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Surface and Porosity of Adsorbents

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The validity of adsorption methods of measuring specific surface areas of solids (and, in particular, of adsorbents) is limited by the characteristics of the porosity. Methods based on the concept of multilayer adsorption, like the BET method and de Boer's *t*-method, are applicable only to non-porous or coarsely porous (including mesoporous) adsorbents.
There is no general method of calculating the surface area of microporous adsorbents from adsorption data. For the "crack" model of the micropores in carbon adsorbents we can calculate the size and the geometrical area of the micropores from the parameters of the adsorption equation given by the theory of the volume filling of micropores, using a standard vapour (benzene). Almost identical results are obtained by using the adsorption of water vapour, which forms continuous monolayers in the micropores because of the dominant role of the hydrogen bond in adsorption. The geometric surface of micropores in carbon adsorbents is not a measure of the adsorption capacity of the sample, which is determined by dispersion forces, but it is relevant in kinetics and catalysis.
The presence of micropores in non-porous or coarsely porous adsorbents makes the measurement of surface area by the BET or the de Boer method physically meaningless. In this case we can use the t/F method of Dubinin and Kadlets, which gives a measure of the volume of micropores and of the specific surface of mesopores. Kistler and Kiselev's capillary condensation method gives similar values for the specific area of the mesopores. 23 References.

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I. INTRODUCTION

The two extreme cases of physisorption are adsorption on non-porous adsorbents and adsorption in the finest pores (the micropores). The porosity of adsorbents is one of the main factors in adsorption. On the basis of adsorption and capillary phenomena pores can be conveniently classified according to their linear size x into micropores (x < 0.6 to 0.7 nm), supermicropores (0.6–0.7 < x < 1.5–1.6 nm), mesopores (1.5–1.6 < x < 100–200 nm), and macropores (x > 100–200 nm).[1] The smallest pores in adsorbents (the micropores) are comparable in size with adsorbed molecules. As a result of the superposition of the fields of dispersion forces from opposite walls of the micropores, adsorption energies in micropores are relatively high. As an example, we show in Fig.1 the dependence of the differential heat of adsorption of benzene on an activated and on a non-porous carbon adsorbent (gas carbon heated *in vacuo* at 950 °C) on the relative adsorption $\theta = a/a_{0.2}$.[2] This large difference in adsorption energy is the fundamental reason for the

difference between adsorption in micropores and adsorption on a non-porous carbon adsorbent. Adsorption in micropores is characterised by volume filling of the adsorption space of the micropores, i.e. of the adsorption field of force.

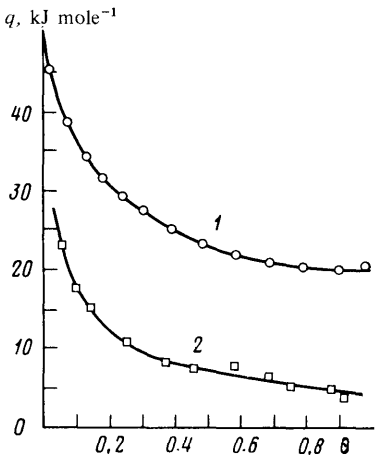


Figure 1. Differential heats of adsorption of benzene (q) for active carbon (*1*) and for "950 carbon" (*2*).[13]

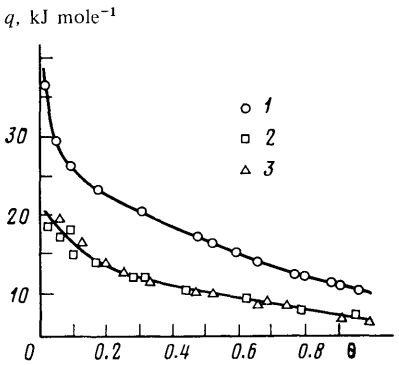


Figure 2. Differential heats of adsorption of benzene for supermicroporous (*1*) and non-porous (*2*, *3*) silicas[13].

Adsorption in mesopores, like adsorption on non-porous adsorbent surfaces, leads to the formation of successive adsorbed layers on the mesopore walls, and ultimately results in filling of the mesopores by the capillary condensation mechanism. Supermicropores occupy a porosity region intermediate between those of micropores and mesopores, in which the properties of micropores gradually disappear and those of mesopores become evident. We note from Fig. 2 that the adsorption energy is increased also in the supermicropores of silica adsorbents, but the effect is less marked than in micropores.

Pores having a diameter greater than 100–200 nm cannot be filled by capillary condensation in practice, and therefore they are usually treated as a form of macropore. Macropores (and, in many cases, mesopores) act as transport pores in adsorption. On the other hand, micropores and supermicropores determine the capacity of the adsorbent towards gases and vapours, and therefore they are called adsorption pores.

The linear dimensions of zeolite holes, usually less than 0.5–0.6 nm, are typical of micropores. Their adsorption space contains cations whose charge is compensated by the excess of negative charge in the alumino-silicate skeleton. The cations behave as active centres, giving a locally enhanced electrostatic interaction (especially for the adsorption of polar molecules). Therefore in many cases the adsorption energy in zeolites is greater than in microporous carbon adsorbents, i.e. the adsorption capacity of the zeolites is greater, especially towards adsorbates having a low equilibrium pressure. The mesopores in formed zeolites are the gaps between adjacent crystallites, held together by the binder.

II. SPECIFIC SURFACE OF NON-POROUS AND OF RELATIVELY COARSELY POROUS ADSORBENTS

In mesoporous (and even more so in macroporous) adsorbents the effect of surface curvature on adsorption is negligible. Therefore we can assume that the adsorption of gases and vapours per unit surface area occurs by the same mechanism in non-porous, macroporous, and mesoporous adsorbents of the same chemical type.

A general theory of physisorption of gases and vapours on non-porous adsorbents has not yet been developed. The Brunauer, Emmett, and Teller (BET) multimolecular vapour adsorption theory[3] is applicable only over a narrow range of equilibrium relative pressures: for example, 0.05–0.35 for the low-temperature adsorption of nitrogen. Therefore the BET isotherm equation is more useful for calculating (from one of its parameters) the specific surface area than for describing the dependence of the physisorption of a vapour on its equilibrium relative pressure. The equation is usually written

$$a = a_m ch/(1-h)[1+(c-1)h],$$

where a is the adsorption at the equilibrium relative pressure p/p_s, and $h = p/p_s$. The parameters of the equation are the adsorption a_m, corresponding to the formation of a monolayer of adsorbed molecules (the monolayer capacity), and the constant c, related to the adsorption energy. These parameters are easily determined graphically by linearising the equation. If ω is the area occupied by one molecule in the filled monolayer (the molecular area), and the monolayer capacity a_m is given in mmole g^{-1}, the surface area per unit mass of adsorbent (or specific surface) S can be written

$$S = a_m \omega N, \qquad (1)$$

where $N = 6.02 \times 10^{20}$ is the number of molecules in 1 mmole of adsorbate.

The standard adsorbate usually chosen for measuring specific surfaces of adsorbents is nitrogen at its boiling point (78 K) and atmospheric pressure: its molecular area ($\omega = 0.162$ nm^2 or 16.2 Å^2) is calculated from the density of liquid nitrogen. This molecular area gives the best agreement with measurements of the specific area of porous solids by other methods (for example, by electron microscopy). However, if molecular areas calculated in the same

way for other vapours are used, significant deviations in the BET specific surface areas are obtained. Table 1 (from Ref.4) lists ω values and the corresponding ratios of the specific surface obtained experimentally to the surface obtained with nitrogen, S/S_{N_2}. We note that the deviation can be as high as 34%. The BET method is basically empirical, and it can be used to measure the specific surface of non-porous or coarsely porous adsorbents by the low-temperature adsorption of nitrogen to a precision of ~15–20%.

The reduced adsorption isotherm method[5] is far simpler to use in estimating specific surfaces of non-porous or coarsely porous adsorbents.

Table 1.

Vapour	T, K	ω, nm^2	S/S_{N_2}
Nitrogen	78	0.162	1.00
Krypton	78	0.152	0.73
n-Butane	273	0.321	0.68
Freon-21	273	0.204	0.66

The method is based on the isotherm equation for the adsorption of the experimental vapour on a non-porous adsorbent whose specific surface has been determined with nitrogen by the BET method. Calculation of the adsorption γ for unit surface of the adsorbent gives the adsorption isotherm

$$\gamma = f(h). \qquad (2)$$

For the coarsely porous adsorbent (with a chemically similar surface) whose specific surface area is required we can write the isotherm as

$$a = S\gamma = Sf(h). \qquad (3)$$

Eqns.(2) and (3) for each adsorbent can be displayed as tables of the parameters γ and a for identical equilibrium relative pressures, obtained by interpolation from plots of the experimental adsorption isotherms. According to Eqn.(3) the plot of $a = \psi(\gamma)$ is a straight line passing through the origin, with a slope numerically equal to the specific surface of the adsorbent. The reduced isotherm method is not limited by the nature of the adsorbed vapour: the only validity condition is chemical similarity between the two surfaces, which determines the similarity of the adsorption isotherms (2) and (3). A solution of the problem in the absence of similar isotherms has also been proposed[6].

The t-method (de Boer and Lippens[7]) is very similar to the above. The only difference is that in the analogue of Eqn.(3) adsorptions are expressed as the volume of liquid adsorbate V. Eqn.(3) then becomes

$$V = St = S\varphi(h), \qquad (4)$$

where t is the average thickness of the adsorbed layer of nitrogen. In this case an equation of the type of (2), i.e.

$$t = F(p/p_s),$$

expresses the dependence of the thickness of the adsorption layer on the relative pressure. This dependence is called the t-curve, and for nitrogen at 78 K it is summarised below[7]:

p/p_s	0.050	0.080	0.100	0.160	0.200	0.240	0.280	0.340	0.400	0.450
t, nm	0.321	0.348	0.359	0.401	0.428	0.455	0.486	0.533	0.575	0.607

By plotting, as above, V against t according to Eqn.(4) we obtain a straight line passing through the origin whose slope is numerically equal to the wanted specific surface. The t-method was proposed by de Boer and Lippens to study the low-temperature adsorption of nitrogen on alumina or silica minerals. The t-curves for these types of mineral are almost identical.

III. ADSORPTION IN MICROPORES AND GEOMETRIC SURFACE AREA OF MICROPOROUS ADSORBENTS

The effective increase in the heat of adsorption or adsorption potential in micropores radically changes the way in which the adsorption space is filled during adsorption in the case of micropores. The formation of successive adsorbed layers (on non-porous adsorbents) is replaced by the volume filling of the adsorption space, i.e. of the field of adsorption forces[8,9]. The writer's theory of adsorption in micropores[10–13], which has been called the theory of volume filling of micropores (TVFM), has been widely used, especially in systems involving microporous carbon adsorbents or active carbons.

The basic equation of this theory is

$$a = \frac{W_0}{v^*} \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right], \qquad (5)$$

where a is the adsorption at the equilibrium relative pressure p/p_S and temperature T, and A is the change in Gibbs free energy, taken with the negative sign and expressed as

$$A = RT \ln(p_s/p). \qquad (6)$$

Also, W_0 is the maximum volume of the adsorption space (or micropore volume), E_0 is the characteristic adsorption energy for the standard vapour, β is a similarity coefficient, defined in terms of physical constants of the experimental and the standard substance, and n is a parameter (integer). The molar volume (v^*) of the substance in the adsorbed state, i.e. of the adsorbate at unit relative pressure, is a function of temperature and can be calculated from the physical constants of the adsorbate or adsorband.

The TVFM adsorption equation (5) has three parameters: W_0, E_0, and n. For microporous adsorbents we usually have $n = 2$. In the case of the adsorption of gases or vapours on zeolites the integer n can take values between 2 and 6, depending on the size of the zeolite holes and on the density of active centres (i.e. cations) within the holes. An approximate estimate of n can be obtained from the TVFM equation (5) by taking logarithms twice (see Ref.13). Knowing n, we can determine W_0 and E_0 by plotting Eqn.(5) in a linearised form (taking logarithms of both sides).

Very many examples of the satisfactory application of the TVFM equation (5) to the adsorption of vapours on active carbons in temperature ranges over 100–150 K wide have been reported. Some examples of the application of the TVFM equation to zeolites are given below. A detailed discussion of the determination of the parameters of the equation is given in Ref.13.

1. Adsorption of methane on zeolite L between 156 and 243 K.[14] The parameters of Eqn.(5) at normal temperature and pressure, determined from the adsorption isotherm for 192 K, were: $W_0 = 46.8$ cm^3 g^{-1} and $E = 9.84$ J mole^{-1} (for CH_4) with $n = 3$. Experimental and calculated adsorption isotherms are compared in Fig.3.

2. Adsorption of carbon dioxide on K,Na-erionite at 293–413 K (from data obtained by Meerson and Stepanov, see Ref.13). The parameters of Eqn.(5) were determined

from the adsorption isotherm for 383 K: $W_0 = 12.4\%$, $E = 21.9$ kJ mole^{-1}, and $n = 3$. Calculated and experimental adsorption isotherms are shown in Fig. 4.[13] In both cases the agreement between calculation and experiment is satisfactory.

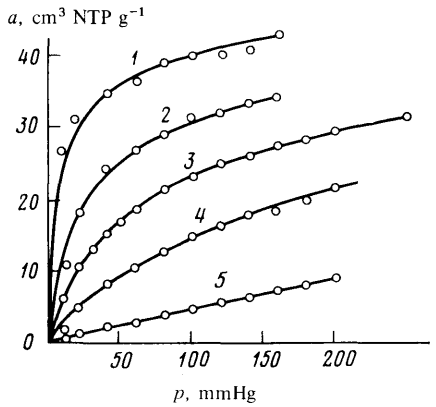


Figure 3. Calculated (curves) and experimental (points) isotherms for the adsorption of methane on zeolite L at: *1*) 156, *2*) 178, *3*) 193, *4*) 212, *5*) 243 K.[13]

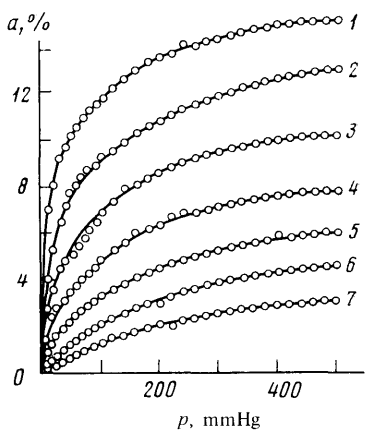


Figure 4. Calculated (curves) and experimental (points) isotherms for the adsorption of carbon dioxide on K,Na-erionite at: *1*) 293, *2*) 313, *3*) 333, *4*) 353, *5*) 373, *6*) 393, *7*) 413 K.[13]

It is interesting to compare the adsorption properties of natural clinoptilolite from the Dzegbi deposits with those of active carbon from coconut shells (combustion loss 50%) for CO_2 at 293 K and $n = 2$:[15]

Sorbent	Clinoptilolite	Carbon
W_0, cm³ g⁻¹	0.100	0.230
E, kJ mole⁻¹	28.5	10.3

In clinoptilolite the micropore volume is one-half that of active carbon, and the characteristic energy of adsorption of carbon dioxide is higher by a factor of 3. The adsorptions (a, mmole g^{-1}) of carbon dioxide on clinoptilolite and on active carbon at 293 K are compared in Table 2: at relatively low pressures (up to $p \approx 400$ mmHg) the adsorption on clinoptilolite is between 17 and 1.4 times greater than on active carbon in spite of the smaller (2.3-fold) adsorption volume in the zeolite than in the carbon. This is due to the higher characteristic energy of adsorption in the zeolite.

Table 2. Adsorption of carbon dioxide at 293 K.[15]

p/p_s	a, mmole g⁻¹	
	clinoptilolite	active carbon
$5 \cdot 10^{-5}$	1.26	0.075
$1 \cdot 10^{-4}$	1.46	0.12
$5 \cdot 10^{-4}$	1.61	0.29
$1 \cdot 10^{-3}$	1.72	0.49
$5 \cdot 10^{-3}$	1.99	1.38

Active carbons and zeolites are the most widely used microporous adsorbents. Their pores are the smallest of all adsorbents, comparable in size with adsorbed molecules. The volume of the micropores usually lies between 0.1 and 0.6 cm^3 g^{-1}. However, the micropore structure of zeolites (unlike that of active carbons) is due to the crystal structure of these materials and hence is strictly regular. This allows us to calculate with great precision the size, volume, and geometric surface of the micropores from X-ray diffraction data. Thus, for CaA zeolite crystals we found[16] a total volume of large holes $v = 0.278$ cm^3 g^{-1} and a geometric surface area of pore walls $S_g = 1640$ m^2 g^{-1}, and for NaX zeolite $v = 0.322$ cm^3 g^{-1} and $S_g = 1400$ m^2 g^{-1}.

However, in contrast to non-porous and coarsely porous adsorbents (for which the adsorption is directly proportional to the specific surface), in the case of volume filling of micropores the adsorption is not determined by the geometric surface of the micropores. The concept of a monolayer also becomes meaningless for adsorption in micropores. Formally, a "monolayer capacity" a_m can be obtained according to formula (1) if the geometric surface area of the pores is known. For a CaA zeolite with $S_g = 1640$ m^2 g^{-1} we obtained $a_m = 16.6$ mmole g^{-1} for the adsorption of nitrogen ($\omega = 0.162$ nm^2) at 78 K. Experimentally, the limiting adsorption of nitrogen on CaA zeolite for $h = 1$ is $a_0 = 8.27$ mmole g^{-1}, i.e. approximately one-half of the estimated monolayer capacity. We conclude that for zeolites the geometric specific surface cannot be determined from adsorption measurements.

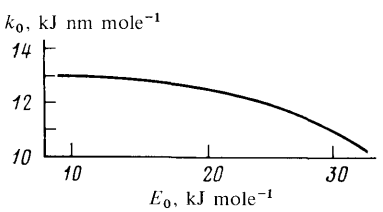


Figure 5. Dependence of the parameter k_0 on E_0.[19]

Unlike those of zeolites, the geometric surface areas of microporous carbons can be calculated and determined experimentally from adsorption data. According to

currently held views the micropores in carbon adsorbents resemble flat cracks, and their main parameter is the half-width x of the crack. We have used[17] X-ray diffraction and adsorption data to show that the half-width x of the micropores is inversely proportional to the characteristic adsorption energy of the standard vapour (benzene):

$$x = k_0/E_0 , \qquad (7)$$

where the parameter k_0 is only weakly dependent on E_0 (see Fig.5).[17,18].

Knowing the parameters of the TVFM equation (5) for $n = 2$, i.e. the micropore volume W_0 ($cm^3\ g^{-1}$) and the characteristic adsorption energy E_0 (kJ $mole^{-1}$), we can easily calculate by Eqn.(7) the half-width of the plane-parallel micropores (x, nm), and by using the elementary formula (8) we can arrive at the geometric surface of the micropore walls in active carbon[19]:

$$S_g,\ m^2\ g^{-1} = 10^3 W_0/x . \qquad (8)$$

Unlike the adsorption of organic vapours on active carbons, in which the role of dispersion forces is predominant, the adsorption of water is controlled by hydrogen bonds both between the primary adsorption centres (oxygen surface compounds) and between the water molecules. In this case the dispersion interaction energies are weaker than the hydrogen bond energies and can be ignored. Since the interactions arising from hydrogen bonding are not amplified in the micropores the adsorption on micropore walls takes place by the same mechanism as on the surface of a non-porous carbon adsorbent (gas carbon heated at 950 °C in vacuum[19]).

Table 3. Specific surface areas ($m^2\ g^{-1}$) of model microporous carbon adsorbents (benzene, 293 K, $W_0 = 0.500\ cm^3\ g^{-1}$).[19]

E_0, kJ mole^{-1}	x, nm	S_g	S_{BET}	S_t
18.9	0.67	750	1200	1450
13.3	0.97	520	1170	1280
9.4	1.38	360	1040	1050

From the experimental results, an average monolayer of water molecules adsorbed on "950 °C" carbon black of known specific surface area is formed at an equilibrium relative pressure of water vapour $h = 0.60$ at 293 K. Taking the molecular area of water as $\omega = 0.105\ nm^2$ we conclude that 1 mmole of water in the form of a monolayer occupies an adsorbent surface $K = \omega N = 63.2\ m^2\ mmole^{-1}$. If the adsorption of water on an active carbon at $T = 293$ K and with $h = 0.6$ is $a_{0.6}$ mmole g^{-1}, the geometric surface of the pore walls can be expressed as[19]

$$S_g^{H_2O},\ m^2\ g^{-1} = Ka_{0.6} = 63.2a_{0.6} . \qquad (9)$$

The geometric surface areas of micropores in different types of active carbon, obtained[19] from the adsorption isotherms of benzene and of water by using Eqns.(8) and (9) respectively, are compared below:

Active carbon	KL2	KL3	AG1	V3	KL4	EK3	V4	KL5	KL6
S_g	560	680	640	540	720	580	680	840	870
$S_g^{H_2O}$	610	620	740	660	710	690	730	880	990
$S_g^{H_2O}/S_g$	1.09	0.91	1.16	1.22	0.99	1.19	1.07	1.05	1.14

The discrepancies between the two sets of results are well within the uncertainty limits of different methods of measuring the surface area of adsorbents.

It may be useful also to compare different methods of calculating the surface area of micropores in order to assess their physical reality. In this analysis we used model adsorption isotherms for benzene, calculated by the TVFM equation for $n = 2$ and $W_0 = 0.50\ cm^3\ g^{-1}$ and for a range of E_0 values determined by low-angle X-ray diffraction measurements[19]. As we have already shown, the TVFM equation is satisfactorily consistent with experimental data. The adsorption isotherms obtained in this way were treated by the BET method and by the de Boer t-method. The geometric surface areas of micropores S_g were calculated by formula (8): the results are shown in Table 3.

Table 4. Specific surface areas ($m^2\ g^{-1}$) of industrial active carbons[9].

Active carbon	S_g	$S_g^{H_2O}$	S_{BET}
AG2	460	470	800
SKT	1350	1460	2160

The geometric surfaces S_g seem to give a realistic indication of the surface area of the walls of the plane-parallel micropores. Their physical reality is confirmed by two independent methods, whose results for water and benzene adsorption are mentioned above[19]. The BET and de Boer specific surfaces are mutually consistent, but far from compatible with real values. The results shown in Table 4 were obtained in a similar way for industrial active carbons from the experimental adsorption isotherms for benzene and water at 293 K. We again note the almost identical geometric surface areas for each type of carbon given by the adsorption isotherms for benzene and for water, and the large discrepancies with the S_{BET} values. Hence we conclude that the specific surface areas of microporous adsorbents based on the multilayer adsorption model, i.e. the values given by the BET and the de Boer t-method, are physically unjustifiable. On the other hand the geometric surfaces have a clear physical meaning. However, they are only relevent to the adsorption of water, and possibly of ammonia, whose isotherms on active carbons have similar shapes. The geometric surface area of micropores bears no relationship whatever to the adsorption characteristics of other vapours on active carbon.

Nevertheless, the geometric surface of micropores could be kinetically significant in the description of surface mass transfer processes and in catalysis, when the microporous carbon adsorbents are used as catalysts or as carriers of catalytically active additives.

IV. ADSORPTION IN MICROPORES AND MESOPORES

If the adsorbent contains micropores as well as mesopores we can expect adsorption on both types of pore under the conditions in which the t-method is applied. The total adsorption V (expressed as volume of liquid adsorbate) will include contributions from the adsorption in micropores (V^{mi}) and in mesopores (V^{me}). The adsorption on the surface of macropores is negligibly small and will be ignored in this analysis. Therefore we have

$$V = V^{mi} + S_{me}t , \qquad (10)$$

where the product $S_{me}t$ gives the adsorption in mesopores. For equilibrium relative pressures in the range $h = 0.05-0.4$, for example in the case of the low-temperature adsorption of nitrogen, the changes in adsorption in the micropores (ΔV^{mi}) are comparable to the changes in adsorption in the mesopores. Therefore the dependence of the total adsorption on the thickness of the adsorption layer is not linear, and the t-method is not applicable.

According to the TVFM equation (5) the extent of filling of the micropore volume F for $n = 2$ can be expressed, in this case as

$$F = V^{mi}/W_0 = \exp[-(A/E)^2] ,$$

where E is the characteristic adsorption energy for the vapour being studied. Dividing both sides of Eqn.(10) by F gives

$$V/F = W_0 + S_{me}t/F . \qquad (11)$$

This is the basic equation of the Dubinin–Kadlets t/F method[20]. To a good approximation W_0 is equal to the volume of micropores ($v_{mi} = W_0$). In V/F against t/F coordinates Eqn.(11) gives a straight-line plot which intersects the vertical axis at v_{mi}. The slope of the straight line is a measure of the specific surface area of the mesopores S_{me}.

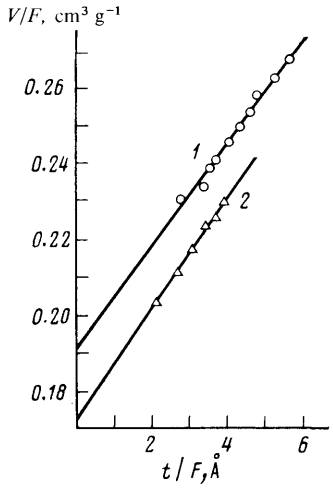


Figure 6. Plots of the t/F method for AU11 active carbon: *1*) nitrogen at 78 K, *2*) benzene at 293 K.[20]

As an example we show in Fig.6 some plots by the t/F method for the AU11 active carbon. According to the almost identical slopes of the two straight lines the specific surfaces of mesopores given by experiments with nitrogen and with benzene are also identical (133 and 140 $m^2\ g^{-1}$ respectively). The micropore volumes of the carbon measured with nitrogen are greater by 0.02 $cm^3\ g^{-1}$ than those measured with benzene. This difference can be explained by the molecular sieve properties of the carbon. Thus the t/F method allows us to determine from a single adsorption isotherm the specific surface of mesopores and the volume of micropores in the adsorbent. The parameter E is obtained from the low relative pressure region ($p/p_S = 10^{-6}-10^{-3}$) of the same isotherm, in which the adsorption on the mesopore surfaces is negligible in comparison to the adsorption in micropores.

In conclusion we should mention the thermodynamic method of determining the specific surface of mesopores from the surface of adsorbed film which disappears when the mesopores are filled by capillary condensation. The method was first formulated by Kistler[21] but its development into a practically useful form is due to Kiselev[22]. The method assumes that the specific surface of the adsorbed multilayer in the mesopores is indistinguishable from the specific surface of the mesopores themselves.

The differential molar heat of adsorption of a vapour initially saturated at the stated temperature is given by Eqn.(6). The ratio of the integral work of adsorption of the vapour between a_0 (the adsorption corresponding to the onset of capillary condensation) and the limiting adsorption a_S for $p/p_S = 1$ to the surface free energy of the adsorbed film σ gives the specific surface area of the adsorbed film S':

$$S' = \frac{1}{\sigma}\int_{a_0}^{a_S} A\,da .$$

The integral is usually evaluated graphically.

Table 5. Specific surface areas ($m^2\ g^{-1}$) of mesopores in active carbons[23].

Active carbon	S_{me}	S'	S_{me}	S'
	benzene, 273 K		nitrogen, 78 K	
AU 10	100	93	95	87
AU 11	140	117	133	105
AU 12	135	157	165	135
AU 13	110	93	90	77
AU 14	197	186	190	166

The specific surface areas of mesopores in highly porous active carbons listed in Table 5 were calculated from experiments with benzene and with nitrogen[23]. The results most closely consistent with experiments for different vapours were obtained by the t/F method. Comparing the average values for each method, the specific surfaces of the adsorbed films are found to be slightly low, as expected from the assumed equality of the surface of the adsorbed film and that of the adsorbent.

In formed zeolites the micropores are part of the zeolite crystallites, and the gaps between crystallites in contact are equivalent to mesopores. Hence the t/F method is applicable (in principle) to formed and to natural zeolites.

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