ASSESSMENT OF ADSORPTION IN MICROPOROUS CARBONS

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ABSTRACT

This paper discusses the formation and fine structure of microporous carbons and the nature of adsorption in micropores. Some experimental factors are also considered. The two principal groups of methods used to analyse adsorption in microporous carbons; are (i) developments of the BET theory, such as the t-plot of de Boer and the α-method of Sing, and (ii) developments of the Dubinin-Polanyi theory, including the Dubinin-Radushkevich, Dubinin-Astakhov, Kaganer and Stoeckli equations. Methods which attempt to separate adsorption in micropores from adsorption in wider pores, e.g. the Dubinin-Kadlec method, the nonane preadsorption technique and the isotherm subtraction method are also considered.

1. INTRODUCTION

Microbalance techniques are often used to measure gas adsorption isotherms in order to determine surface areas and pore structures of solid adsorbents. The experimental measurements are straightforward relative to the interpretation of the resultant isotherms, particularly when micropores are present. (Micropores have been defined[1] as pores of width less than 2 nm; a mesopore has width between 2 and 50 nm and a macropore has width greater than 50 nm). The presence of micropores makes interpretation of isotherms difficult because theories of microporous adsorption are not as well-developed as those for adsorption on a free surface or for adsorption in macropores and mesopores.

In this paper the principal theories applied to adsorption on microporous carbons are reviewed critically. Many carbons contain mesopores and macropores as well as micropores but, to restrict the scope of the paper, methods of analysing mesoporous structure (e.g. by analysis of closed-loop hysteresis[2,3]) or macroporous structure (e.g. by mercury porosimetry[4,5]) are not discussed. However, some consideration is given to methods which attempt to separate microporous adsorption from non-microporous adsorption. Also, space does not allow consideration of techniques for the study of micropores which are complementary to gas adsorption, including small angle x-ray scattering[6,7], high resolution electron microscopy[8,9] adsorption from solution[10,11] and apparent density determinations[12,13]. The production and

fine structure of microporous carbons and the nature of adsorption in micro-
pores are first considered followed by a summary of some experimental factors
in determining gas adsorption isotherms using vacuum microbalances.
Applications of the BET equation are discussed in detail as is the development
of Polanyi Potential theory by Dubinin and his collaborators. Finally, some
treatments which combine BET and Dubinin theories are discussed.

2. THE PRODUCTION OF MICROPOROUS CARBONS

Many commercial microporous carbons are produced by carbonisation of
cellulosic precursors such as wood, cononutshell and a wide range of organic
by-products of agricultural and industrial processes. A large proportion are
produced by carbonization of coals from lignites to anthracites[14,15].
Activated carbons have micropores and mesopores which are developed either by
reaction with oxidising gases, e.g. CO_2, H_2O, or by incorporation of inorganic
additives, e.g. $ZnCl_2$, prior to the carbonisation process. In recent years a
range of activated carbon textiles have been developed by carbonization of
textile precursors such as viscose[16,17]. Details of manufacturing methods,
properties and the wide range of applications of activated carbons are given
in standard reference works[18-20].

Carbonisation processes are complex. In general, the organic precursor is
thermally degraded to form products which undergo either condensation
reactions or volatilization, the competition between these processes determin-
ing the carbon yield. For example, Tang and Bacon[21] have proposed the
following mechanism for the primary carbonisation of cellulosic plant tissues:
(i) dehydration of the cellulose units between 150^0 and 240^0C; (ii) thermal
cleavage of glycosidic linkages and scission of other C-O and some C-C bonds
between 240^0 and 400^0C; (iii) aromatization above 400^0C. Secondary carboniz-
ation in the range 400^0-800^0C involves condensation of polynuclear aromatic
compounds and expulsion of side chain groupings. The carbon will contain
significant amounts of heteroelements, especially O and H, bound to the carbon
and 'ash', the thermally-transformed residue of the inorganic constituents of
the precursor; ash content can be reduced by washing.

3. THE FINE STRUCTURE OF MICROPOROUS CARBONS

Microporous carbons have a very disordered structure. X-ray diffraction
shows some evidence for 2-dimensional order revealed by a broad 002
reflection[22-24]. This is created by parallel orientation of graphite layer
planes formed from the condensation of polynuclear aromatic compounds; there is
very little evidence for 3-dimensional graphitic ordering in the structure.
Biscoe and Warren[22] coined the term 'turbostratic' to describe a graphite-like

structure with random translation of layer planes along the a-axis and rotation of layer planes about the c-axis. There is also strong X-ray scattering at low angles due to the presence of micropores[6,7].

The structure of microporous carbons has been elaborated by application of high resolution electron microscopy[25,26] (HREM). A typical micrograph for a cellulose-based microporous carbon is in Fig.1[27]. Based on HREM, various models for the microstructure of carbons have been proposed. The essential feature of all models is a twisted network of carbon layer planes cross-linked by aliphatic bridging groups. A schematic of a volume element from such a model, Fig. 2, shows micropores as spaces between the carbon layer planes. It can be seen that a slit-shaped pore is a plausible model for micropores in carbons. Another feature of the structure is constrictions in the microporous network which control access to much of the pore space. Entrances to micropores may also be blocked by aliphatic groupings attached to the edges of layer planes and by carbon deposits formed by thermal cracking of volatiles.
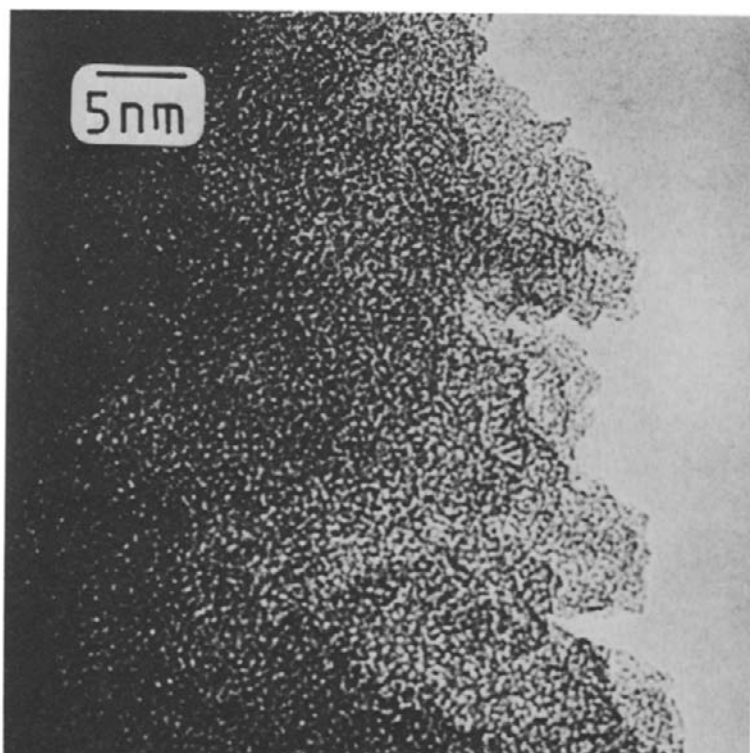

Fig. 1. High resolution, phase contrast, electron micrograph of a microporous cellulose carbon heat-treated to 1170 K.
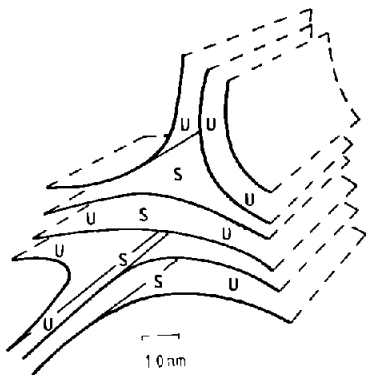
Fig. 2. A model of the fine structure of a microporous carbon showing micropores as spaces between carbon layer planes. S, possible super-microporous spacings; U, possible ultra-microporous spacings.
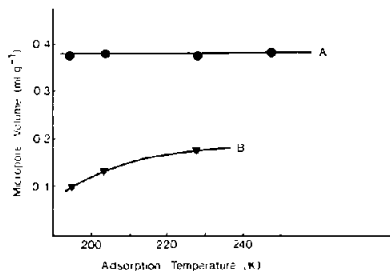
Fig. 3. The effect of activated diffusion upon the DR micropore volume of a wide pore carbon (A) and a narrow-pore carbon (B). Adsorptive CO_2.

4. ACTIVATED DIFFUSION AND MOLECULAR SEIVE EFFECTS

Constrictions and blockages in the microporous network cause activated diffusion effects at low adsorption temperatures when the adsorptive has insufficient kinetic energy to completely penetrate the pore space. Fig. 3 shows the influence of adsorption temperature upon the micropore volume of two carbons (micropore volumes were determined using the DR equation, see below). For carbon A with wide micropores, the micropore volume is independent of adsorption temperature, but for the narrow-pore carbon B, the micropore volume apparently decreases as temperature falls[28]. This is an artefact due to activated diffusion. At low temperature the adsorptive has failed to completely penetrate the pore space and an anomalously low value for micropore volume is obtained.

The related phenomenon of molecular seive action (also found with microporous zeolite adsorbents) is the selective adsorption of small molecules in narrow micropores. Carbons also exhibit molecular shape selectivity by preferential adsorption of flat molecules[29], as expected from the slit-shape of micropores, Fig. 2. Molecular seive action can be exploited to effect separation of gas mixtures by microporous carbons. A measure of a micropore size distribution may be obtained by determining adsorption isotherms using a range of adsorptives of different molecular size[30,31], the molecular probe technique.
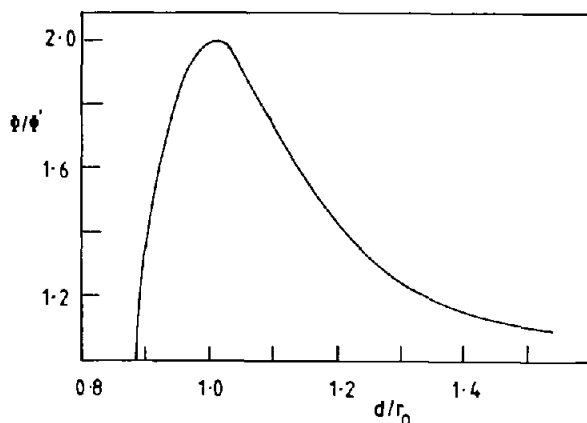
Fig. 4. Interaction energy in a slit-shaped micropore, Φ, relative to that in a free surface Φ'; energies calculated using a 10:4 potential function. Data of Everett and Powl[34].

7. ADSORPTION FORCES IN MICROPORES

Gas is strongly adsorbed by microporous carbons because there is enhancement of the adsorption potential due to overlap of the force fields of opposite pore walls. Calculations of the enhancement of potential in different shaped micropores have been made by numerous authors[32,33,34]. Fig. 4. shows the interaction potential, Φ, relative to that on a free surface, Φ', plotted against pore half-width, d, relative to the collision radius of the adsorptive molecule, r_0, for a slit-shaped pore between parallel slabs of solid[34]. Φ/Φ' has a maximum of 2 for $d/r_0 = 1$ and enhancement of interaction potential disappears at $d/r_0 \approx 2$. For Ar at 77 K, $r_0 = 0.23$ nm so that the enhancement due to overlap of force fields is not found for micropores of width more than about 0.9 nm. Pores with enhanced adsorption potential have been termed ultra-micropores[35] and larger micropores (up to 2 nm[1]) are termed super-micropores. Examples of possible super-microporous and ultra-microporous spacings in the model for microporous carbon are shown in Fig. 2.

It has been postulated[36] that the enhancement effect may persist in super-micropores due to co-operative effects between the adsorptive and pre-adsorbed molecules, although there is no quantitative treatment to test this idea. Furthermore, the boundary between (i) enhanced adsorption in micropores due to cooperative effects between adsorptive molecules and (ii) the normal interactions between adsorptive molecules during multilayer adsorption in mesopores is ill-defined. This highlights the arbitrary nature of the mesopore/

micropore boundary proposed by IUPAC[1] and further work is necessary to clarify this important point.

8. EXPERIMENTAL CONSIDERATIONS

The volumetric method[37] using N_2 at 77 K as adsorptive is the commonest technique for determination of the surface area of solids by gas adsorption. However, the gravimetric method using vacuum microbalances has a number of advantages, particularly for solids of low surface area. For solids with a surface area less than about 10 m^2/g, krypton is preferred as adsorptive for the volumetric method, but there are complications in its use[38]. This restriction does not apply to the gravimetric method. A monolayer of N_2 on 1 m^2 of solid weighs 289 µg so that N_2 can be used for surface area determinations by gravimetric means for solids with surface areas significantly less than 1 m^2/g. Microbalance measurements must be corrected for buoyancy effects and for thermomolecular flow, i.e. spurious mass changes in the Knudsen pressure range caused by temperature gradients in the balance assembly[39,40].

The choice of adsorptive poses problems when working with microporous carbons. Gregg and Sing give a useful summary of the advantages and limitations of adsorptives used to determine surface area by the BET method[38] and conclude that N_2 or Ar at 77 K are the most reliable. Unfortunately, Ar and N_2 at 77 K may be subject to activated diffusion effects in ultra-microporous adsorbents and, partly for this reason, CO_2 at 195, 273 or 293 K has been used for adsorption on microporous carbons and microporous coals[41,42]. A disadvantage of CO_2 is its high quadrupole moment $(3.1 - 3.4 \times 10^{-20}$ esu) which may make it susceptible to localised interaction with polar groups on carbon surfaces. A wide range of adsorptives has been used in attempts to obtain micropore size distributions by the molecular probe technique[31].

Outgassing of specimens is necessary before commencing adsorption isotherms. For most microporous carbons heating under vacuum at 250°C overnight is usually sufficient to achieve a residual pressure of about 10^{-5} mbar. Such treatment removes physically absorbed species but also decomposes some of the chemisorbed surface complexes which are present at room temperature. Careful temperature measurement and control are necessary during the determination of adsorption isotherms. The reversibility of adsorption should always be checked by means of an adsorption - desorption cycle. Low pressure hysteresis is sometimes found with microporous carbons due to trapping of adsorptive molecules in the microporous network. This is probably associated with adsorption-induced deformation of the carbon structure[43]. Closed-loop hysteresis at P/P_o greater than 0.35 is due to capillary condensation in mesopores[2,3].

9. APPLICATION OF THE BET EQUATION

The equation which is most widely used to analyse adsorption isotherms to obtain surface areas is that derived by Brunauer, Emmett and Teller[44] (BET) for adsorption of multiple molecular layers, multilayers, on a non-porous adsorbent. The principles of the BET theory may be found in standard texts[38]. In essence the theory assumes that adsorption builds up as successive molecular layers. The first layer forms by localised, Langmuirian[45] adsorption while formation of subsequent layers is analogous to condensation of the bulk liquid adsorptive. For adsorption on a non-porous surface where an infinite number of molecular layers may be formed, the BET equation is

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{P}{P_0} \tag{1}$$

where V is the amount adsorbed at relative pressure P/P_0, V_m is the amount of adsorptive required to form a monolayer and C is a constant given by the approximate expression

$$C = \exp[(q_1 - L_v)/RT]$$

where q_1 and L_v are heats of adsorption in the monolayer and in multilayers respectively, the latter being equivalent to the molar heat of condensation.

This form of the BET equation is very often used to analyse adsorption in microporous carbons, although the assumption of an infinite number of molecular layers is clearly inappropriate. If the number of multilayers is restricted to N then the BET equation becomes.

$$\frac{\Xi}{V} = \frac{1}{V_m C} + \frac{\theta}{V_m} \tag{2}$$

where Ξ and θ are functions of N and P/P_0[46]. The specific surface area S of the solid can be obtained from V_m (g/g) if the cross-sectional area of the adsorptive molecule, $\sigma(nm^2)$, is known using

$$S = \frac{V_m}{M} \sigma N_A \ 10^{-18} \ (m^2/g) \tag{3}$$

where M is the molecular weight of the adsorptive and N_A is Avogadro's Number. Problems associated with the choice of σ have been summarised by Gregg and Sing[38].

Application of the BET equation to adsorption in microporous carbons is subject to severe limitations. The values of surface areas (up to about 4000 m^2/g for some highly activated carbons[47]) are unrealistically high, since the calculated area of an extended graphite layer plane, counting both sides, is about 2800 m^2/g. Adsorption in micropores does not take place by successive build-up of molecular layers as supposed in the BET theory. Rather, the

enhanced interaction potential in micropores induces an adsorption process described as micropore filling[35]. Because of its widespread use for other adsorbents, the BET surface area has and will continue to be used for microporous carbons, but the notional character of the surface area should be recognised and, following Barrer[48], the term 'monolayer equivalent area' should be used.

Similar, unrealistically high surface areas are obtained if the 'N' form of the BET equation, Equation (2), is used. Moreover, for an activated series of carbons it has been shown that the value of 'N' decreases with increasing activation[49], apparently signifying a decrease in pore width, Table 1. The overwhelming balance of other evidence suggests that activation increases micropore and mesopore widths, so that the change in N is an artefact resulting from the limitations of the BET equation when applied to microporous carbons.

10.   t-PLOTS AND α-PLOTS

Useful developments of the BET equation have arisen from the early realisation[50] that isotherms of a given adsorptive on a series of related solids can be reduced to a 'compound' isotherm[51] by plotting adsorption uptake in normalised coordinates, e.g. V/V_m. This reflects the fact that while the adsorptive capacity of the adsorbents may differ, the shape of the isotherms are similar. The best known development along these lines is the t-plot of de Boer and collaborators[52,53]. t is the statistical thickness of the adsorbed layer given by $t = V/S$; when $V = V_m$, t is t_m the monolayer thickness which can be calculated by making assumptions about molecular packing in the monolayer. If a suitable, non-porous, standard or reference adsorbent of known S is available, then the standard isotherm, $V = f(P/P_0)$, may be transformed into a standard t-plot, $t = f'(P/P_0)$. Using the same adsorptive, an isotherm on another adsorbent may be compared with the standard isotherm by re-plotting it as $V = f''(t)$ using the standard t-plot to effect the transformation. If the standard and test adsorbents are nonporous, then a linear t-plot is usually found, $V = kt$, where $k = V_m/t_m = S$. In this way S for the test adsorbent may be determined.

TABLE 1
BET Surface Areas for CCl_4 Adsorption at 293 K in Activated Cellulose Carbons using Equn (2)

% Burn-Off	S/ (m²/g)	N
25	786	1.3
45	1382	1.25
75	2400	1.15
89	3576	1.10

Of course, if the sole object was to determine S, then application of the BET equation to the test adsorbent isotherm is a more direct method. However, the t-plot is useful when comparing adsorption on a porous solid with that on a non-porous reference material. Curves of t-plots for non-porous, microporous and mesoporous solids are sketched in Fig. 5. Because of enhanced adsorption in micropores, there is strong adsorption at low relative pressures. This is reflected in a steep rise in the t-plot at low t values. On the presumption that the linear portion of the t-plot, represents non-microporous adsorption, Sing[54] proposed that extrapolation of the linear portion of the t-plot to the ordinate will give a measure of the micropore volume. Effectively, the linear portion of the t-plot for microporous adsorbents is of the form.

$$V = V_o + V_m' \, t/t_m \tag{4}$$

where V_o, is the micropore volume and V_m' is the monolayer value for the non-microporous part of the surface and $V_m'/t_m = S'$, the non-microporous surface area. Use of Equation (4) leads to an underestimate of V_o, however, since it implies that micropores are completely filled at $P/P_o = 0$. Further, if micropore filling extends into the linear range of the t-plot, then the value of S' will be overestimated. The problem of separating adsorption in micropores from adsorption on the rest of the surface is considered in Section 15. If mesopores are present, then an upward deviation of the t-plot is found at large t values, Fig. 5. If both micropores and mesopores are present, then a t-plot with a limited linear range or no linear range is found.

Sing[55] argues persuasively that, if the objective is simply to compare a given isotherm with a standard isotherm, then the t-plot is unnecessarily
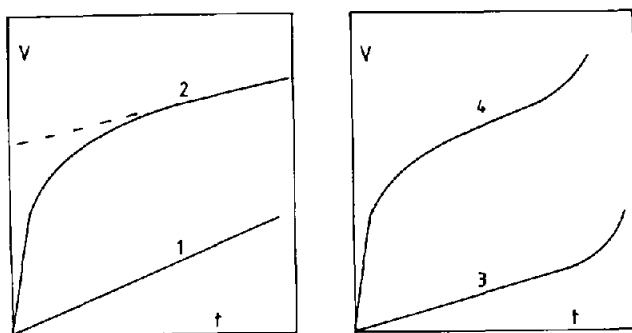

Fig. 5. Schematic t-plots. 1, a non-porous adsorbent; 2, a microporous adsorbent; 3, a mesoporous adsorbent; 4, an adsorbent containing mesopores and micropores.
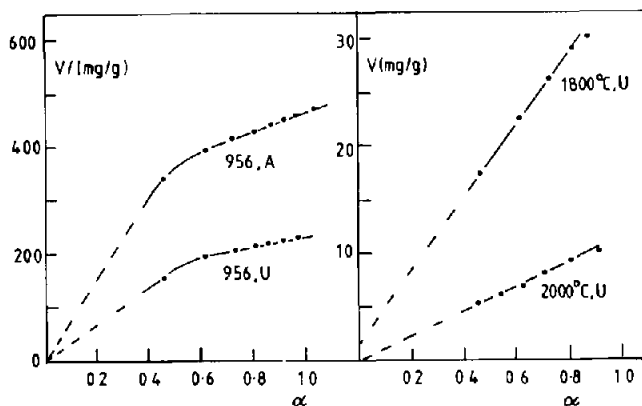
Fig. 6. α-plots for adsorption of CO_2 at 195 K on activated (A) and unactivated (U) cellulose triacetate carbons, using the 2000° U carbon as reference adsorbent.

elaborate. He proposed empirically that the amount adsorbed at P/P_o = 0.4 may be used as a normalising factor and defined the term α = $V/(V$ at P/P_o = 0.4). Standard isotherms and α-plots are constructed in a similar way to t-plots. If S for the reference adsorbent is determined without recourse to the BET equation, the α-plot method is rendered independent of BET theory.

The choice of standard adsorbent for carbons poses difficulties. Graphitised carbon black has been used[56] and, although it is a carbonaceous solid with a well characterised surface, the surface structure is quite different from most microporous carbons (except microporous carbon blacks)[26]. An alternative which merits further consideration is a microporous carbon which has been heat-treated to about 2000°C to close off microporosity[57]. The non-microporous surface of a heat-treated carbon will more closely resemble that of an open microporous carbon than does that of graphitised carbon black. Use of this type of reference solid is illustrated in Fig. 6 in which α-plots for heat-treated and activated carbons prepared from cellulose triacetate are compared. α-plots for the 956° unactivated and activated carbons are similar to t-plots for micro-porous adsorbents[58]. The linear portions of the curve may be extrapolated to give estimates of V_o and S'; the analogue of Equation (4) is

$$V = V_o + m\alpha \qquad (5)$$

where m is the slope of the linear portion of the α-plot and $S' = S_r m/m_r$ where S_r is the surface area of the reference adsorbent and m_r is the slope of α-plot

for the reference adsorbent. Use of Equation (5) will give underestimates of V_o and may possibly give an over-estimate of S' as noted for Equation (4). The α-plots for the 2000°C reference carbon and a carbon heat-treated to 1800°C are also compared in Fig. 6. Micropores are closed off by heat-treatment to about 1400°C and, as expected, the 1800°C carbon gives an α-plot which indicates that it is virtually non-microporous, although of higher surface area than the reference carbon.

11. THE DUBININ-RADUSHKEVICH EQUATION

Because of the enhanced interaction potential in pores, adsorption is better described as micropore filling rather than successive build up of multilayers, as implied by the BET theory. Micropore-filling may be modelled by the Polanyi Potential theory[59]. Polanyi likened the adsorption force field emanating from a surface to a gravitational field. The field is characterised by an adsorption potential, ε, defined as the isothermal work done in transferring an adsorptive molecule from the free gaseous state to a point above the adsorbent surface. The adsorption potential ε decreases with distance from the surface and when $\varepsilon = 0$, the volume enclosed by a equipotential surface, $V = V_o$ the total adsorption space. When the temperature is below the critical temperature of the adsorptive, it is assumed that the potential is sufficient to compress the adsorptive to a liquid-like state and in this case $\varepsilon = RT \ln P_o/P$. Isotherms plotted as V (ml liquid/g) vs ε are called characteristic curves and Polanyi[59] showed that isotherms obtained at different temperatures can often be reduced to a single characteristic curve. After analysing characteristic curves for a wide range of microporous carbons, Dubinin and Radushkevich proposed the following equation[60] (the DR Equation)

$$V = V_o \exp{(-\varepsilon/E)^2} \tag{6}$$

where the constant E is termed the characteristic energy and is a function of the adsorptive-adsorbent system. Dubinin[60] sought to separate the two contributions to E by use of the similarity coefficient β, a scaling factor, which is determined by comparing the isotherm of a given adsorptive with that for a standard adsorptive (benzene) for which $\beta = 1.00$; $\beta^2 = E^2 k$, where k is a constant characteristic of the microporous structure.

If the adsorption space is confined to micropores, then V_o is the micropore volume which may be found by extrapolation to P_o using the linear form of the DR equation

$$\ln V = \ln V_o - \left(\frac{RT}{E}\right)^2 \ln(P_o/P)^2 \tag{7}$$

Characteristic curves for adsorption of CO_2 on active carbons at different temperatures plotted in DR coordinates, Fig. 7., show the temperature-invariant

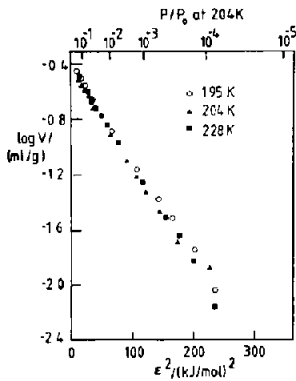nature of the curves and conformity with the DR Equation.

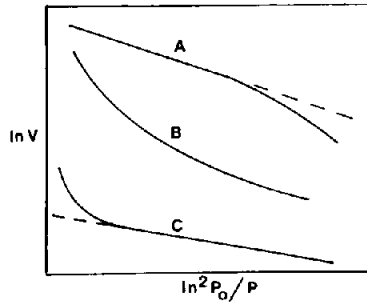Fig. 7. Characteristic curves for adsorption of CO_2 on an activated carbon, plotted in DR co-ordinates.

Fig. 8. The Marsh Rand[61] classification of deviations from the DR equation.

The assumption that adsorption is confined to micropores is more appropriate at lower relative pressures and, where possible, the DR equation should be applied to data obtained at P/P_0 less than 0.1. The DR equation is sometimes linear over a wide relative pressure range, e.g. Fig. 7, but deviations from linearity are often found (see below). When linear DR plots are obtained the resultant value of V_0 is a more realistic measure of micropore adsorptive capacity than is the BET surface area. Furthermore, the value of E gives a measure of the heterogeneity of the micropore structure. Deviations from a linear DR equation were classified by Marsh and Rand[61], into types A, B and C, Fig. 8. When such deviations occur the extrapolation to the ordinate to obtain V_0 becomes uncertain. To overcome this problem a number of approaches for generalising the DR equation have been proposed.

12. THE DUBININ ASTAKHOV EQUATION[62]

If Equation (7) is differentiated, a distribution of adsorption volume with adsorption potential is obtained

$$dF/d\varepsilon = -[2\varepsilon. \exp(-\varepsilon/E)^2]/E^2 \tag{8}$$

where $F = V/V_0$ is the fraction of the micropores filled. Equation (8) has the form of a Rayleigh distribution where the only independent variable is E. The influence of E on the Rayleigh distribution is illustrated in Fig. 9. An adsorptive-adsorbent system of low E, which conforms to the DR equation has
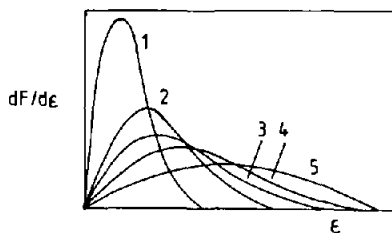
Fig. 9. The influence of the characteristic energy, E, upon the shape of the Rayleigh distribution function. Curve 1, low E; Curve 5, High E.
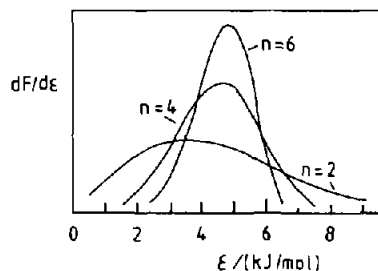
Fig. 10. The influence of the exponent n of the DA equation upon the shape of the Weibull distribution function. E = 5 kJ/mol.

a narrower range of ε values, i.e. a more homogeneous micropore structure, than a system of a high E value.

The Rayleigh distribution is an example of the more general Weibull function[63] where the exponent 2 in equation (6) is replaced by n. The isotherm is described by the Dubinin-Astakhov (DA) equation

$$V = V_o \exp(-\varepsilon/E)^n \qquad (9)$$

The exponent n mainly affects the breadth and to a lesser extent the mode of the Weibull type of $dF/d\varepsilon$ distribution, Fig.10. For a given value of E, the range of ε increases as n decreases. Thus a small value of n denotes a heterogeneous micropore structure, while a large value of n denotes the opposite; experimental values of n[64] range between 1.0 and 3.4. Dubinin and Radushkevich[60] had earlier proposed an equation with n = 1.0 for well-activated carbons with a wide range of micropore sizes. Stoeckli[65] has shown that the DA Equation can be related to the generalised adsorption isotherm equation and the shape of the site energy distribution function is influenced by n in a similar way to the curves in Fig. 10. Type B deviations from the DR Equation, Fig. 8, can be linearised by application of the DA equation, but types A and C cannot be linearised over the whole pressure range[64]. Also, methods for determining n are not precise. The DA equation is most successful at low relative pressures where the chosen value of n has greatest effect, but, for high pressure data, the DA equation appears to offer no advantage over the DR equation.

13. THE STOECKLI EQUATION

An alternative approach to generalising the DR equation by Stoeckli[66] proposed that adsorption in a heterogeneous system of micropores consists of a weighted sum of DR equations, each corresponding to a given class of micropores. The resultant equation is:

$$V = V_0 \exp(-B_0 Y) \exp (Y^2 \Delta^2/2)(1-\mathrm{erf}(x))/2 \tag{10}$$

where $Y = (T/\beta)^2 \ln^2 P_0/P$ and $X = (Y-B_0/\Delta^2)\Delta/2^{0.5}$.

The distribution of the structure constant k with micropore volume is assumed to be Gaussian with B_0 and Δ being the maximum and half-width respectively of the distribution. The isotherm constants, B_0 and Δ are similar to the constants E and n of the DA equation, i.e. measures of the heterogeneity of the micropore structure. It is debatable whether the extra computation involved in the use of Equation (10) offers any advantage over the use of the DA equation.

14. QUALITATIVE STRUCTURAL ANALYSIS OF DEVIATIONS FROM THE DR EQUATION

An alternative to the use of generalised equations, is to plot the isotherm in DR co-ordinates and examine any deviations. This can be useful because some deviations are structural in origin and others are not. Recent evidence[67] shows clearly that Type A deviations, Fig. 8, are due to activated diffusion. An example is shown in Fig. 11 for a cellulose carbon heat-treated to 1470 K for 5 and 30 minutes. This treatment progressively closes micropore entrances[68,69]. When isotherm equilibration times of 2 hr were used, the type A deviation increased with increasing heat-treatment time. However, with 12 hr equilibration times, the type A deviation is eliminated and a positive deviation is found at low pressures (see below). Clearly, activated diffusion is associated with the progressive narrowing of micropore entrances with increasing heat-treatment time. Similar effects were noted by Toda et al[70] for adsorption of CO_2 at 195K on coals heat-treated in the range 773 to 1173 K.

Negative deviations from the DR equation are also found at high pressures, e.g. adsorption of CO_2 at 295 K on unactivated carbon cloth, Fig. 12. It was concluded[67] that the micropores in carbon cloth are smaller and the size distribution narrower than for a carbon with the same values of V_0 and E which conforms to the DR Equation. Similar deviations are also found with microporous zeolites which have discrete micropore sizes rather than a distribution of sizes. Partial gasification (activation) of carbons increases micropore sizes and widens their distribution. In the case of activated carbon cloth a DR plot is obtained which is curved (Type B), Fig. 12. A Type B deviation therefore indicates a micropore structure that is more heterogeneous
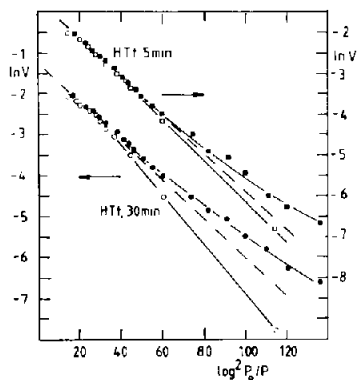
Fig.11. Adsorption of CO_2 at 295 K on cellulose carbon heat-treated to 1470 K for 5 and 30 minutes. Open symbols, adsorption equilibration time, 2 hr; closed symbols, adsorption equilibration time 12 hr.
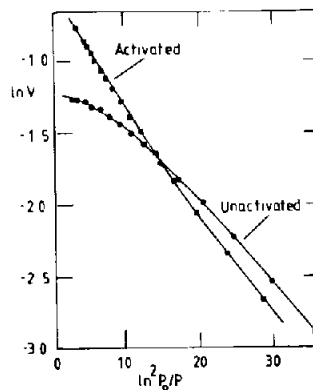
Fig.12. Adsorption of CO_2 at 295 K on unactivated and activated carbon cloth.

than a carbon with the same values of V_o and E which conforms to the DR equation.

The positive deviations at low relative pressures, Fig. 11, are found at low degrees of micropore filling (V/V_o less than 0.03). At such low surface coverage it is possible that the concept of micropore filling is not appropriate, as previously noted by Dubinin[71]. In such a case it is not possible to relate deviations from the DR equation to the microporous structure of the adsorbent.

15. COMBINATIONS OF THE BET AND DR THEORIES

The first to introduce concepts of the BET theory into the DR Equation was Kaganer[72] who replaced V_o by V_m. As noted previously, the BET and DR Equations are based on quite different mechanisms for the adsorption process and so the justification for using V_m for V_o is not clear. As may be expected, values of surface areas calculated using the Kaganer equation for adsorption of activated carbons can reach unrealistically high values.

A basic difficulty in attempting to separate adsorption in micropores from non-microporous adsorption (and especially mesoporous adsorption) is that there is often a wide range of relative pressure when significant amounts of adsorption is occurring in both micropores and on the rest of the surface. The use of t-plots and α-plots on microporous adsorbents (Equations 4,5) to obtain

V_o and S' is based on the assumption that adsorption in micropores is complete before the experimental range of the isotherm.

One method for attempting to separate adsorption in micropores from non-microporous adsorption is the V/F, t/F method of Kadlec and Dubinin[73,74]. They proposed that the total adsorption V was the sum of a microporous contribution calculated from the DR equation and a non-microporous contribution calculated from a t-plot, i.e.

$$V = V_o F + S't \tag{11}$$

where F is given by $F = \exp(-\varepsilon/E)^2$; thus a plot of V/F vs t/F gives a slope of S' and an intercept of V_o. This is an improvement on Equation (4) since it takes account of the progressive filling of micropores with increasing P/P_o, and when F = 1, Equation (11) reduces to Equation (4). A difficulty with this method is the unambiguous determination of E; Kadlec[73] used an empirical, iterative method.

Another more direct method for separating microporous and non-microporous adsorption[75] is illustrated in Fig.13. Carbons which contain significant amounts of micropores and mesopores usually give a DR plot which is Type C in the Marsh-Rand classification, Fig.8; Fig.13 is an example. Because of the high adsorption potential in micropores, it is reasonable to assume that microporous adsorption dominates at low P/P_o. If it is further assumed that adsorption on the non-microporous surface may be neglected in the low pressure, linear regions of the DR isotherm (ab, Fig.13), then extrapolation will give the microporous contribution at high P/P_o (bd, Fig.13) which can then be
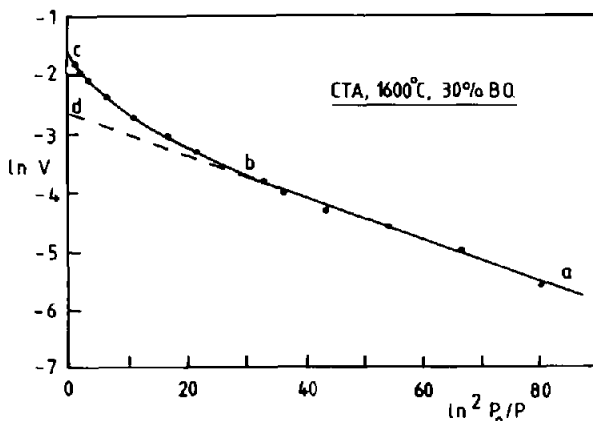

Fig.13. Adsorption of CO_2 at 195 K of cellulose triacetate carbon heat-treated to 1600°C and subsequently activated to 30% burn-off. See text for explanation of symbols a to d.

TABLE 2

Adsorption Parameters for Microporous Carbons

Carbon	Total Surface Area $S/(m^2/g)$	Non-microporous surface area $S'/(m^2/g)$	Micropore volume $V_0/(ml(liquid/g))$
Cellulose carbon % B.O.			
35	1081	450	0.28
50	1138	694	0.21
70	1167	768	0.20
Cellulose Triacetate Carbon, 30% B.O.			
HTT/^{o}C			
1400	411	233	0.09
1600	399	267	0.07
1800	338	250	0.05
2000	193	200	0.02

subtracted from the total isotherm at high pressures to give the non-microporous contribution. The non-microporous isotherm may then be analysed by the BET equation to give S'. Some results of this approach are given in Table 2 for an activated series of cellulose carbons and a heat-treated series of carbons which had been subsequently activated. From previous work, both processes are known to develop mesoporosity. In both cases the proportion of non-microporous surface increases as expected.

A further method for estimating the adsorptive capacity of micropores is the nonane pre-adsorption techniques[76]. The basis of this method is that, if a porous solid with adsorbed nonane is outgassed at room temperature, nonane will rapidly desorb from the non-microporous surface but be retained in micropores. Measurement of N_2 or Ar isotherms on such a solid before and after nonane pre-adsorption should enable the micropore volume to be determined. The effectiveness of this method was first demonstrated using microporous carbon black[76].

Table 3 shows values of S' obtained by the isotherm subtraction technique[75], Fig. 13, and the nonane pre-adsorption technique for a series of activated anthracite carbons; the agreement between the two methods is remarkable.

16. MICROPORE SIZE MEASUREMENTS FOR ADSORPTION ISOTHERMS

A form of micropore size distribution can be obtained using molecular probes, but this method is very laborious and is at best semi-quantitative, since differences in uptake with a range of adsorptives may reflect differences in

the adsorptive-adsorbent interactions in addition to the effects of molecular size. Everett and Powl[34] obtained a measure of micropore sizes from Henry's Law adsorption isotherms. The measurement of Henry's Law isotherms requires specialised apparatus and a very precise technique. Dubinin and Stoeckli[78,79] have proposed a simple inverse relation between the Guinier radius of gyration, R_G, determined from small angle x-ray scattering and the characteristic energy for benzene adsorption: $R_G \simeq 14.8/E_o$ nm. As admitted by these authors, the relationship is an approximate one and much more work is required to substantiate or modify this equation. A reliable method of obtaining pore sizes distributions from a single adsorption isotherm is a highly desirable goal which has so far proved elusive. Kadlec[78] has proposed a relation between ε, and the radius of a cylindrical micropore, r, of the form $\varepsilon = k/r^3$ to obtain micropore size distributions, but this approach has been criticised by Stoeckli[79] because the expression used ignores the repulsive part of the adsorption potential.

17. CONCLUSIONS

The enhanced adsorption potential in micropores leads to adsorption by pore-filling rather than by successive build up of molecular layers, as implied by the BET equation. Consequently, application of the BET equation is subject to serious limitations when applied to microporous carbons. The DR equation, which derives from the Polanyi Potential theory, is better suited to microporous carbons and the isotherm constants V_o and E give information on the micropore volume and the heterogeneity of the micropore structure respectively. Deviations from the DR equation are often found and more generalised, three constant, isotherm equations (Dubinin-Astakhov and Stoeckli) have been proposed. Alternatively, analysis of deviations from the DR equation can yield qualitative information on the microporous structure of carbons.

TABLE 3

Comparison of Surface Areas for Anthracite-based Active Carbons using Ar at 77 K

Sample Number	Total Surface Area $S/(m^2/g)$	Non-microporous Surface Area $S'/(m^2/g)$	
		Nonane Method	Isotherm Subtraction
1457	547	178	189
1459	711	297	280
1480	807	324	325
1461	926	387	416

t-plots or α-plots can be used to obtain estimates of micropore volume and non-microporous surface area, but these are often subject to error, particularly when there is significant overlap between microporous and non-microporous adsorption. The V/F, t/F method, the isotherm subtraction method, and the nonane-preadsorption technique are alternative ways for separating the two types of adsorption. There is as yet no satisfactory method for obtaining a micropore size distribution from a single adsorption isotherm. It is clear that, despite the vast amount of published work on adsorption in microporous carbons, much remains to be done.

ACKNOWLEDGEMENTS

NOTATION

B_0 structure constant, Stoeckli Equation (Equation (10)).

C constant of BET Equation (Equation (1,2)).

d half-width of a slip-shaped pore

E characteristic energy, constant of DR equation (Equation (6))

F fraction of micropores filled

k structure constant, DR equation.

L_V latent heat of condensation of bulk liquid adsorptive

M molecular weight of adsorptive

m gradient of α-plot

m_r gradient of α-plot of reference adsorbent

N number of molecular layers, BET equation (Equation (2))

N_A Avogadro's Number

n exponent of DA equation (Equation (9))

P/P_0 relative pressure

q_1 heat of adsorption in monolayer

R gas constant

R_G Guinier radius of gyration

r radius of cylindrical pore

r_0 collision radius of adsorptive

S total specific surface area of adsorbent

S' non-microporous surface area of adsorbent

S_r surface area of reference adsorbent

T temperature

t statistical thickness of adsorbed layer

t_m statistical thickness of monolayer

V amount adsorbed

100

V_m monolayer value

V'_m non-microporous monolayer value

V_o micropore volume

X function of Stoeckli Equation (Equation (10))

Y function of Stoeckli Equation

α normalised adsorption uptake, $V/(V$ at $P/P_o = 0.4)$

β similarity coefficient of DR Equation

Δ structure constant of Stoeckli Equation (Equation (10))

ε adsorption potential

Σ function of the BET Equation (Equation (2))

σ cross-sectional area of an adsorptive molecule

υ function of the BET Equation (Equation (2))

Φ interaction potential in micropores

Φ' interaction potential on a free surface.

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