

When the major catalytic surface is in the interior of a solid particle, the resistance to transport of mass and energy from the external surface to the interior can have a significant effect on the global rate of reaction. Quantitative treatment of this problem is the objective in Chap. 11. It is sufficient here to note that this treatment rests on a geometric model for the extent and distribution of void spaces within the complex porous structure of the particle. It would be best to know the size and shape of each void space in the particle. In the absence of this information the parameters in the model should be evaluated from reliable and readily obtainable geometric properties. In addition to the surface area, three other properties fall into this classification: void volume, the density of the solid material in the particle, and the distribution of void volume according to void size (pore-volume distribution). The methods of measurement of these four properties are considered in Secs. 8-5 to 8-7.

8-5 Determination of Surface Area

The standard method for measuring catalyst areas is based on the physical adsorption of a gas on the solid surface. Usually the amount of nitrogen adsorbed at equilibrium at the normal boiling point (-195.8°C) is measured over a range of nitrogen pressures below 1 atm. Under these conditions several layers of molecules may be adsorbed on top of each other on the surface. The amount adsorbed when one molecular layer is attained must be identified in order to determine the area. The historical steps in the development of the Brunauer-Emmett-Teller method¹ are clearly explained by Emmett.² There may be some uncertainty as to whether the values given by this method correspond exactly to the surface area. However, this is relatively unimportant, since the procedure is standardized and the results are reproducible. It should be noted that the surface area so measured may not be the area effective for catalysis. For example, only certain parts of the surface, the active centers, may be active for chemisorption, while nitrogen may be physically adsorbed on much more of the surface. Also, when the catalyst is dispersed on a large-area support, only part of the support area may be covered by catalytically active atoms. For example, a nickel-on-kieselguhr catalyst was found to have a surface of $205 \text{ m}^2/\text{g}$ as measured by nitrogen adsorption.³ To determine the area covered by nickel atoms, hydrogen was chemisorbed on the catalyst at 25°C . From the amount of hydrogen chemisorbed, the surface area of nickel atoms was calculated to be about $40 \text{ m}^2/\text{g}$. It would be most useful to know surface areas for

¹S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

²P. H. Emmett (ed.), "Catalysis," vol. I, chap. 2, Reinhold Publishing Corporation, New York, 1954.

³G. Padberg and J. M. Smith, *J. Catalysis*, **12**, 111 (1968).

chemisorption of the reactant at reaction conditions. However, this would require measurement of relatively small amounts of chemisorption at different, and often troublesome, conditions (high temperature and/or pressure), for each reaction system. In contrast, nitrogen can be adsorbed easily and rapidly in a routine fashion with standard equipment.

In the classical method of determining surface area an all-glass apparatus is used to measure the volume of gas adsorbed on a sample of the solid material.¹ The apparatus operates at a low pressure which can be varied from near zero up to about 1 atm. The operating temperature is in the range of the normal boiling point. The data obtained are gas volumes at a series of pressures in the adsorption chamber. The observed volumes are normally corrected to cubic centimeters at 0°C and 1 atm (standard temperature and pressure) and plotted against the pressure in millimeters, or as the ratio of the pressure to the vapor pressure at the operating temperature. Typical results from Brunauer and Emmett's work² are shown in Fig. 8-3 for the adsorption of several gases on a 0.606-g sample of silica gel. To simplify the classical experimental procedure a flow method has been developed in which a mixture of helium and the gas to be adsorbed is passed continuously over the sample of solid.³ The operating total pressure is constant, and the partial pressure of adsorbable gas is varied by changing the composition of the mixture. The procedure⁴ is to pass a mixture of known composition over the sample until equilibrium is reached, that is, until the solid has adsorbed an amount of adsorbable component corresponding to equilibrium at its partial pressure in the mixture. Then the gas is desorbed by heating the sample while a stream of pure helium flows over it. The amount desorbed is measured with a thermal-conductivity cell or other detector. This gives one point on an isotherm, such as shown in Fig. 8-3. Then the process is repeated at successively different compositions of the mixture until the whole isotherm is obtained.

The curves in Fig. 8-3 are similar to the extent that at low pressures they rise more or less steeply and then flatten out for a linear section at intermediate pressures. After careful analysis of much data it was concluded that the lower part of the linear region corresponded to complete monomolecular adsorption. If this point could be located with precision, the

¹For a complete description of apparatus and techniques see L. G. Joyner, "Scientific and Industrial Glass Blowing and Laboratory Techniques," Instruments Publishing Company, Pittsburgh, 1949; see also S. Brunauer, "The Adsorption of Gases and Vapors," vol. 1, Princeton University Press, Princeton, N.J., 1943.

²S. Brunauer and P. H. Emmett, *J. Am. Chem. Soc.*, **59**, 2682 (1937).

³F. M. Nelson and F. T. Eggertsen, *Anal. Chem.*, **30**, 1387 (1958).

⁴A description of the operating procedure and the data obtained are given by S. Masamune and J. M. Smith [*AIChE J.*, **10**, 246 (1964)] for the adsorption of nitrogen on Vycor (porous glass).

volume of one monomolecular layer of gas, v_m , could then be read from the curve and the surface area evaluated. The Brunauer-Emmett-Teller method locates this point from an equation obtained by extending the Langmuir isotherm to apply to multilayer adsorption. The development is briefly summarized as follows: Equation (8-3) can be rearranged to the form

$$\frac{p}{v} = \frac{1}{Kv_m} + \frac{p}{v_m} \quad (8-8)$$

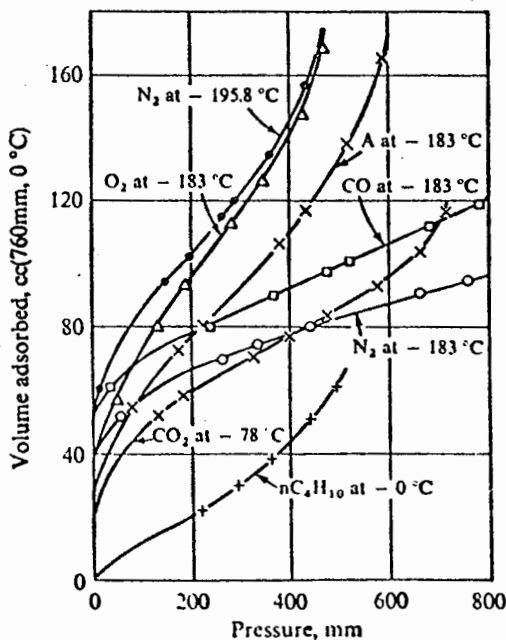
Brunauer, Emmett, and Teller adapted this equation for multilayer adsorption and arrived at the result

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c - 1)p}{cv_m p_0} \quad (8-9)$$

where p_0 is the saturation or vapor pressure and c is a constant for the particular temperature and gas-solid system.

According to Eq. (8-9), a plot of $p/v(p_0 - p)$ vs p/p_0 should give a straight line. The data of Fig. 8-3 are replotted in this fashion in Fig. 8-4.

Fig. 8-3 Adsorption isotherms for various gases on a 0.606-g sample of silica gel [by permission from P. H. Emmett (ed.), "Catalysis," vol. I, Reinhold Publishing Corporation, New York, 1954]



p_0 = vapor pressure of gas adsorbing
 p = partial pressure of gas
 V = volume of gas adsorbed (at p , 0°C , 760 mm)

c = a constant
 v_m = volume of gas that would occupy a monolayer

Of additional significance is the fact that such straight lines can be safely extrapolated to $p/p_0 = 0$. The intercept I obtained from this extrapolation, along with the slope s of the straight line, gives two equations from which v_m can be obtained,

$$I = \frac{1}{v_m c} \quad \text{at } p/p_0 = 0 \quad (8-10)$$

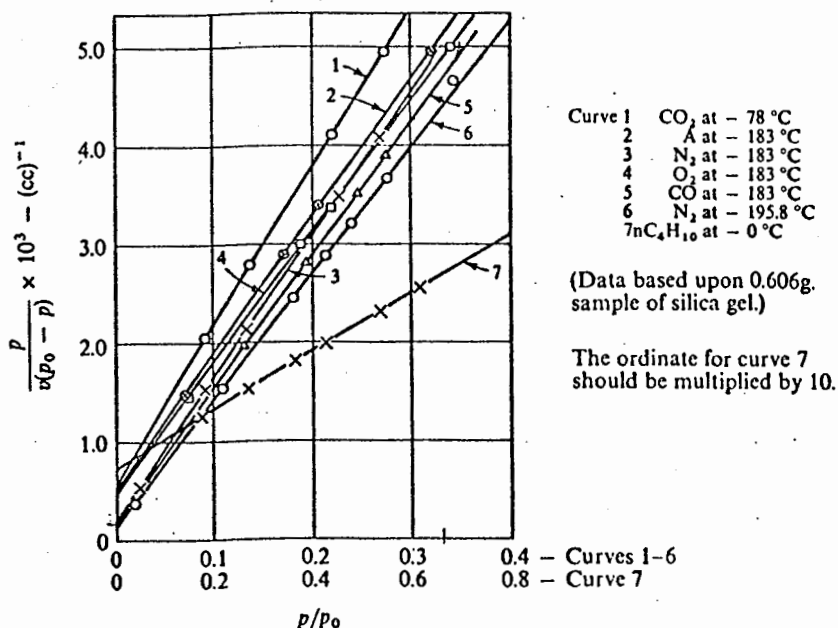
$$s = \frac{c - 1}{v_m c} \quad (8-11)$$

Solving these equations for the volume of adsorbed gas corresponding to a monomolecular layer gives

$$v_m = \frac{1}{I + s} \quad (8-12)$$

The volume v_m can be readily converted to the number of molecules adsorbed. However, to determine the absolute surface area it is necessary to select a value for the area covered by one adsorbed molecule. If this is α , the total surface area is given by

Fig. 8-4 Plot of Brunauer-Emmett-Teller equation [Eq. (8-9)] for data of Fig. 8-3 [by permission from P. H. Emmett (ed.), "Catalysis," vol. I, Reinhold Publishing Corporation, New York, 1954]



$$S_g = \left[\frac{v_m N_0}{V} \right] \alpha \quad (8-13)$$

where N_0 is Avogadro's number, 6.02×10^{23} molecules/mole, and V is the volume per mole of gas at conditions of v_m . Since v_m is recorded at standard temperature and pressure, $V = 22,400 \text{ cm}^3/\text{g mole}$. The term in brackets represents the number of molecules adsorbed. If v_m is based on a 1.0 g sample, then S_g is the total surface per gram of solid adsorbent.

The value of α has been the subject of considerable investigation. Emmett and Brunauer¹ proposed that α is the projected area of a molecule on the surface when the molecules are arranged in close two-dimensional packing. This value is slightly larger than that obtained by assuming that the adsorbed molecules are spherical and their projected area on the surface is circular. The proposed equation is

$$\alpha = 1.09 \left[\frac{M}{N_0 \rho} \right]^{1/2} \quad (8-14)$$

where M is molecular weight and ρ is the density of the adsorbed molecules. The term in brackets represents the volume of one adsorbed molecule. The density is normally taken as that of the pure liquid at the temperature of the adsorption experiment. For example, for N_2 at -195.8°C , $\rho = 0.808 \text{ g/cm}^3$.

In theory, the adsorption measurements can be made with a number of different gases. However, it has been found that even when values of α are calculated from Eq. (8-14) for each gas the results are somewhat different (see Example 8-3). Therefore it has become standard procedure to employ N_2 at its normal boiling point (-195.8°C). The reason for the variation in areas obtained with different gases is not well understood. Nevertheless, if the measurements are carried out with one gas at one temperature, the results for different catalysts may be compared with confidence.

With the value of ρ for N_2 at -195.8°C , the area per molecule from Eq. (8-14) is $16.2 \times 10^{-16} \text{ cm}^2$, or $16.2 \text{ \AA}^2$. If this result is used in Eq. (8-13), along with the known values of N_0 and V , the surface area per gram is

$$S_g = 4.35 \times 10^4 v_m \quad \text{cm}^2/\text{g solid adsorbent} \quad (8-15)$$

Remember in using Eq. (8-15) that it is based on adsorption measurements with N_2 at -195.8°C .

Table 8-2 shows surface areas determined by the Brunauer-Emmett-

¹ P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, 59, 1553 (1937).

Table 8-2 Surface area, pore volume, and mean pore radii for typical solid catalysts

Catalyst	Surface area, m ² /g	Pore volume, cm ³ /g	Mean pore radius, Å
Activated carbons	500-1,500	0.6-0.8	10-20
Silica gels	200-600	0.4	15-100
SiO ₂ -Al ₂ O ₃ cracking catalysts	200-500	0.2-0.7	33-150
Activated clays	150-225	0.4-0.52	100
Activated alumina	175	0.39	45
Celite (Kieselguhr)	4.2	1.1	11,000
Synthetic ammonia catalysts, Fe	...	0.12	200-1,000
Pumice	0.38		
Fused copper	0.23		

SOURCE: In part from A. Wheeler, "Advances in Catalysis," vol. III, pp. 250-326, Academic Press, Inc., New York, 1950.

Teller method for a number of common catalysts and carriers. Calculations of surface areas from adsorption data are illustrated in Examples 8-2 and 8-3.

Example 8-2 From the Brunauer-Emmett-Teller plot in Fig. 8-4 estimate the surface area per gram of the silica gel. Use the data for adsorption of nitrogen at -195.8°C .

Solution From curve 6 of Fig. 8-4, the intercept on the ordinate is

$$I = 0.1 \times 10^{-3} \text{ cm}^{-3}$$

The slope of the curve is

$$s = \frac{(5.3 - 0.1) \times 10^{-3}}{0.4 - 0} = 13 \times 10^{-3} \text{ cm}^{-3}$$

These values of s and I may be substituted in Eq. (8-12) to obtain v_m .

$$v_m = \frac{10^3}{0.1 + 13} \frac{1}{0.606} = 126 \text{ cm}^3/\text{g catalyst}$$

The factor 0.606 is introduced because the data in Fig. 8-4 are for a silica gel sample of 0.606 g, and v_m is the monomolecular volume per gram. For nitrogen at -195.8°C , the application of Eq. (8-15) yields

$$S_g = 4.35(126) = 550 \text{ m}^2/\text{g}$$

Example 8-3 For comparison, estimate the surface area of the silica gel by using the adsorption data for oxygen at -183°C . The density of the liquefied oxygen at -183°C , from the International Critical Tables, is 1.14 g/cm.

$$V_m = 65.4$$

Solution First the area of an adsorbed molecule of O_2 must be calculated from Eq. (8-14):

$$\alpha = 1.09 \left[\frac{32}{(6.02 \times 10^{23}) 1.14} \right]^{\frac{1}{2}} = 14.2 \times 10^{-16} \text{ cm}^2$$

$$1.56 \times 10^{-15}$$

$$1.71 \times 10^{-15}$$

With this value of α the area equation [Eq. (8-13)] becomes

$$S_g = \frac{v_m (6.02 \times 10^{23})}{22,400} 14.2 \times 10^{-16} = 3.8 \times 10^4 v_m \quad \text{cm}^2/\text{g}$$

From curve 4 of Fig. (8-4),

$$I = 0.40 \times 10^{-3} \text{ cm}^{-3}$$

$$s = \frac{(5.4 - 0.4) \times 10^{-3}}{0.38 - 0} = 13.2 \times 10^{-3} \text{ cm}^{-3}$$

Then the monomolecular volume per gram of silica gel is, from Eq. (8-12),

$$v_m = \frac{10^3}{0.4 + 13.2} \frac{1}{0.606} = 122 \text{ cm}^3/\text{g catalyst}$$

Finally, substituting this value of v_m in the area expression gives

$$S_g = 3.8 \times 10^4 (122) = 465 \times 10^4 \text{ cm}^2/\text{g} \quad \text{or } 465 \text{ m}^2/\text{g}$$

The difference in area determined from the N_2 and O_2 data is somewhat larger than expected for these gases. The adsorption curve for N_2 at -183°C gives a value in closer agreement with $550 \text{ m}^2/\text{g}$ (see Prob. 8-1).

8-6 Void Volume and Solid Density

The void volume, or pore volume, of a catalyst particle can be estimated by boiling a weighed sample immersed in a liquid such as water. After the air in the pores has been displaced, the sample is superficially dried and weighed. The increase in weight divided by the density of the liquid gives the pore volume.

A more accurate procedure is the *helium-mercury method*. The volume of helium displaced by a sample of catalyst is measured; then the helium is removed, and the volume of mercury displaced is measured. Since mercury will not fill the pores of most catalysts at atmospheric pressure, the difference in volumes gives the pore volume of the catalyst sample. The volume of helium displaced is a measure of the volume occupied by the solid material. From this and the weight of the sample, the density of the solid phase, ρ_s , can be obtained. Then the void fraction, or porosity, of the particle, ϵ_p , may be calculated from the equation