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Errors in the Determination of Specific Surface Area in Transitional Porous Bodies

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The dependence of the pore radius on the factor S_0 used to determine the specific surface is examined.

It is always considered that the factor S_0 is equal to A_mN_m, where N_m is the number of molecules of adsorbate/ml at standard conditions, and A_m is the transversal area of one of these molecules. Thus S_0 or A_mN_m depends both on the molecule or adsorbate, and on the temperature of the experiment.

Really, the pore radius affects the quantity S_0 by means of the factor $2r/(2\bar{r}-\sigma)$ where σ is the equivalent diameter of the adsorbate molecule. For nitrogen at its normal boiling point, for example, it is found:

$$S_0 = 4.37\,\frac{2\bar{r}}{2\bar{r}-\sigma}$$

In dealing with macropores, the effect of the pore radius is not at all important. For mesopores however, it is important to take it into account.

Determining the surface area without corrections can give an error of about 10% when the pore radius is of the order of 20 Å.

NOMENCLATURE

A_m	Transverse area of one molecule of adsorbate.
A_w	Area of the wall of the pore that covers one molecule of adsorbate
S_0	Square meters occupied by 1 cm³ of adsorbate (standard conditions).
N^0	Avogadro's number.
M	Molecular weight of adsorbate.
N_m	Number of molecules that exist in 1 cm³ of adsorbate at standard conditions.
r	Radius of a pore.
$\bar{r}$	Mean pore radius.
S	Area of the wall of a pore.
S_s	Surface area (m²/g).
$S_{s'}$	Surface area obtained in neglecting the correction due to the curvature of the pore wall.
v	Volume of a pore.
V_m	Volume of a monolayer (cm³/g) (standard).
$V_{m'}$	Volume of a monolayer (cm³/g) (liquid).
V_p	Pore volume (cm³/g).
l	Length of a pore.
ρ_l	Density of adsorbate (liquid phase).
ρ_g	Density of adsorbate (gas phase, standard conditions).
σ	Equivalent diameter of a molecule of adsorbate = thickness of a monolayer of adsorbate.

INTRODUCTION

The specific surface of porous bodies is estimated normally by the equation:

$$S_s = N_mA_mV_m, \tag{1}$$

where

$$N_m = \frac{N^0\rho_g}{M}, \tag{2}$$

and

$$A_m = 1.091\left(\frac{M}{\rho_lN^0}\right)^{2/3}. \tag{3}$$

When hexagonal packing is considered for the molecules in the adsorbed state (*1*),

V_m is calculated by means of BET method (2).

Generally, surface determinations are made with nitrogen at normal boiling point, because at that temperature its properties (area/molecule, diameter of molecule, thickness of adsorbed layer with pressure, etc.) are known with accuracy.

For nitrogen at its normal boiling point

$$S_0 = A_m N_m = 4.37\text{m}^2/\text{cm}^3(\text{STP}).$$

It is generally accepted that S_0 for nitrogen is a function of the temperature of the experiment (or the saturation pressure).

Dollimore and Heal (3) show the errors involved in the calculation of the area of the microporous bodies when there are steric obstructions (inner porous structure) in the construction of hexagonal packing in the adsorbed phase.

This effect is found with adsorbents whose pore diameters are of the order of one molecule; for this reason S_0 varies widely.

In this article, it is proposed that S_0 also is a function of the porous structure (therefore of the pore radius).

OUTLINE

1. *Influence of the pore radius on the constant S_0*

1.1. First derivation. First it is assumed that the pores have a cylindrical geometry, then for each the volume is:

$$v = \Pi r^2 l, \tag{4}$$

and the surface of its wall:

$$S = 2\Pi r l, \tag{5}$$

this is:

$$S = \frac{2v}{r}. \tag{6}$$

Taking a model of a porous body with a mean pore radius $\bar{r}$, it is found:

$$S_s = \frac{2V_p}{\bar{r}}; \tag{7}$$

V_p is the total pore volume (cm^3/g).

The quantity $V_p/V_{m'}$ may be expressed as (see Fig. 1):

$$\frac{V_p}{V_{m'}} = \frac{\Pi \bar{r}^2}{\Pi[\bar{r}^2 - (\bar{r} - \sigma)^2]} = \frac{\bar{r}^2/\sigma}{2\bar{r} - \sigma} \tag{8}$$

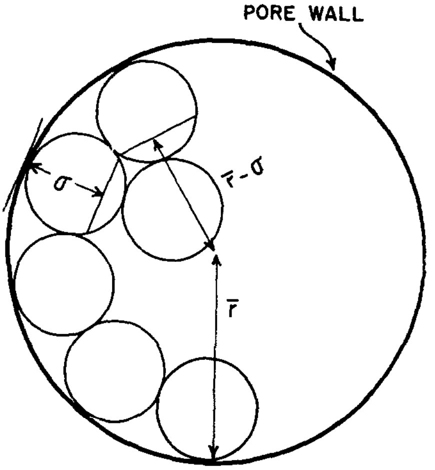

FIG. 1. Pore with molecules of adsorbate (axial view).

From Eqs. (7) and (8) it follows that:

$$S_s = \frac{2}{\sigma}\frac{\bar{r}}{2\bar{r} - \sigma} V_{m'}. \tag{9}$$

To express S_s as a function of V_m (for nitrogen):

$$\frac{V_{m'}}{V_m} = \frac{\rho_g}{\rho_l} = 0.00156.$$

Taking $\sigma = 3.6$ Å (the case of N_2) and expressing S_s (m^2/g), V_m (cm^3, STP):

$$S_s = 4.37 \frac{2\bar{r}}{2\bar{r} - \sigma} V_m \tag{10}$$

Finally:

$$S_0 = 4.37 \frac{2\bar{r}}{2\bar{r} - \sigma} \text{m}^2/\text{cm}^3\text{STP} \tag{11}$$

$2\bar{r}/(2\bar{r} - \sigma)$ is a factor that accounts for the influence of pore radius on the constant S_0.

1.2. Second derivation. A cylindrical shape for the pore is also supposed, and in Fig. 2, a pore with a mean radius is showed.

The area projected by one molecule in the pore wall is a function not only of the diameter of the molecule and of its packing but also of the pore curvature.

The relation between the curved surface of the wall, and the projection of the transverse cross of the molecule is (see Fig. 2):

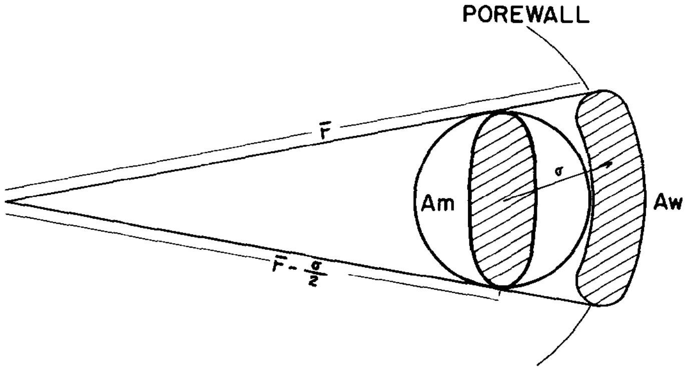

FIG. 2. Projected area of a molecule over the pore wall.

$$\frac{A_w}{A_m} = \frac{\bar{r}}{\bar{r} - (\sigma/2)}, \tag{12}$$

or

$$\frac{A_w}{A_m} = \frac{2\bar{r}}{2\bar{r} - \sigma}. \tag{13}$$

The correction factor caused by the pore wall curvature is found again.

2. Estimation of Errors

Estimation of errors involved when the wall curvature correction factor is missing:

$$S_0 = N_m A_m,$$

usually S_0 is corrected by means of the operation temperature.

Temp (°K)	Saturation pressure (mm Hg)	$S_0 = A_m N_m$ m²/ml (STP)
77.36	760	4.372
77.80	800	4.379
78.33	850	4.388
78.83	900	4.396

Actually the influence of the pore radius which is never taken into account by other authors is really much more important (Fig. 3):

$\bar{r}$(Å)	$S_0 = N_m A_w$	P_{sat} = 760 mm Hg.
150	1.012 × 4.37	
100	1.018 × 4.37	
50	1.037 × 4.37	
25	1.077 × 4.37	
20	1.098 × 4.37	
10	1.219 × 4.37	

3. Example of the Computation of Specific Surface with the Correct Method

The case of a silica obtained by precipitation with potassium metasilicate and sulfuric acid, working at pH 1.5 and heated for 24 hr at 110°C has been examined. This porous solid presents the following values obtained with nitrogen at its normal boiling point.

$$V_p = 0.56 \text{ cm}^3/\text{g} \tag{14}$$

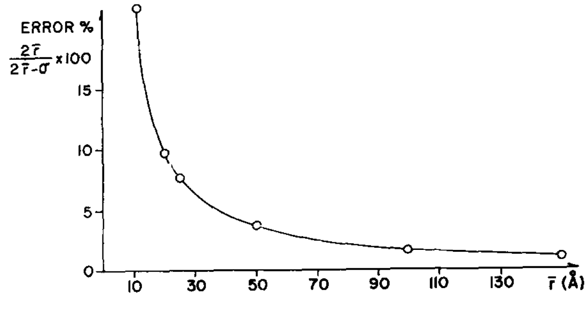

FIG. 3. Error in missing the influence of $\bar{r}$ over S_0.

$$V_m = 92 \text{ cm}^3/\text{g} \tag{15}$$

For that silica the relationship can be proposed:

$$S_s = 4.37 \times \frac{2\bar{r}}{2\bar{r} - 3.6} \times 92, \tag{16}$$

$$S_s = \frac{2V_p \times 10^4}{\bar{r}} = \frac{2 \times 0.56 \times 10^4}{\bar{r}}. \tag{17}$$

Solving those simultaneous equations it is obtained:

$$S_s = 432.0\text{m}^2/\text{g}.$$

with $\bar{r} = 25.92$ Å the correction factor is 1.074. On the other hand the specific area estimated without taking the correction factor into account is:

$$S_{s'} = 402.2\text{m}^2/\text{g}.$$

An error of 7.4% is avoided.

CONCLUSIONS

1. The constant S_0 in the equation:

$$S_s = S_0 V_m,$$

used for the determination of the specific surface area, is a function of the mean pore radius of the porous solid.

2. The errors made when the correction given by Eq. (13) is missing, are of the order of 3.7; 7.7; 9.8 and 21.9% if the mean pore radius is of 50, 25, 20 and 10 Å, respectively.

3. The method "t" involves an error of the same kind, since it is always based on assuming a constant $A_m N_m$, independent of the pore radius.

4. We propose the relationship:

$$S_s = A_m N_m \frac{2\bar{r}}{2\bar{r} - \sigma} V_m = A_w N_m V_m,$$

which accounts for the influence of the pore radius on the area of the pore, covered by one molecule of adsorbate.

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