200,000 and the smaller possibly below 10,000. Both these types are believed to consist of organic complexes of ferrous iron[8]. It is interesting to note that one of these molecular types contains calcium. This has been confirmed by continuous electrophoresis experiments, which indicate that about 3/4 of the calcium in the fractions of peak *B* (Fig. 1 *a*) is associated with the coloured iron complexes. The manner in which this calcium is bound to the humus is unknown.

E. T. GJESSING

Norwegian Institute for Water Research,
Blindern, Norway.

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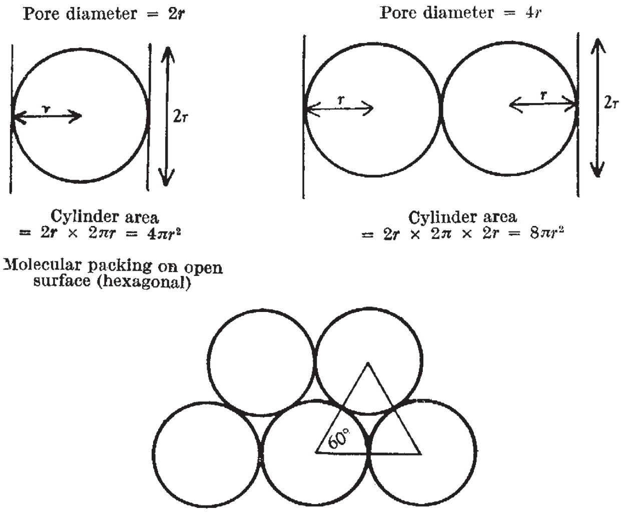
Errors in the Calculation of Surface Area and Average Pore Radius

IN the determination of surface areas from adsorption data the area of the adsorbed molecules A_m is usually calculated from the liquid density, assuming hexagonal close packing in the liquid state on the surface, namely:

$$A_m = 1{\cdot}091\left(\frac{M}{d_l N}\right)^{\frac{2}{3}} \qquad (1)$$

where M is the molecular weight of adsorbate, d_l is liquid density in g/cm³, N is Avogadro's number.

The constant 1·091 is a packing factor to account for hexagonal close packing. This calculation assumes that the molecule only covers an area on one flat, or almost flat, surface. In very small pores, which occur in certain zeolites, charcoals, and silica[1], this is not true. To take an extreme case, if only one molecule can fit into the pore touching the walls (as shown in Fig. 1), it actually covers an area of $4\pi r^2$, the area of the cylinder into which it fits, where r is the radius of the pore. The simple adsorption theory assumes it to cover an area of $2\sqrt{3}r^2$. Thus the actual area is $\frac{2\pi}{\sqrt{3}}$ (= 3·63) times the apparent area.



The area of the triangle is the area that three 60° angle segments of the projected area of one molecule cover; that is, half the total projected area. Area of triangle = ½ base × height = ½ × 2r × $\sqrt{3}r$ = $\sqrt{3}r^2$. Therefore area covered by a molecule = $2\sqrt{3}\,r^2$. Area covered by two molecules = $4\sqrt{3}\,r^2$.

$$\frac{\text{True area}}{\text{Apparent area}} = \frac{4\pi r^2}{2\sqrt{3}\,r^2} = \frac{2\pi}{\sqrt{3}} = 3{\cdot}63$$

$$\frac{\text{True area}}{\text{Apparent area}} = \frac{8\pi r^2}{4\sqrt{3}\,r^2} = \frac{2\pi}{\sqrt{3}} = 3{\cdot}63$$

Fig. 1. Apparent and actual molecular coverage in molecular sized pores

If the pore is two molecular diameters wide, the factor is again 3·63. For increasing pore size the factor will decrease quickly to unity, but substances with pores approaching molecular size will show apparent surface areas which are really too low. Silica samples of this type have been shown to have areas of the order of 300 m²/g or less[1] compared with commercial silica gel with areas of 600–700 m²/g. This is the reverse of what might have been expected assuming a similar total pore volume in the two types of silica.

Average pore radius is often calculated from total pore volume V_p cm³/g and surface area S cm²/g. Assuming the pores to be open cylinders of radius $\bar{r}_p$ cm, then

$$\bar{r}_p = \frac{2V_p}{S} \qquad (2)$$

However
$$V_p = \frac{X_T}{1{,}000 d_l}\ \text{cm}^3/\text{g} \qquad (3)$$

where X_T is adsorption at saturation in mg/g and d_l is density of liquid adsorbate in g/cm³

Also
$$S = \frac{X_m N A_m}{1{,}000\ M}\ \text{cm}^2/\text{g} \qquad (4)$$

where X_m is monolayer adsorption in mg/g and the other terms are as previously defined.

Then
$$\bar{r}_p = \frac{2X_T}{1{,}000 d_l}\,\frac{1{,}000\ M}{X_m N A_m} = \frac{X_T}{X_m}\,\frac{2M}{d_l A_m N}\ \text{cm} \qquad (5)$$

Substances with very fine pores, similar to those already mentioned, give type I adsorption isotherms with very sharp 'knees'. In these cases the monolayer capacity (calculated by the use of the Langmuir equation) is found to be very nearly equal to the total adsorption. Thus X_m and X_T in equation (5) are equal and this leaves $\bar{r}_p$ as a constant. Substituting the values for nitrogen adsorption

$$\bar{r}_p = \frac{2\times 28}{0{\cdot}808\times 6{\cdot}03\times 10^{23}\times 16{\cdot}2\times 10^{-16}} = 7{\cdot}08\times 10^{-8}\ \text{cm} \qquad (6)$$

Thus whatever the true pore size might be, a value less than about 7 Å radius cannot be obtained from adsorption data. This error in radius is connected with the error previously described in that 16·2 Å is not the area covered by the nitrogen molecule in these pores.

Combining equations (1) and (5), cancelling X_m and X_T and ignoring the packing factor gives

$$\bar{r}_p = 2\left(\frac{M}{d_l N}\right)^{\frac{1}{3}}$$

where $\left(\frac{M}{d_l N}\right)^{\frac{1}{3}}$ may be taken to be approximately equal to the molecular diameter D_m. Thus in general pore radius never appears less than twice the adsorbate diameter from calculation. This type of error has also been shown for very fine-pored silica[2] where radii appear always 7–10 Å by calculation based on nitrogen adsorption, whereas molecular sieve effects show the pores to be mainly 3·8 to 4·8 Å in diameter[3].

D. DOLLIMORE
G. R. HEAL

Department of Chemistry
and Applied Chemistry,
Royal College of
Advanced Technology,
Salford, Lancashire.

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