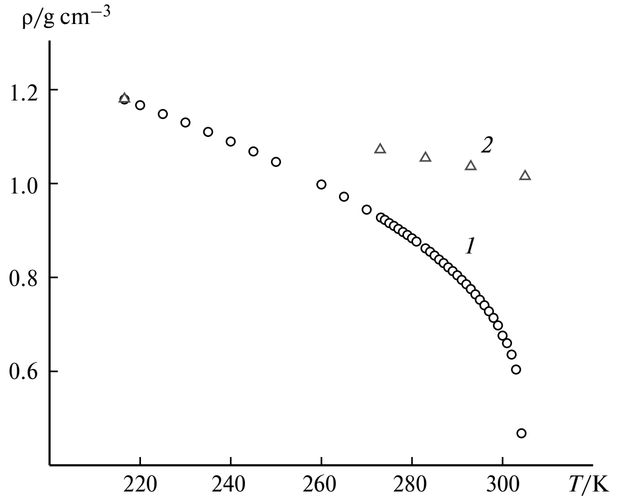

Fig. 2. Temperature plots of the density of CO_2: *1*, density of liquid CO_2; and *2*, ultimate density of CO_2 adsorbed on NaX.[7]

As can be seen from Fig. 1, with the pressure increase the excess adsorption isotherms (Γ) pass through the maximum and reach zero values ($\Gamma \approx 0$). In this region, the adsorbate density is equal to the density of the equilibrium gas phase $a = \Gamma + \rho_{gas}W_0$ and, in this case, $a/W_0 = \rho_{ad} \approx \rho_{gas}$ (a is the total content adsorption). This shape of excess adsorption isotherms is observed for the adsorption of nitrogen, argon, and krypton on zeolite NaA at temperatures 305, 334, and 334 K, respectively,[11,12] and for methane adsorption on the carbon adsorbent CMS at 313 K.[13] Therefore, the amount adsorbed at $\Gamma \approx 0$ can be used to determine the adsorbate density. The results of calculation of the density of the adsorbates from the measured isotherms are presented in Table 1. It is seen that the densities of adsorbed gases differ insignificantly from the densities of the corresponding liquids at the boiling temperatures. Table 1 also contains the densities of liquid nitrogen, argon, krypton, and methane at the boiling temperatures and the critical parameters of these liquids. It follows from Table 1 that Eq. (5) can be used for the calculation of the adsorbate density at temperatures above the critical temperature.

As can be seen from the data in Fig. 2, in the temperature range from T_b to T_{cr} the density of the liquid decreases sharply when the critical temperature is approached. In contrast to condensation which shows a sharp decrease in the density of liquid with temperature, adsorption leads to weak changes of sorbate density in the vicinity of the critical temperature (see Fig. 2, curve *2*). The reason is that the heat of adsorption considerably exceeds the heat of condensation. Therefore, a substantial decrease in the adsorbate density can be expected only at temperatures considerably exceeding the critical temperature. It has previ-

Table 1. Comparative data on adsorption of gases at high pressures

Adsorbent	Gas	T/K	$P(\Gamma \approx 0)$/atm	$\rho_{ad} \approx \rho_{gas}$/g cm^{-3}	T_b/K	ρ_{liq}/g cm^{-3}	P_{cr}/atm	T_{cr}/K	ρ_{cr}/g cm^{-3}
NaA	N_2	305	1390	0.635	77.36	0.807	33.54	126.25	0.304
	Ar	334	1515	1.067	87.29	1.393	48.0	150.86	0.536
	Kr	334	1400	2.01	119.75	2.42	54.182	209.4	0.911
CMS	CH_4	313	1400	0.363	111.67	0.434	45.8	190.55	0.162

ously been established[11—13] that for adsorption there is the region of P and T in which the adsorbate density approaches the density of the equilibrium gas $\rho_{ad} \approx \rho_{gas}$ (see Table 1). However, this is observed not at the critical point of the adsorptive but at substantially higher temperatures (see Table 1). This specific feature of the temperature dependence of the adsorbate density allows us to use Eq. (5) in the calculation of ρ_{ad} for the ultimate value of amount adsorbed at temperatures above the critical temperature.

Determination of the thermal coefficient of ultimate adsorption. To determine the adsorbate density by formulas (5) and (5a), one should know the thermal coefficient of ultimate value of adsorption. It is assumed that the adsorbate density at the critical temperature and pressure can be determined by the formula $\rho^*_{cr} = M/b$, where M is the molecular weight of the adsorptive, and b is the constant in the van der Waals equation of state. Some authors[7,14] believe that the thermal coefficient of ultimate value of adsorption is independent of the properties of the adsorbent but is a characteristic of the adsorptive (liquid) only. However, when determining the adsorbate density and, hence, the value of thermal coefficient α by the formula

$$\alpha = -1/a_0 \cdot \mathrm{d}a_0/\mathrm{d}T \qquad (6)$$

(a_0 is the ultimate amount adsorbed), one should take into account not only the properties of the adsorbate but these of the adsorbent—adsorbate pair as well. The thermal coefficient of ultimate value of adsorption depends on the adsorbent structure, and the values of α for the same adsorptive can vary for adsorbents of different structure. For instance, it was determined[15] by the measurement of CO_2 adsorption on macroporous silica gel that $\alpha = 3.3 \cdot 10^{-3}$ K^{-1}, and approximately twofold lower value of α was obtained[9] for the adsorption of the same CO_2 on microporous zeolite NaX (see below, Table 2).

At the same time, the value of α calculated by Eq. (5a) is close to the values determined for adsorption on zeolites.

Adsorbent	$\alpha \cdot 10^3$/K^{-1}
NaX	1.7
Silica gel C-1	3.3
Calculation by Eq. (5a)	1.6

Thus, the character of adsorbent porosity should be taken into account when the adsorbate density is calculated by Eq. (6) and, therefore, when the value of α is chosen. The adsorption of CO_2 and other gases on montmorillonite NaMt occurs in micropores and in meso- and macropores of crystals, and the adsorption volume of mesopores is three times that the micropore volume (Table 3). Accordingly, the average value of $\alpha = 2.9 \cdot 10^{-3}$ K^{-1}, which was obtained with allowance for the contribution of the volume of pores of the both types, was used in the calculation of ρ_{ad}. In the case of adsorption on supermicroporous carbon AC-71 with pore size range intermediate between micropore and mesopore ranges, the values of α determined by Eq. (5a) was chosen for the calculation of ρ_{ad}. The same value of α as that for zeolite NaX (see above) was used for the calculation of ρ_{ad} from the data for CO_2 adsorption on such microporous carbons as CMS and PAC.

To calculate the limiting value of the density of adsorbate SF_6 by Eq. (5) for $T > T_{cr}$ (T_{cr} = 318.7 K, P_{cr} = = 37.67 bar)[16] on the microporous adsorbents PAC and CMS, the value of $\alpha = 2.7 \cdot 10^{-3}$ K^{-1} was used, which was derived from our experimental data for carbon CMS at temperatures below T_{cr} by formula (6).

For the adsorption of SF_6 on supermicroporous carbon AC-71, the value of α determined from the experimental data was $3.5 \cdot 10^{-3}$ K^{-1}. Since Eq. (5) is fulfilled in a wide temperature range, it can be used for the calculation of ρ_{ad} also at temperatures exceeding T_{cr}.

The highest value of amount adsorbed Δm_{ad}, to which the maximum adsorption volume ΔW corresponds, is achieved at $P = P_s$. For temperatures $T > T_{cr}$, it is necessary to preliminarily elucidate what gas pressure can be accepted as an analog of the saturation vapor pressure "P_s". In some cases, the linear extrapolation of the dependence $\ln P_s = f(1/T)$ is often used. However, for some systems another approach to the determination of the an-

Table 2. Calculated parameters P_s, "P_s", and W_0 for the CO_2—NaX system at various temperatures

T/K	P_s, "P_s"/MPa	W_0* at P_s, "P_s"/cm^3 g^{-1}
305	7.47	0.29
323	8.32	0.3
353	9.94	0.3
383	11.7	0.3
423	14.27	0.3

* According to the data,[9] W_0 = 0.3.

alog "P_s" can be advised. In particular, the value analogous to the saturation vapor pressure was calculated[7] by the equation

$$«P_s» = \tau^2 P_{cr} \quad (7)$$

in the temperature range from T_b to T_{cr} + (30—40 K). In this equation $\tau = T/T_{cr}$ (T is the temperature of the experiment). Equation (7) was used in our experiments for the temperatures $T > T_{cr}$. The results of calculations are presented in Figs 3—10.

Experimental

All measurements of adsorption were carried out on a high-pressure setup that combines volumetric and gravimetric techniques. This dedicated equipment was developed by us and described in detail earlier.[17] Adsorption isotherms were measured in the temperature range 298—423 K in pressure ranges for CO_2 and SF_6 of 0.01—6.0 and 0.01—2.20 MPa, respectively. Adsorbents with different porosities and different chemical compositions were used: zeolite NaX, sodium montmorrilonite NaMt, active carbon AC-71 prepared from brown coal and referred to the class of supermicroporous carbons, microporous carbon CMS (Switzerland), and active carbon PAC produced from the polymer material. Carbon dioxide (99.99%) and sulfur hexafluoride (99.999%) were used as adsorptives. The volume of the empty autoclave was precalibrated. The density of the equilibrium gas phase ρ_{gas} was calculated by the multi-constant equation of state $P = f(T,\rho)$ for CO_2 and SF_6.[16] The values of ΔW for different P were determined by Eq. (4) from the experimentally found values of P, T, and Δm and calculated values of ρ_{gas} and ρ_{ad}. For some adsorption systems, we failed to measure adsorption at pressures close to the saturation vapor pressure P_s, especially at pressures P close to the analog "P_s" and at temperatures substantially higher than T_{cr} of the adsorptive. The values of adsorption volume W_0 can be determined by extrapolating the linear branch of the curve smoothing the points calculated to P_s or "P_s" by formula (4). For example, the dependence

$$\Delta W = \frac{k_0(k_1P + 2k_2P^2 + 3k_3P^3)}{(1 + k_1P + k_2P^2 + k_3P^3)}, \quad (8)$$

where k_0, k_1, k_2, and k_3 are the selected coefficients, which provide the best agreement with the experiment, is suitable for the extrapolation. Therefore, we may believe than the value of W_0 can be determined in such a way.

Results and Discussion

The range of the studied temperatures included the temperatures both below and above the critical temperature for the adsorptives. This makes it possible to compare the results of different lines of approach to the determination of W_0. Our results of application of the proposed procedure of determination of W_0 for various adsorption systems are shown in Figs 3—10. In all figures, solid lines correspond to the approximation by Eq. (8).

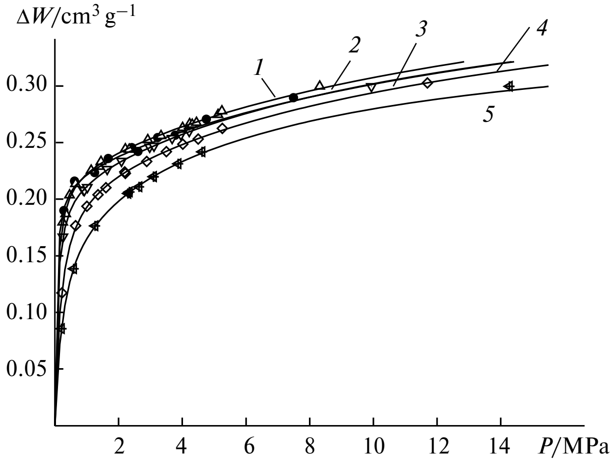

Fig. 3. Change in the adsorption volume ΔW *vs* pressure in the CO_2—NaX system for temperatures 305 (*1*), 323 (*2*), 353 (*3*), 383 (*4*), and 423 K (*5*).

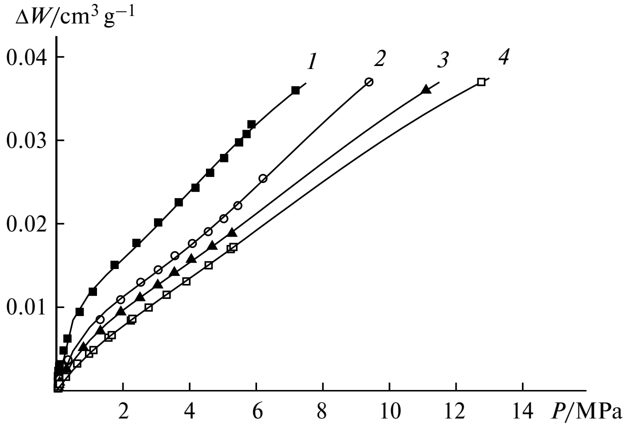

Fig. 4. Change in the adsorption volume ΔW *vs* pressure in the CO_2—NAMt system for temperatures 303 (*1*), 343 (*2*), 373 (*3*), and 400 K (*4*).

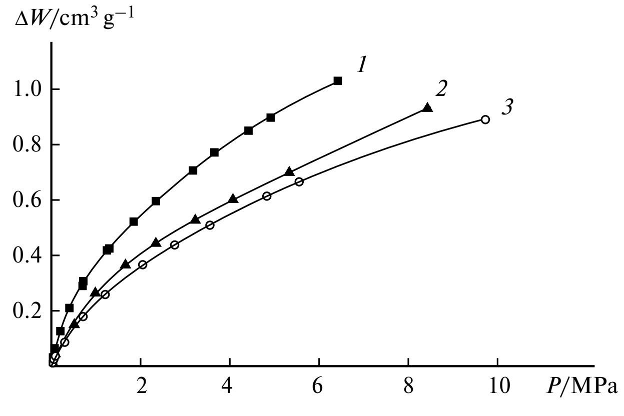

Fig. 5. Change in the adsorption volume ΔW *vs* pressure in the CO_2—AC-71 system for temperatures 298 (*1*), 323 (*2*), and 343 K (*3*).

Table 3. Calculated parameters P_s, "P_s", and W_0 for the CO_2—NaMt system at various temperatures

T/K	P_s, "P_s"/MPa	W_0* at P_s, "P_s"/cm^3 g^{-1}
305	7.18	0.04
343	9.39	0.04
373	11.1	0.04
400	12.76	0.04

* At 303 K W_0 = 0.015 cm^3 g^{-1} was obtained by the Dubinin—Radushkevich method, and W_0 = 0.05 cm^3 g^{-1} was obtained for the Ar—NaMt system by the MDAVG method (see Ref. 5).

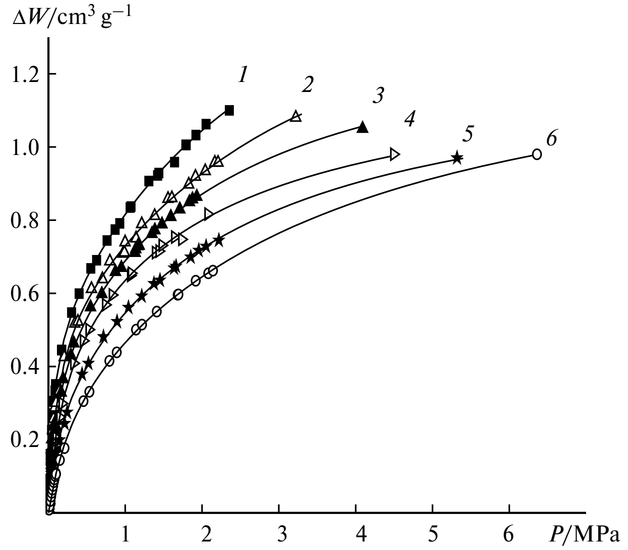

Fig. 6. Change in the adsorption volume ΔW *vs* pressure in the SF_6—AC-71 system for temperatures 298 (*1*), 313 (*2*), 327 (*3*), 343 (*4*), 373 (*5*), and 408 K (*6*).

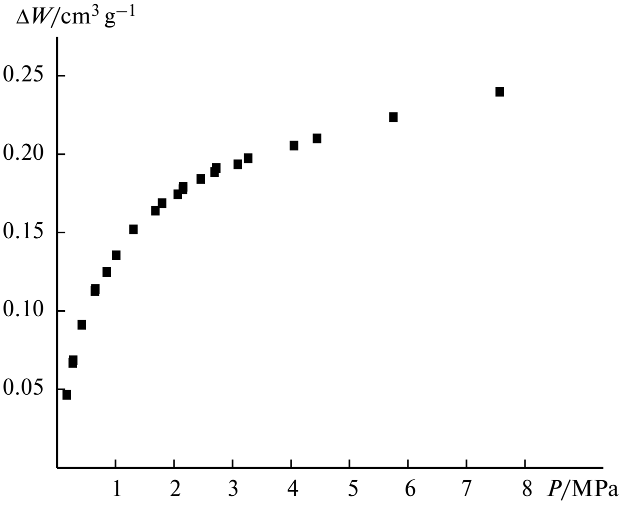

Fig. 7. Change in the adsorption volume ΔW *vs* pressure in the CO_2—CMS system at T = 310 K.

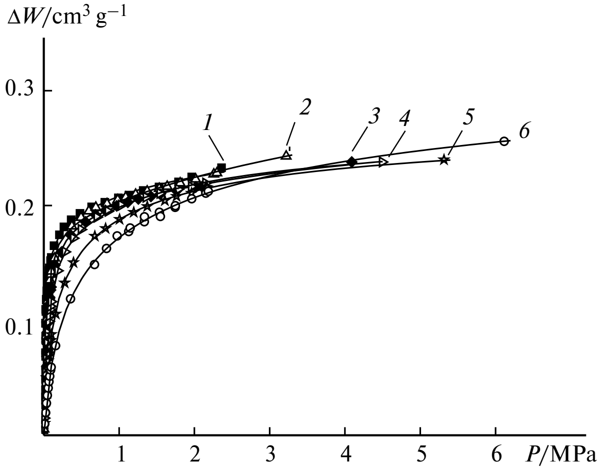

Fig. 8. Change in the adsorption volume ΔW *vs* pressure in the SF_6—CMS system for temperatures 298 (*1*), 313 (*2*), 327 (*3*), 343 (*4*), 373 (*5*), and 408 K (*6*).

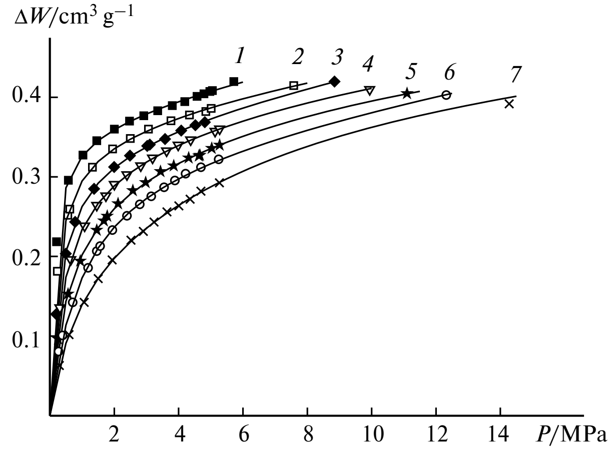

Fig. 9. Change in the adsorption volume ΔW *vs* pressure in the CO_2—PAC system for temperatures 293 (*1*), 313 (*2*), 333 (*3*), 353 (*4*), 373 (*5*), 393 (*6*), and 423 K (*7*).

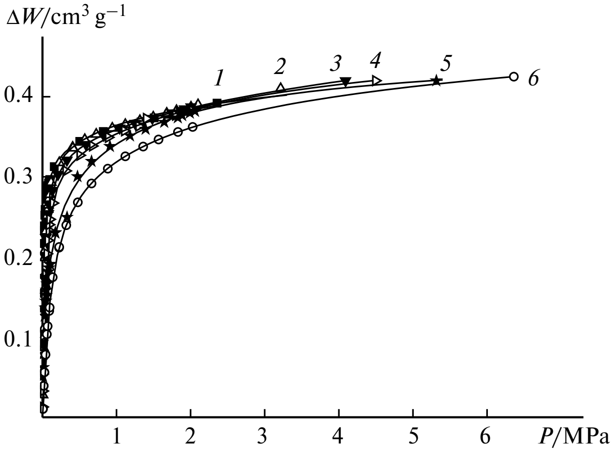

Fig. 10. Change in the adsorption volume ΔW *vs* pressure in the SF_6—PAC system for temperatures 298 (*1*), 313 (*2*), 327 (*3*), 343 (*4*), 373 (*5*), and 408 K (*6*).

The adsorption isotherms of CO_2 on synthetic microporous zeolite NaX calculated by formula (4) are shown in Fig. 3. Adsorption measurements of this system were carried out at temperatures 305, 323, 353, 383, and 423 K in the pressure range 0.01—6.0 MPa. The pressure P_s for $T = 303$ K was taken from the manual,[18] and "P_s" and ρ_{ad} were calculated by Eqs (7) and (5), respectively, using the data[18] for CO_2: $T_{tr.p} = 216.55$ K (temperature of the triple point), $\rho_{liq} = 1.18$ g cm^{-3}. The experimentally determined[9] value of $\alpha = 1.7 \cdot 10^{-3}$ K^{-1} was used in the calculation of the adsorbate density by Eq. (5) for different temperatures. The values of ΔW for this system calculated by formula (4) are presented in Fig. 3. Extrapolating these values to P_s and "P_s", W_0 were determined, whose values for all temperatures almost coincided with each other and other data[9] (see Table 2).

The adsorption isotherms of carbon dioxide on montmorrilonite NaMt calculated by formula (4) are presented in Fig. 4.

Adsorption measurements of this system were carried out at temperatures 303, 343, 373, and 400 K in the pressure range 0.01—6.0 MPa. The pressure P_s for $T = 303$ K was taken from the manual,[18] and "P_s" and ρ_{ad} were calculated by Eqs (7) and (5), respectively. For the calculation of ρ_{ad} by formula (5), $\alpha = 0.0029$ K^{-1} was used. The values of ΔW for the system considered calculated by formula (4) are shown in Fig. 4. In spite of the fact that ΔW is a function of P and T, the values of W_0, *i.e.*, ΔW at P_s and "P_s", are almost temperature-independent (Table 3). Even the far extrapolation by P to "P_s", for instance, by Eq. (8), at all temperatures gives similar values of W_0. Thus determined volume W_0 is a characteristic of this adsorption system as a whole. The volume of micropores W_{mi} of montmorrilonite studied was determined also by the DR method (see Ref. 1) from the excess adsorption isotherm at $T = 303$ K, which corresponds to the ultimate value of amount adsorbed found by Eq. (5). The volume of the system of micropores of montmorrilonite determined by the DR method is presented in Table 3, whose data show that this value is lower than the adsorption volume W_0 determined according to the proposed procedure. The volume of micropores of this adsorbent determined by the DR equation is equal to volume ΔW corresponding to the beginning of the linear branch of the plot of ΔW *vs* P (see Fig. 4). The adsorption volume W_0 determined by the proposed procedure includes the micropore volume and also the volume related to the adsorption of carbon dioxide on the adsorbent surface, *i.e.*, the near-surface adsorption volume. The comparison of the values of W_{mi} determined by the DR equation and the values of W_0 determined according to the proposed procedure shows that adsorption on the surface predominates for the systems CO_2—NaMt. The measured excess adsorption isotherms of argon on NaMt in the pressure range 0.1—6.0 MPa at temperatures 303, 343, and 373 K made it possible to calculate $W_0 = 0.05$ cm^3 g^{-1} using the earlier developed MDAVG method.[5] This value turned out to be close to that determined by the proposed method (see Table 3).

The isotherms of CO_2 on active carbon AC-71 at temperatures 298, 323, and 347 K in the pressure range 0.1—6 MPa are shown in Fig. 5. Domestic active carbon AC-71 produced from brown coal refers to the class of supermicroporous carbons. The results of calculations of ΔW by the proposed procedure for this system at different pressures of the equilibrium gas phase and different temperatures are listed in Table 4. As can be seen, the volumes ΔW calculated by formula (4) depend on the temperature of the experiment, but the values of W_0 are close for all isotherms (see Table 4). The value $W_{mi} = 0.91$ cm^3 g^{-1}, obtained from the excess adsorption isotherm at $T = 298$ K by the DR equation, lies in the interval of W_0 calculated according to the proposed procedure (see Table 4).

The adsorption isotherms of sulfur hexafluoride on active carbon AC-71 calculated by Eq. (4) are presented in Fig. 6. Adsorption measurements on this system were carried out at temperatures 298, 313, 327, 343, 373, and 400 K in the pressure range 0.01—2.2 MPa. The pressure P_s for $T = 298$ and 313 K was determined by the interpolation of the tabulated dependence $\ln P_s$—$1/T$, and the values of "P_s" and ρ_{ad} at $T > T_{cr}$ were calculated by Eqs (7) and (5), respectively. The value $\alpha = 3.5 \cdot 10^{-3}$ K^{-1} obtained by the study of adsorption of SF_6 (see above) was used for the calculation of ρ_{ad} by Eq. (5). As can be seen from Fig. 6, in the whole range of measured pressures ΔW depends on temperature but, as in the case of CO_2 adsorption on this carbon, the values of W_0 for temperatures 303, 313, and 327 K agree satisfactorily with each other (Table 5). The values of W_0 for temperatures 343, 373, and 400 K obtained by extrapolation by Eq. (8) are somewhat lower. The comparison of W_0 determined for the systems CO_2—AC-71 and SF_6—AC-71 (see Figs 5, 6 and Tables 4, 5) shows that for CO_2 adsorption the values of W_0 are slightly lower than those for SF_6 adsorption on the same carbon. The volume of supermicropores for this system determined by the DR equation at $T = 298$ and 313 K was 0.97 and 1.07 cm^3 g^{-1}, respectively, which satisfactorily coincides with the values of W_0 obtained by the proposed procedure (see Table 5). It is most likely that the adsorption of sulfur hexafluoride, as well as the adsorption of CO_2, on the surface of this adsorbent is insignificant. The average value of $<W_0>$ obtained by the MDAVG method (see Ref. 5) from the adsorption

Table 4. Calculated parameters P_s, "P_s", and W_0 for the CO_2—AC-71 system at various temperatures

T/K	P_s, "P_s"/MPa	W_0 at P_s, "P_s"/cm^3 g^{-1}
298	6.41	1.01
323	8.32	0.96
347	9.61	0.91

Table 5. Calculated parameters P_s, "P_s", and W_0 for the SF_6—AC-71 system at various temperatures

T/K	P_s, "P_s"/MPa	W_0 at P_s, "P_s"/cm^3 g^{-1}
298	2.355	1.1
313	3.267	1.08
327	3.965	1.05
343	4.359	0.98
373	5.154	0.97
408	6.166	0.98

of Ar on the same carbon at $T = 303$, 343, 373, and 400 K and pressures below 100 MPa was 0.89 cm^3 g^{-1}.

The CO_2 adsorption isotherm calculated by formula (4) on active carbon CMS at $T = 310$ K in the pressure range 0.1—6.0 MPa is shown in Fig. 7. This carbon adsorbent is classified as a microporous carbon with an average pore width of 0.75 nm. The value of W_0 calculated by Eq. (8) is 0.244 cm^3 g^{-1}, which agrees with $W_0 = 0.246$ cm^3 g^{-1} obtained earlier[13] by the MDAVG method with allowance for methane adsorption measured in a wide pressure range of 0.1—150 MPa at $T = 313$, 373, and 408 K.

The adsorption isotherms of SF_6 on carbon CMS calculated by formula (8) are presented in Fig. 8. Adsorption measurements were carried out in the pressure range from 0.01 to 2.2 MPa at temperatures 298, 313, 327, 343, 373, and 408 K. As can be seen from Fig. 8, the values of ΔW calculated by formula (4) are temperature-dependent, and the values of W_0 for this system determined by the procedure described above nearly coincided (Table 6). Coincidence of the ultimate values of W_0 for the same carbon in the systems with CO_2 and CH_4 (see Ref. 13) confirms that the results obtained by the proposed procedure are reliable.

The adsorption isotherms of CO_2 on PAC calculated by formula (4) are shown in Fig. 9. Carbon PAC prepared from poly(vinilydene chloride) refers to the class of microporous carbons and has a very narrow pore size distribution. Adsorption measurements for this system were carried out in the pressure range from 0.1 to 6.0 MPa at temperatures 293, 313, 333, 353, 373, 393, and 423 K. For all isotherms of the considered system, the values of W_0 are similar (Table 7). The values of W_{mi} of this carbon determined using the DR equation for temperatures 298 and 313 K were 0.416 and 0.41 cm^3 g^{-1}, respectively. The values of W_{mi} calculated by the TVFM coincided with the values of W_0 determined by our method (see Table 7), which indicates that this carbon adsorbent contains mainly micropores.

Table 7. Calculated parameters P_s, "P_s", and W_0 for the CO_2—PAC system at various temperatures

T/K	P_s, "P_s"/MPa	W_0 at P_s, "P_s"/cm^3 g^{-1}
293	5.72	0.42
313	7.82	0.41
333	8.85	0.41
353	9.94	0.40
373	11.1	0.39
293	12.4	0.39
423	14.27	0.39

The adsorption isotherms of SF_6 on PAC calculated by Eq. (4) are presented in Fig. 10. Adsorption measurements for this system were carried out in the pressure range from 0.01 to 2.2 MPa at temperatures 298, 313, 327, 343, 373, and 408 K. As can be seen from Fig. 10, the dependence of ΔW calculated by formula (4) in the range of measured pressures is temperature-dependent, but the values of adsorption volume W_0 determined using Eq. (8) almost coincided for all temperatures (Table 8). The calculated values of W_0 for this system agree well with the values of W_0 in the case of adsorption of CO_2 on the same carbon (see Fig. 9). The value of microporous formation volume in this carbon determined for this system using the DR equation by the excess adsorption isotherm for 298 K was $W_{mi} = 0.35$ cm^3 g^{-1}, which is somewhat lower than W_0 determined by the proposed procedure.

Coincidence of the values of W_0 obtained for the adsorption of various adsorptives on the same adsorbent at different temperatures indicates that the procedure proposed for the calculation of W_0 can find use in practical calculations.

We attempted to extend this procedure of calculation of W_0 to temperatures substantially exceeding the critical temperature of the adsorptives and to pressures consider-

Table 6. Calculated parameters P_s, "P_s", and W_0 for the SF_6—CMS system at various temperatures

T/K	P_s, "P_s"/MPa	W_0 at P_s, "P_s"/cm^3 g^{-1}
298	2.355	0.23
313	3.267	0.24
327	3.965	0.24
343	4.358	0.24
373	5.154	0.24
400	5.927	0.24

Table 8. Calculated parameters P_s, "P_s", and W_0 for the SF_6—PAC system at various temperatures

T/K	P_s, "P_s"/MPa	W_0 at P_s, "P_s"/cm^3 g^{-1}
298	2.355	0.39
313	3.267	0.41
327	3.965	0.42
343	4.358	0.42
373	5.154	0.42
408	6.166	0.43

ably exceeding P_{cr}. For instance, for the systems Ar—NaA, N_2—NaA, Ar—AC-71, and CH_4—CMS, the measurements were carried out in the temperature range from 300 to 408 K and the pressure range 0.1—150 MPa. However, the calculations of W_0 gave no reliable results for these adsorption systems. Therefore, it can be concluded that the approach proposed for determination of W_0 is applicable to adsorption systems, whose density of the equilibrium gas at P_s or "P_s" is substantially (several times) lower than the calculated density of the adsorbate.

Thus, the new approach was proposed to determine the total adsorption volume of porous adsorbents, The method is based on the use of experimental data on adsorption at temperatures both above and below the critical temperature for the adsorptives used. It is assumed that the adsorbate density depends on temperature only.

The method proposed makes it possible to determine the adsorption volume both in micropores and on the surface of meso- and macropores. The values of W_0 for adsorbents with different chemical compositions and adsorbents agree with the results obtained by other methods.

References

1. M. M. Dubinin, V. A. Astakhov, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1971, 5 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1971, **20**, 3].
2. Ya. I. Frenkel´, *Kineticheskaya teoriya zhidkostei* [*Kinetic Theory of Liquids*], Izd. Akad. Nauk SSSR, Moscow, 1945, 369 pp. (in Russian).
3. G. D. Helsey, *J. Chem. Phys.*, 1948, **16**, 931.
4. T. L. Hill, *J. Chem. Phys.*, 1949, **17**, 590; 688.
5. A. A. Pribylov, O. G. Larionov, I. A. Kalinnikova, L. G. Shekhovtsova, L. D. Belyakova, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 707 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 722].
6. A. N. Matveev, *Molekulyarnaya fizika* [*Molecular Physics*], Vysshaya Shkola, Moscow, 1981, 396 pp. (in Russian).
7. K. M. Nikolaev, M. M. Dubinin, *Izv. Akad. Nauk SSSR*, *Otd. Khim. Nauk* [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*], 1958, 1165 (in Russian).
8. A. M. Arkharov, B. P. Bering, I. A. Kalinnikova, V. V. Serpinskii, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1972, 1434 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1972, **21**, 1389].
9. V. V. Zhukov, V. V. Serpinskii, *Zh. Fiz. Khim.*, 1971, **45**, 2959 [*J. Phys. Chem. USSR* (*Engl. Transl.*), 1971, **45**, No. 11]; deposited with VINITI of 16.08.1971, 3329.
10. A. A. Pribylov, S. Z. Muminov, I. A. Kalinnikova, L. G. Shekhovtsova, *Kolloid. Zh.*, 2010, **72**, 409 [*Colloid J.* (*Engl. Transl.*), 2010, **72**].
11. A. A. Pribylov, V. V. Serpinski, S. M. Kalashnikov, *Zeolites*, 1991, **11**, 846.
12. A. A. Pribylov, T. S. Yakubov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1996, 1138 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1996, **45**, 1078].
13. A. A. Pribylov, G. F. Stekli, *Zh. Fiz. Khim.*, 1998, **72**, 306 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 1998, **72**].
14. A. V. Shkolin, A. A. Fomkin, V. A. Sinitsin, *Fizikokhimiya poverkhnosti i zashchita materialov* [*Physicochemistry of Surface and Protection of Materials*], 2010, **46**, 151 (in Russian).
15. B. N. Vasil´ev, Ph. D. (Phys.-Math.) Thesis, Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow, 1957, p. 14 (in Russian).
16. A. A. Opalovskii, E. U. Lobkov, *Usp. Khim.*, 1975, **44**, 197 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1975, **44**].
17. A. A. Pribylov, S. M. Kalashnikov, V. V. Serpinskii, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1990, 1238 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1990, **39**, 1105].
18. N. B. Vargaftik, *Spravochnik po teplofizicheskim svoistvam gazov i zhidkostei* [*Manual on Thermophysical Properties of Gases and Liquids*], Nauka, Moscow, 1972, 720 (in Russian).

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