QUARTERLY REVIEWS

A STUDY OF THE POROUS STRUCTURE OF ACTIVE CARBONS USING A VARIETY OF METHODS

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Active carbon is a porous carbonaceous adsorbent. It is to the highly porous structure that the extensive specific surface area of active carbon, amounting to hundreds of square metres per gram, is due. The density, δ, of the porous material of commercial active carbon as a rule is 0·55 to 0·90 g. $cm.^{-3}$ while the true density of the organic substance of carbon, d, is close to that of graphite, *i.e.*, 2·25 g. $cm.^{-3}$. Hence the total volume of pores of a unit mass of carbon, equal to

$$v = 1/\delta - 1/d \qquad . \quad . \quad . \quad . \quad (1)$$

lies between 1·40 and 0·65 $cm.^3 g.^{-1}$.

The surface area of active carbon significant for adsorption consists of the total internal wall area of the pores. Different methods of assessing the specific surface area of active carbons usually give results lying between 400 and 900 $m.^2 g.^{-1}$. From data on the volume and surface area of the pores of active carbon it is possible to conclude that its pores are extremely small. By using mean values and making the crude assumption that the pores are cylindrical and equal in size, we find that their mean radii are about 3×10^{-7} cm. However this mean value does not correspond to the actual dimensions of the pores of active carbon.

The specific surface area of active carbon is determined by the total volume and the dimensions of the pores; in other words it is, in general, a function of the pore-volume distribution. The main problem in studying the porous structure of active carbon consists in finding this distribution function from the experimental data.

There are two conceivable extreme cases of the pore-volume distribution function. In the first case active carbon is considered a polydisperse system, where pores of all possible sizes are represented more or less equally. A second extreme case might be a monodisperse system with pores lying within a narrow range of dimensions. An intermediate form is polymode distribution, with several relatively narrow maxima of the distribution curve. Such a porous carbon system, although polydisperse, possesses groups or varieties of pores with definite intervals between the dimensions of each variety.

The whole body of experimental data, and in particular the results of our investigations, point to the conclusion that the dimensional distribution of pore volume in active carbon is a polymode one, and consequently lead to the conception of different varieties and types of pores in active carbon.[1—3] A description of the physical principles of this investigation follows.

An examination of sections of polished surfaces of active carbon by means of an optical microscope shows that relatively large pores exist which can be called macropores. Fig. 1 illustrates a photomicrograph of macropores of charcoal active carbon.

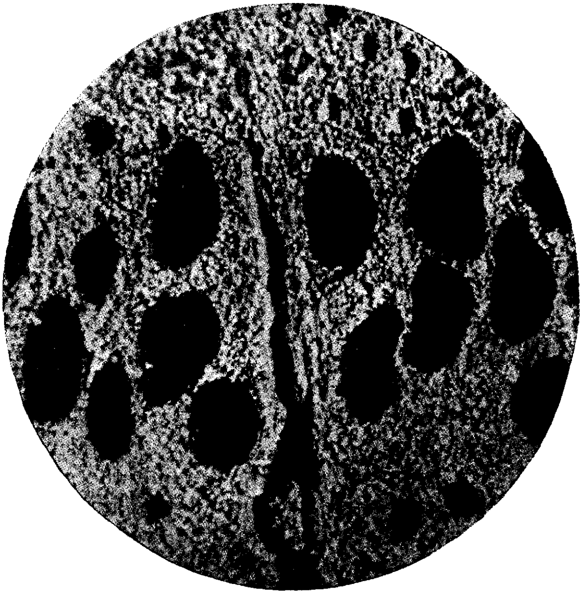

FIG. 1

Photomicrograph of the macropores of active carbon.

More detailed information concerning the volume distribution of the macropores can be obtained by measuring the volume of mercury (which does not wet the walls of carbon pores) which can be forced into the pores under various pressures. If P is the hydrostatic pressure corresponding to the volume V of mercury pressed into the carbon pores, then the effective radius r (in Å) of the smallest pores filled is given by the simple formula

$$r = 2\sigma \cos \theta / P \quad . \quad . \quad . \quad . \quad (2)$$

where σ is the surface tension of mercury and θ is the contact angle (142° in this case). A macropore-distribution curve for the carbon can easily

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[1] M. M. Dubinin, *Yubileyni sbornik Akad. Nauk S.S.S.R.*, 1947, **1**, 562.

[2] *Idem*, *Viestnik Akad. Nauk S.S.S.R.*, 1949, **19**, 19.

[3] *Idem*, *Uspekhi Khim.*, 1952, **11**, 513.

be constructed from the experimental data. The most convenient form for this curve corresponds to the equation

$$\Delta V/(\Delta \log r) = f(\log r) \quad . \quad . \quad . \quad . \quad (3)$$

where the left-hand side represents the differential volume of the carbon pores.

In Fig. 2 an example of a macropore distribution curve for active carbon is shown. The area lying below the curve at $\log r \geqslant 3{\cdot}6$ ($r \geqslant 4{\cdot}2 \times 10^{-5}$ cm.) expresses the volume of macropores for the given carbon specimen (0·32 cm.^{3} g.$^{-1}$). In assessing the order of magnitude of the specific surface area of the macropores we can assume the carbon pores to be cylindrical. Then the specific surface area of this variety of pore for the example considered will be

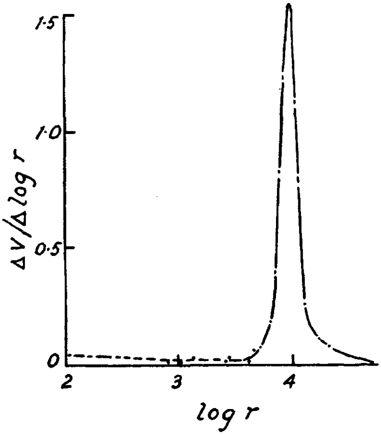

FIG. 2

Differential macropore-volume distribution curve for active carbon.

$$S_{\mathrm{ma}} = \frac{2V_{\mathrm{ma}}}{r_{\mathrm{m}}} = \frac{2 \times 0{\cdot}32}{1 \times 10^{-4}} = 0{\cdot}64 \times 10^4 \ \mathrm{cm.}^2 \mathrm{g.}^{-1} \quad . \quad (4)$$

$$= 0{\cdot}64 \ \mathrm{m.}^2 \mathrm{g.}^{-1}$$

where r_m is the effective pore radius corresponding to the maximum in the distribution curve. Thus the specific surface area of active carbon macropores is rather small, and amounts to tenths of a square metre per gram of carbon.

The results of our studies of the macroporosity of various active carbons by forcing mercury into the pores and by direct microscopical measurements show that the volume of the macropores lies within the limits 0·2—0·5 cm.^{3} g.$^{-1}$, that the most probable dimensions of the macropores, corresponding to the maxima of the distribution curves, lie between 5×10^{-5} and 2×10^{-4} cm., and that the specific surface areas are from 0·6 to 1·3 m.^{2} g.$^{-1}$.

A smaller kind of pore in active carbon, called " transitional pores ", can be directly observed with the electron microscope. Radushkevich and Lukianovich of our laboratory have achieved notable success in preparing specimens, in developing electron-microscopical techniques, and in statistical evaluation of photographs.[4] Transitional pores with diameters of approximately 200 Å are distinctly visible in Fig. 3, an electron micrograph of active carbon.

The method of forcing mercury into the pores can often be used to study transitional porosity of active carbons. For example, a curve of distribution of pore volume according to effective radii for one of the specimens of active carbon with a well-developed volume of pores of this variety is shown in Fig. 4. The right-hand part of this curve corresponds to the macropores of the carbon, which in this case are represented in a wider interval of sizes. The left-hand part of the curve, also having a maximum (at $r = 1{\cdot}36 \times 10^{-6}$ cm.), shows the volume distribution for most of the transitional pores, which can be filled with mercury at pressures up to 800 atm.

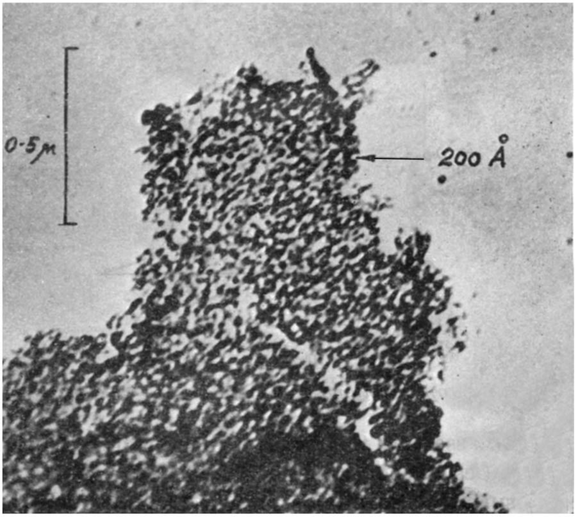

FIG. 3
An electron-microscope photograph of transitional pores of active carbon.

For the study of the transitional porosity of active carbon sorption methods are generally used, based usually on measuring the isotherms for capillary condensation of vapours in the carbon pores. Fig. 5 shows, in semilogarithmic co-ordinates, a typical isotherm for the sorption of benzene vapour by active carbon with a highly developed transitional porosity. The reversible part of the isotherm, up to the beginning of capillary condensation (*O* on the isotherm), corresponds to the adsorption of benzene

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[4] L. B. Radushkevich and V. M. Lukianovich, *Zhur. fiz. Khim.*, 1950, **24**, 21.

vapour. In the region of capillary condensation the sorption and desorption branches do not coincide and form a characteristic hysteresis loop.

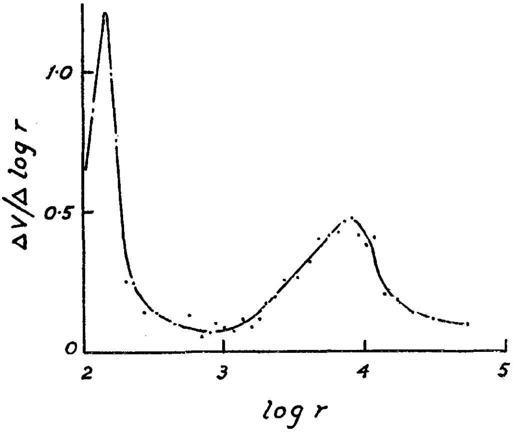

FIG. 4

Differential pore-volume distribution curve for macropores and transitional pores of active carbon.

It is in the transitional pores that capillary condensation of benzene vapour takes place. The space between adsorbed films in these pores is large

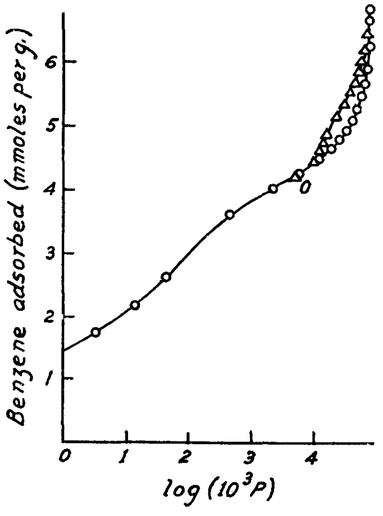

FIG. 5

Isotherm for sorption of benzene vapour on active carbon with highly developed transitional porosity.

enough compared with the dimensions of a molecule for the idea of a concave liquid meniscus in such pores to have physical significance.

For each point of the desorption branch of the isotherm in this region of sorption in the case of full wetting the radius of curvature of the meniscus corresponding to the effective radius of the space between adsorbed films can be calculated from the Kelvin equation. For the determination of the pore radius a correction must be made for the thickness, h, of the adsorbed films. On the other hand, the total adsorption expressed as the volume of condensed vapour per unit mass of carbon represents the sum of the volumes of both adsorbed and capillary condensed vapour. In calculating the volume of the carbon pores filled it is necessary to make a correction for the volume of the adsorbed films, both for the completely filled pores and for the pores already cleared of capillary condensed vapour at the equilibrium pressure being considered.

To make all these adjustments the thickness of the adsorbed films is calculated from the isotherm of adsorption of benzene vapour on a non-porous carbon adsorbent (a heat-treated carbon-black with spherical particles), which is practically identical in nature and whose specific surface area is known. In this case the mean statistical adsorption-film thickness for each equilibrium pressure will be the ratio of the volume of adsorbed vapour, taken as liquid, to the specific surface area of the carbon-black. Details of the calculation are given in our papers.[5, 6]

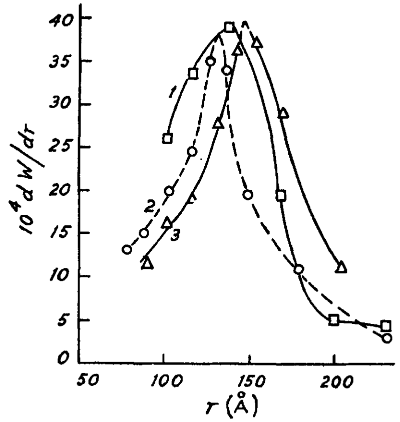

FIG. 6

Differential pore-volume distribution curves for transitional pores of active carbon.

In Fig. 6, in which radii are plotted along the horizontal axis in place of their logarithms, a comparison is made of transitional pore-volume distribution curves of active carbon, calculated from experiments on forcing mercury into the pores (curve 1), from the capillary condensation of benzene vapour without a correction for the adsorbed quantity (curve 2), and with an adjustment made for the thickness and volume of the adsorption layers

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[5] V. A. Alexandrov, M. M. Dubinin, E. D. Zaverina, T. G. Plachenov, and S. G. Chepurnoy, *Doklady Akad. Nauk S.S.S.R.*, 1952, **84**, 301.

[6] M. M. Dubinin and E. D. Zaverina, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1952, 577.

(curve 3). As a result of the adjustment the shape of curve 3 approaches that of curve 1. The shift of 10 Å, amounting to 6% of the effective radius of the pores, cannot be regarded as of great significance and, on the whole, it may be concluded that there is satisfactory agreement of the results obtained by the various methods by which transitional pore-volume distribution curves have been calculated.

Statistical treatment of electron micrographs of transitional porosity in carbon gives an idea of the number and volume distribution of transitional pores according to their size. For the series of specimens investigated we again attained generally satisfactory agreement with the results of calculations based on the capillary condensation theory.[3] Thus, the use of different methods of investigation has led to sufficiently well-founded conclusions of the physical reality of the transitional pores in active carbon.

The transitional pore volume for common specimens of active carbon is relatively small and lies between 0·02 and 0·1 cm.^{3} g.$^{-1}$. We have developed methods for obtaining active carbon with high transitional porosity from saccharose. The volume of the transitional pores for these carbon specimens[7] lies between 0·30 and 0·85 cm.^{3} g.$^{-1}$. The sorptive properties of such carbons in the region of high relative pressures are similar to those of silica gel with large pores.[8]

The specific surface area of transitional pores can be assessed from the surface area of the adsorbed film covering the pore walls at the beginning of capillary condensation. Completion of the capillary condensation process, when the relative pressure becomes equal to unity, leads to the filling of the entire volume of transitional pores with condensed vapour and consequently to the disappearance of the surface of the adsorbed films. If

$$A_a = RT \ln P_s/P \quad . \quad . \quad . \quad . \quad (5)$$

is the differential molar work of adsorption of a substance from the vapour, whose initial state is that of a saturated vapour at pressure P_s or of a liquid, then the ratio of the integral work of sorption from vapour to the free surface energy of the adsorption film, σ, will represent the surface area of the adsorption film of the practically equal specific surface area of the transitional pores :

$$S_t = 1/\sigma \int_{a_0}^{a_s} A_a \mathrm{d}a \quad . \quad . \quad . \quad . \quad (6)$$

In this equation a_0 is the adsorption at the origin of the hysteresis loop, *i.e.*, at the beginning of capillary condensation, and a_s the sorption limit when the adsorbent is saturated. For the table of multimolecular boundary surface adsorption films values of the free surface energy σ can be used. In using equation (6) the value of the integral is calculated graphically. A thermodynamic proof of this method for calculating the surface area of adsorbed films was given by Kiselev.[9]

The specific surface areas of the transitional pores of common active

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[7] M. M. Dubinin and E. D. Zaverina, *Doklady Akad. Nauk S.S.S.R.*, 1952, **84**, 93.

[8] A. V. Kiselev, *Zhur. fiz. Khim.*, 1949, **23**, 452.

[9] *Idem, Uspekhi Khim.*, 1945, **14**, 367.

carbons evaluated in this way lie between 20 and 50 m.^{2} g.$^{-1}$, and for specimens with high transitional porosity it reaches[5] 150 m.^{2} g.$^{-1}$. The most probable values of the effective radii of the transitional pores at the maxima of the distribution curves lie between 4×10^{-7} and 2×10^{-6} cm. Consequently the transitional pores are larger by more than one order of magnitude than adsorbed molecules of vapour. For such pores, the thickness of the multimolecular films on the surface, two or three monolayers thick, is not sufficient to diminish the diameter seriously. There can, therefore, be scarcely any doubt of the reality of the process of capillary condensation of vapour in such pores, still so large in comparison with molecular dimensions.

The smallest variety of active carbon pores are micropores that cannot be observed directly even by means of an electron microscope. Study of the adsorption of dissolved substances with molecules of different sizes, *i.e.*, by the method of " molecular probes " developed by us,[10] led to the conclusion that the dimensions of micropores approach molecular dimensions in order of magnitude.

When organic vapours are adsorbed on the surface of micropores as a result of compression the adsorbed vapour is transformed into a liquid. The swift increase in thickness of the adsorbed layers resulting from the significantly higher adsorption potentials in fine micropores leads to the combining of the adsorption layers, *i.e.*, to the filling of the whole volume of the micropores with condensed vapour. Reversibility of adsorption equilibrium, *i.e.*, coincidence of adsorption and desorption branches of the isotherm, is characteristic of the adsorption process.

There are many reasons for believing that for the relative pressure corresponding to the beginning of the hysteresis loop of the isotherm, which is a result of the combination of the adsorption layers, the micropores become completely filled with condensed vapour. Then for active carbons with a weakly developed transitional porosity where the adsorption on the surface of the transitional pores, and especially of the macropores, may be neglected, the volume of adsorbed vapour in liquid form at the beginning of the hysteresis loop will directly correspond to the volume of the carbon micropores :

$$V_{\mathrm{mi}} = a_0 V \qquad (7)$$

where V is the volume of a millimole of adsorbed substance in liquid form. This method for calculating the volume of carbon micropores was proposed by Kiselev.[11]

Since at the sorption limit not only the micropores but the transitional pores also are filled as a result of capillary condensation, the difference between the limiting value of the sorption volume V_s and the volume of the micropores will represent the volume of the transitional pores of the active carbon :

$$V_t = V_s - V_{\mathrm{mi}} \text{ cm.}^3\text{ g.}^{-1} \qquad (8)$$

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[10] M. M. Dubinin and E. D. Zaverina, *Acta Physicochim. U.R.S.S.*, 1946, **4**, 647.

[11] A. V. Kiselev, V. F. Dreving, and A. D. Runov, *Doklady Akad. Nauk S.S.S.R.*, 1945, **46**, 310.

Equations (7) and (8) are only approximate as the volume of micropores is too large by the volume of the adsorption film in the transitional pores. The volume of transitional pores in formula (8) has been decreased to this extent. In formulating our ideas we neglected adsorption on the surface of the macropores and excluded their participation in the process of capillary condensation. The first assumption is clear without discussion, since the specific surface areas of the macropores approach 1 m.^{2} g.$^{-1}$, and the corresponding adsorptions are immeasurably small.

The lowest value for the effective radii of macropores does not differ substantially from $r = 2 \times 10^{-5}$ cm., judging from the experiments on forcing mercury into the pores. Taking into consideration the initial parts of the volume distribution curves for the macropores we can find from the Kelvin equation that a notable filling of macropores would only take place as a result of capillary condensation of vapours, if it were possible to reach a relative equilibrium pressure approaching unity, within a few tenths of one per cent. This is scarcely possible in experimental practice.

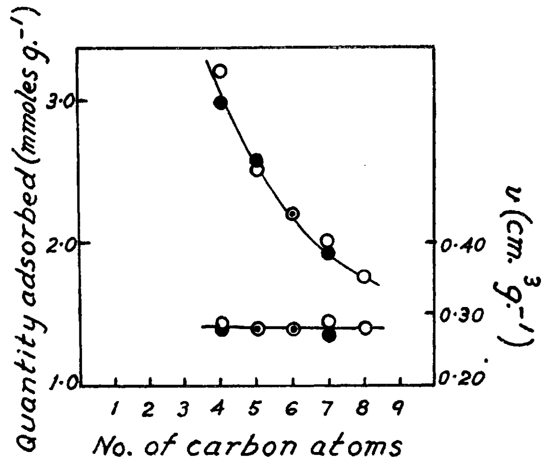

FIG. 7

The limit of the amount and the volume of normal aliphatic acids and alcohols adsorbed from aqueous solution by active carbon.

The micropores of active carbon also become filled with the pure dissolved substance in the form of a liquid when adsorption of partially soluble aliphatic acids or alcohols [12, 13] from aqueous solution reaches its limit. Fig. 7 represents the adsorbed quantities (upper curve) and the corresponding volumes of pure substance v (lower curve) as a function of the number of atoms of carbon in the molecules of normal aliphatic acids (open circles) and alcohols (full circles), for adsorption from aqueous solutions by active carbon. The constant value of the volume of the adsorption limit corresponds to the volume of the micropores of the active carbon.

[12] A. V. Kiselev and K. D. Scherbakova, *Doklady Akad. Nauk S.S.S.R.*, 1944, **45**, 257.

[13] *Idem, Acta Physicochim. U.R.S.S.*, 1946, **21**, 539.

In Table 1 a comparison is made of micropore volumes of several specimens of active carbons determined in different ways.[1, 11]

TABLE 1. *Micropore volumes of active carbon calculated from adsorption measurements* (cm.^{3} g.$^{-1}$)

	Carbon specimen				
	1	2	3	4	5
Aliphatic acids and alcohols from aqueous solution	0·27	0·26	0·38	0·31	0·59
Methyl alcohol vapour	0·26	0·24	0·39	0·31	0·60
Benzene vapour	0·25	0·23	0·38	0·33	0·60

The conclusion can be drawn that there is satisfactory agreement of the micropore volumes for each carbon specimen. Since the methods based on measuring the adsorption of vapours and of dissolved substances are independent of each other, the results obtained serve to confirm the physical reality of the micropores of active carbon.

All experiments described were carried out with ordinary specimens of carbon with poorly developed transitional porosity. The specific surface area of these carbons, therefore, is practically entirely due to the micropores. For active carbon specimens with substantial volumes of transitional pores equations (7) and (8) are not satisfactory.

In more rigid calculations it is necessary to introduce a correction for the quantity of adsorbed vapour on the surface of the transitional pores. If S_t is the specific surface area of the transitional pores, calculated from equation (6), and α is the amount adsorbed, uncomplicated by the rise of the adsorption potential and corresponding to the equilibrium pressure of the vapour at the beginning of hysteresis, for a unit free surface area of the carbon, then a more precise expression for the micropore value will be

$$V_{\mathrm{mi}}^{\mathrm{corr.}} = (a_0 - \alpha S_t)V \quad \text{. . . . .} \quad (9)$$

In conformity with (8) we have for the volume of the transitional pores :

$$V_t^{\mathrm{corr.}} = V_s - (a_0 - \alpha S_t)V \quad \text{. . .} \quad (10)$$

The amount of vapour adsorbed on unit surface area of the carbon can be obtained from the isotherm for vapour adsorption on non-porous heat-treated carbon-black with known specific surface area. If the conditions of heat treatment of the carbon-black *in vacuo* were the same as those used for the specimens of active carbon (for instance, evacuation at 1000°) the chemical nature of carbon surface and that of carbon-black will not differ substantially. In that case the adsorption α for carbon-black corresponds to adsorption on a unit area of the transitional pores of active carbons, the relatively large dimensions of which exclude the effect of a rise in adsorption potential.

In Table 2 typical examples are given of results of calculations of the volumes of micro and transitional pores carried out both in the usual and in the more precise way for specimens of active carbon from sucrose, produced under laboratory conditions.[7] Carbons 1 and 2 of the specimens chosen for comparison are characterised by a highly developed transitional porosity, while carbon 3 is a specimen of the usual kind. Sorption isotherms for benzene vapour at 20°, found by the sorption balance vacuum method,[10] were used for the calculations.

TABLE 2. *Volume of micro and transitional pores of active carbons*

Carbon	P/P_s for point O	$10^3\alpha$ (mmoles m.$^{-1}$)	S_t (m.^{2} g.$^{-1}$)	Pore volume (cm.^{3} g.$^{-1}$)			
				V_{mi} from (7)	$V_{mi}^{corr.}$ from (9)	V_t from (8)	$V_t^{corr.}$ from (10)
1	0·080	3·5	160	0·200	0·153	0·513	0·560
2	0·173	4·4	145	0·267	0·210	0·280	0·336
3	0·173	4·4	30	0·295	0·284	0·046	0·057

Although the more complicated method of calculating the volumes of the micro and transitional pores has no practical importance for the active carbon 3 with the usual structure, for carbon specimens 1 and 2 with a large transitional porosity the use of the more precise calculations is absolutely necessary.

There is no general method for determining the specific surface area of such fine porous adsorbents as active carbon. The strongly pronounced rise of adsorption potential in the micropores of carbon makes it impossible to employ the usual methods for calculating the specific surface area, based on theoretical conceptions of multimolecular adsorption on surfaces of uniform energy.[14] Employment of the hypothesis of capillary condensation of water vapour on active carbons [15, 16] cannot be regarded as physically sound.[17] Therefore the calculation of both the specific surface area and the pore volume distribution of carbon from the isotherms for water-vapour desorption, based on the capillary condensation theory, bears a formal character.

In a few cases the specific surface area of active carbon can be assessed sufficiently reliably when the isotherms for adsorption of water vapour are similar in the region of multimolecular adsorption on carbon, and on non-porous carbon-black with a known surface, if the two specimens being compared are practically identical chemically.[17] The specific surface area of carbon 1, listed in Table 2, assessed in this way is 547 m.^{2} g.$^{-1}$. The sum of the specific surface areas of transitional pores and macropores for this

[14] S. Brunauer, L. Deming, W. Deming, and E. Teller, *J. Amer. Chem. Soc.*, 1940, **62,** 1723.

[15] E. O. Wiig and A. J. Juhola, *ibid.*, 1949, **71,** 561.

[16] A. J. Juhola and E. O. Wiig, *ibid.*, p. 2069.

[17] M. M. Dubinin and E. D. Zaverina, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk,* 1954, 217 ; *Doklady Akad. Nauk S.S.S.R.*, **1953, 92,** 111.

carbon is 161 m.^{2} g.$^{-1}$, and consequently the specific surface area of micropores with a volume of 0·153 cm.^{3} g.$^{-1}$ will be

$$S_{\text{mi}} = 547 - 161 = 386 \text{ m.}^2\text{ g.}^{-1}$$

If, for a rough estimate of the order of magnitude of the dimensions of the micropores, they be considered cylindrical, the mean effective radius of the micropores will be

$$r = \frac{2V_{\text{mi}}^{\text{corr.}}}{S_{\text{mi}}} = \frac{2 \times 0{\cdot}153}{3{\cdot}86 \times 10^6} = 8 \times 10^{-8} \text{ cm.}$$

Thus, the effective radii of micropores of active carbons have an order of magnitude (10^{-8} cm.) comparable with the dimensions of molecules. The cross section of such a pore or gap is large enough to contain four or five molecules of water. If two of them correspond to unimolecular adsorption layers the conception of a concave liquid meniscus in the remaining space equal to two or three molecular diameters has no physical significance.

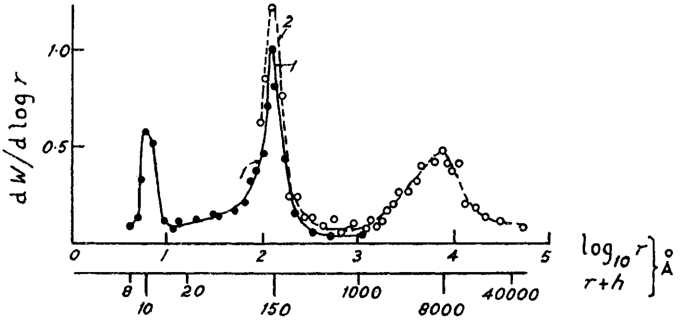

Fig. 8

Differential pore-volume distribution curve for active carbon.

These considerations make capillary condensation of water vapour in the micropores of active carbon unreal.

A detailed study of many specimens of active carbon has led to the conclusion that the volumes of the micropores of carbon lie between 0·15 and 0·50 cm.^{3} g.$^{-1}$. Their effective radii probably do not exceed 10 Å and the approximately assessed values of specific surface areas are between 400 and 900 m.^{2} g.$^{-1}$.

Fig. 8 represents a corrected differential curve for the porosity of one of the carbon specimens studied by us.[6] Curve 1 was calculated from the desorption branch of benzene vapour capillary condensation, and curve 2 from the experiments on forcing mercury into the pores. The left-hand part of the curve corresponding to the micropore distribution and containing a maximum was plotted approximately on the basis of data on the specific surface area and the volume of micropores. The graph clearly shows the polymode volume distribution of pores in active carbon.

Thus, active carbons generally possess a tridisperse porous structure. The volume of the transitional pores for many carbon specimens is extremely small (less than 0·05 cm.^{3} g.$^{-1}$) so that the systems are practically didisperse and contain two varieties of pores, micropores and macropores. On the other hand during activation, approaching the limiting case, the micropores of the carbon grow to the dimensions of transitional pores, and at the same time the dimensions and volume of the macropores also increase. Once again didisperse carbon is obtained with well-developed volumes only for transitional pores and macropores, the volume of micropores remaining negligibly small. In this case the specific surface area of the adsorption film calculated by using equation (6) must practically coincide with the specific surface area of the pore skeleton.

The adsorption properties of active carbon conform to the ideas on their porous structure elaborated above. From the point of view of the potential theory of adsorption one should take into consideration the substantial rise of adsorption potential in the micropores of carbon whose dimensions are comparable with the dimensions of the molecules adsorbed (adsorbents of the first structural type). On the other hand, for carbon specimens that contain practically no micropores the curvature of the pores whose dimensions approach those of transitional pores is too slight to influence adsorption. In this respect such carbons do not differ from non-porous carbon adsorbents, for instance heat-treated carbon-blacks (adsorbents of the second structural type). The equations for the characteristic curves and for the adsorption isotherms of the active carbons belonging to the two border cases of structural types mentioned above differ substantially.[18, 19]

Active carbons of the first structural type	Active carbons of the second structural type
Equation of the characteristic curve	
$W = W_0 \exp(-K\varepsilon^2)$ (11)	$W = W_0' \exp(-m\varepsilon)$ (12)
Equation of the adsorption isotherm	
$a = \frac{W_0}{V} \exp\left[-\frac{BT^2}{\beta^2}\left(\log_{10}\frac{P_s}{P}\right)^2\right]$ (13)	$a = \frac{W_0'}{V} \exp\left(-\frac{AT}{\beta}\log_{10}\frac{P_s}{P}\right)$ (14)

In these equations W_0 and W_0' are the volume limits of the adsorption space, W the volume actually adsorbed, ε the adsorption potential, β the characteristic curve affinity coefficient (for the standard vapour, benzene, $\beta = 1$), V is the volume of a millimole in the liquid state of the substance adsorbed, and T is the absolute temperature.

In the case of active carbons of the first structural type vapour adsorption takes place in the limited volume of the micropore adsorption space. The adsorption fields of opposite pore walls intersect and this is the reason for a higher adsorption potential. As a result, the maximum volume of the adsorption space, from the physical significance of the concept, must

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[18] M. M. Dubinin, E. D. Zaverina, and L. V. Radushkevich, *Zhur. fiz. Khim.*, 1947, **21,** 1351.

[19] M. M. Dubinin and E. D. Zaverina, *ibid.*, 1949, **23,** 1129.

be equal to the volume of the micropores of the carbon. Experiments confirm this conclusion from the theory very well.[20] When there is a substantial development of transitional pores it is necessary to introduce a correction for adsorption on the surface of this variety of pores, which takes place in accordance with equation (14).

The value of the constant B of the isotherm equation (13) depends on the distribution function of the pore volumes according to their dimensions.[21] The smaller the micropore dimensions of the carbon, the smaller will be the value of constant B and the steeper the rise of the isotherm in the region of small relative equilibrium pressures. Experimental proof of this is the growth of the constant B of the isotherm for a series of carbon specimens with progressively increasing activation.[18]

For active carbons of the second structural type the constant A of the isotherm equation (14) does not differ greatly from the corresponding constant for carbon-black. If the carbon specimen contains a considerable quantity of micropores, fictitious decreases of the constant A are observed.[22] Adsorption takes place in a practically unlimited space and therefore $W_0' > W_0$.

The field of employment of an active carbon is determined by its structural type. For gas and vapour adsorption in the region of low relative pressures it is best to use an active carbon of the first structural type with the smallest possible value of the constant B of the adsorption isotherm equation (13). Active carbons of an intermediary or mixed structural type characterised by a relatively weak retaining ability in the process of desorption are better suited for recovery processes.[19] Active carbons of the second structural type with porous structure accessible to the larger molecules and to the colloid particles of the admixtures colouring the solutions, are most suitable for decolorising solutions by adsorption with active carbons.

The conceptions developed in regard to the structural types of adsorbents and the corresponding adsorption isotherm equations can be applied to adsorbents of a different nature chemically, for instance silica gel and alumina gel.[23]

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[20] M. M. Dubinin and E. D. Zaverina, *Zhur. fiz. Khim.*, 1949, **23**, 993.

[21] L. V. Radushkevich, *ibid.*, p. 1410.

[22] M. M. Dubinin, Statia v sbornike " Metody issledovania strukturnykh vysokodispersnykh e poristykh tel." Akademia Nauk S.S.S.R., Moscow, 1953, str. 72.

[23] M. M. Dubinin and A. G. Zuiev, *Doklady Akad. Nauk S.S.S.R.*, 1949, **69**, 209.