CHARACTERIZATION OF MICROPOROUS MATERIALS
By Carlos A. Leon y Leon D.

All solid powders, and in particular those with apparent surface areas > 400 m^2/g, are bound to contain micropores. The importance of micropores lies in that materials containing micropores generally have most of their apparent surface area residing in them. Hence, all applications of materials (adsorbents, catalysts) that depend on their accessible surface area must deal with the possible effects arising from the presence of micropores in the materials.

By convention, IUPAC classifies pores according to their widths as follows [1]:

> Micropores, < 2 nm width
> Mesopores, 2-50 nm width
> Macropores, > 50 nm width

This somewhat arbitrary classification is necessary because pores within these approximate ranges differ considerably in their interactions with adsorbing gases. Physical adsorption in, and desorption from, macropores can be assumed to take place in general via a layer-by-layer buildup mechanism. This type of mechanism, when occurring on an ideal (flat) surface, is described by the popular BET equation [2]. Each mesopore can also adsorb gases on a layer-by-layer fashion, but its capillary size forces desorption to occur from a spherical meniscus rather than a flat wall, thereby inducing a phenomenon called hysteresis [2, 3].

Micropores, on the other hand, have dimensions close to those of molecules. This fact has several important implications for their interactions with gases. First, the diffusion of molecules into micropores may be very slow (i.e., "activated"), or negligible (as in molecular sieving). Second, when the pore walls are so close to each other their adsorption forces overlap. Because of their higher adsorption potential, micropores will be filled first upon adsorption, and emptied last upon desorption. Indeed, most real surfaces are rough (nonideal) and present a distribution of adsorption potentials. Micropore filling in particular entails a cooperative participation by overlapping potentials which result in the micropores being filled before nonmicroporous surfaces begin to be covered with adsorbate. This process cannot be described by a layer-by- layer mechanism. Therefore, the BET equation is strictly applicable to non-microporous materials. (For available strategies to derive information about micropores from BET isotherms, see Ref. [4].)

In 1947, Dubinin and his coworkers introduced a model to describe physical adsorption on micropores based on a "volume-filling" mechanism [3-6]. Dubinin's model, based on thermodynamic considerations, was originally developed on semi-empirical grounds and, consequently, did not meet with general acceptance. It was later shown that the observed success of the Dubinin equations in describing physical adsorption even on non-microporous materials was not coincidental; indeed, their success was related to their ability to account for a statistical distribution of adsorption energies [4-6]. In other words, Dubinin's model provides not only a physical account of the adsorption process, but also (and more importantly) an expression derived from the mathematical manipulation of statistical distributions [5]. In its most general form, the model is represented by the Dubinin-Astakhov (DA) equation, which reads

$$V=V_0\exp[-(\varepsilon/E)^n] \qquad (1)$$

where V is the volume filled at a temperature T and a relative pressure P/P_o, Vo is the total volume of the micropores, $\varepsilon = RT\ln(P_0/P)$ is the free energy change for one mol of adsorbate to go from the vapor to the adsorbed state, $E = \beta E_0$ is an energy constant obtained by multiplying the adsorption energy of the adsorbate, E_0, by a polarity correction factor, β, and n is an exponent related in a complex mathematical manner to the width of the adsorption energy distribution. If the distribution of adsorption energies can be described by a statistical (e.g., Gaussian, Rayleigh, etc.) function, as is often the case, equation (1) becomes the well-known Dubinin-Radushkevich (DR) expression,

$$\log V=\log V_0-D\log^2(P/P_0) \qquad (2)$$

Equation (2) allows one to estimate Vo by extrapolation from the low P/P_0 ($\leq$ 0.1) region of a log V vs. $\log^2 (P/P_0)$ plot of an adsorption isotherm. It can also be shown [5,6] that the average micropore width, L, and the characteristic adsorption energy E_0 are related to the slope D by the expressions

$$L=(\beta/T)[(4.25\times10^6)(-D)]^{1/2} \qquad (3)$$
and

$$E_0 = (T/\beta) [(1.59\times10^{-4})/(-D)]^{1/2} \qquad (4)$$

respectively. (In equations (2),(3) and (4) V and V_0 are in mL(STP)/g of adsorbent, L is in nm, Eo in KJ/mol, and β is the molar volume of the adsorbate relative to that of a standard (benzene); for N2 and C02 adsorption at 77 and 298 K, β = 0.393 and 0.478,respectively.) From the above expressions, the relationship

$$E_0=k/L \qquad (5)$$

where k = 26 nm.KJ/mol can be derived. In practice, k was reported to vary between 16.5 and 36 nm.KJ/mol for activated carbons with L values in the range 0.45-2 nm [6]. It is therefore more informative to derive pore size distributions by, e.g., substituting equation (5) into equation (2). These distributions are directly related to the slope of the DR plot (equation (2)), in that the steeper the slope, the wider the corresponding pore size distribution. In addition, deviations from linear DR plots can be adequately interpreted in terms of structural irregularities, activated diffusion, mesopore filling or adsorbent polarity effects [5]. Finally, equivalent surface areas can be estimated from micropore volumes following two methods:

(a) via the Dubinin-Polanyi (DP) approach, i.e., by assuming that on average two layers of adsorbate cover the micropore walls; in this case Vo is the volume of a monolayer of adsorbed gas, whose equivalent surface area (ESA) in m^2/g is calculated in the same way as the BET surface area, i.e.,

$$ESA_{DP} = (V_O) \ (N_a) \ (a) \ / \ (22{,}404) \qquad (6)$$

where Na is Avogadro's constant and a is the cross-sectional area of an adsorbate molecule, which can be estimated from

$$a = (1.091)[M/Na/p]^{2/3} \qquad (7)$$

where M and p are the molecular weight and liquid density of the adsorbate at temperature T; or

(b) via the Dubinin-Radushkevich (DR) approach, i.e., by assuming a pore shape; activated carbons and coals, for instance, present regions with slit-like micropores sandwiched between planar sheets of fairly aromatic macromolecules. Assuming these slits to be flat cylinders for which the radius of the top and bottom macromolecules far exceeds the distance L between them,it can be shown that

$$ESA_{DR-slit} = V_o/L \qquad (8)$$

Materials which have a cage-like crystallinity (e.g., zeolites) may be better represented by assuming the pores to be long tubes with heights far exceeding the diameter L of their bases. In this case the above relationship becomes

$$ESA_{DR-Tube} = 4V_o/L \qquad (9)$$

For any given material, equivalent expressions can be derived by assuming a pore geometry which most closely resembles the actual physical situation.

To sum up, both the BET and the DR models can be used to describe the physical

adsorption of gases on solids. However, there are important differences between these approaches. On a fundamental level, the BET equation is based on a layer-by-layer adsorbate buildup mechanism, and is applicable to energetically homogeneous nonmicroporous materials. On the other hand, the DR equation accounts for the "volume-filling" of the most energetically favoured adsorption sites on a heterogeneous surface, and is particularly suitable for the analysis of microporous materials. The BET equation uses the $0.05 \leq P/P_o \leq 0.33$ region of an isotherm to derive a monolayer adsorbate volume, and from it an equivalent surface area. In contrast, the DR equation essentially uses the low P/P_o (≤ 0.1) region of the adsorption isotherm to derive a micropore volume, V_o, as well as pore size distribution independent of the limitations of the Kelvin equation [4]. It is possible to estimate equivalent surface areas from Vo values by use of the proper assumptions. Comparison of equivalent surface areas obtained from BET and DR analysis of (a) the same adsorption isotherm, or (b) different isotherms for the same material, can provide valuable information about the structure of a material. Therefore, both the BET and the DR approaches must be viewed as complementary, and used in conjunction whenever possible in order to fully described a porous material.

Because of the slow (activated) diffusion of N2 at 77 K into micropores, the use of C02 adsorption at 273 K or 298 K is often recommended for DR analysis. This is a very fertile area of research which has been the subject of quite a few international conferences [7, 8].

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