# ⟨268⟩ POROSITY BY NITROGEN ADSORPTION–DESORPTION

## INTRODUCTION

*Porosity* is a term typically used to indicate the porous nature of solid material and is more precisely defined as the ratio of the volume of accessible pores and voids to the total volume occupied by a given amount of the solid. Closed or inaccessible pores that are isolated from the external surface are excluded from this definition of pore volume. Pores (or voids) may consist of apertures, channels, or cavities within a solid body or spaces between solid particles in a compact or aggregate. Pores exist in a variety of solid materials beyond compacts and aggregates, such as powders and tablets, and their characterization usually involves the determination of the total pore volume or porosity, as well as the pore size distribution. Pores generally are classified by size into the following groups:

- Micropores—less than 2 nm
- Mesopores—2 to 50 nm
- Macropores—greater than 50 nm

The method in *Porosity by Nitrogen Adsorption–Desorption ⟨268⟩* is complementary to that in general chapter *Porosimetry by Mercury Intrusion ⟨267⟩*. Mercury porosimetry may, in principle (in theory), be used with pore diameters from 3 nm to 400 µm but is most applicable in the range from 100 nm to 200 µm. Nitrogen adsorption–desorption may be used to characterize pores smaller than about 300 nm but is most appropriate for the analysis of mesopores and into the low macropore range from 2 to 100 nm.

## APPARATUS

Measurements are most commonly performed using the static volumetric procedure, although dynamic flow methods also may be employed. Users of commercially available equipment should refer to the manufacturer's literature and manual for a description of their particular apparatus. For example, a static volumetric apparatus must provide: evacuation of the system to a pressure of less than 10 Pa, delivery of known volumes of high-purity nitrogen and helium, accurate measurement of pressure and temperature, and a means of cooling the sample to liquid nitrogen temperature.

## MEASUREMENT PRINCIPLE

The adsorption of an inert gas onto solid surfaces at low temperatures is a well-known phenomenon and is the basis for measurement of the surface area of solids (see general chapter *Specific Surface Area ⟨846⟩*). As gas adsorbs to a surface, it can condense into accessible pores. The total pore volume and pore size distribution can be derived from the gas adsorption isotherm, which is the measure of amount adsorbed as a function of adsorbate partial pressure. Adsorption isotherms fall into six general categories, depending on the relative energetics of adsorption and the presence of pores. *Figure 1* shows six general categories of adsorption isotherms.
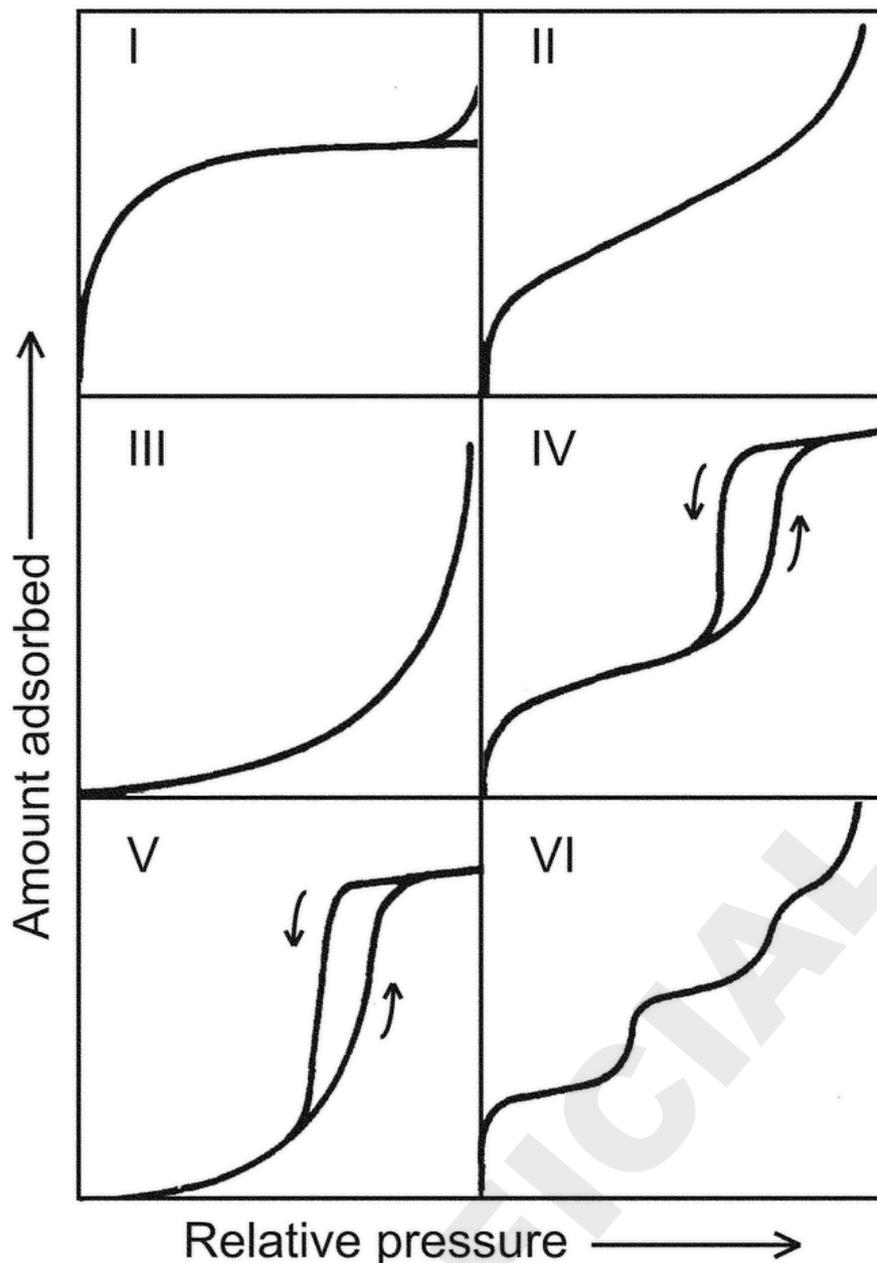
Figure 1. Isotherm Types. [Reproduced with permission and modification from: Sing KSW, Everett DH, Haul RAW, et al. Reporting physisorption for gas/solid systems with special reference to the determination of surface area and porosity (recommendations 1984). *Pure Appl Chem.* 1985;57(4):603–619, *Figure 2*.]

Micropores (pore sizes less than 2 nm) frequently give rise to type I isotherms. Mesopores and macropores normally yield type IV isotherms, but for pores greater than about 100 nm hysteresis may be difficult to observe, thus yielding a type II isotherm. Although some information, such as the total porosity, can be derived for microporous materials, the determination of pore size distributions in that size range is outside the scope of this chapter.

The preferred adsorbate is nitrogen, and the isotherm is determined at liquid nitrogen temperature (77.4 K). Other adsorbates may be used for special purposes but are not discussed in this chapter.

## PROCEDURE

### Sample Preparation

Before analysis, analysts should outgas the sample to remove gases and vapors that may have become physically adsorbed onto the surface. The outgassing conditions must be demonstrated to yield reproducible adsorption–desorption, a constant sample weight, and no detectable physical or chemical changes in the sample. Outgassing of many substances often is achieved by applying a vacuum, by purging the sample in a flowing stream of a nonreactive, dry gas, or by applying an adsorption–desorption cycling procedure. If appropriate, analysts can apply elevated temperatures to increase the rate at which the contaminants leave the surface. Analysts should be cautious when outgassing samples using elevated temperatures to avoid affecting the nature of the surface and the integrity of the sample. If heating is employed, the recommended temperature and time of outgassing should be the minimum needed to achieve reproducible measurement of the adsorption–desorption isotherm.

Analysts should determine the sample mass after outgassing or, alternatively, should determine the mass after the adsorption–desorption measurement. The total surface area of the sample should be greater than 1 m$^2$ and preferably greater than 5 m$^2$.

## Isotherm Measurement

Specific details of the measurement process depend on the procedure used. Analysts should follow the manufacturer's instructions for the particular instrument used. The following description is applicable generally:

- Analysts should determine the saturated vapor pressure of the adsorbate, $p_0$. It is preferable to determine $p_0$ experimentally at the time of measurement, but analysts can use a calculated value.

- Analysts should determine the nitrogen sorption isotherm and should measure the volume adsorbed, $V_a$, at the lowest desired relative pressure ($p/p_0$, the ratio of the measured adsorbate pressure to its saturated vapor pressure).

- Analysts repeat the measurement of $V_a$ at successively higher relative pressure values to the maximum desired relative pressure (generally 0.99). Then they successively decrease the relative pressure to determine sorbed amounts on the desorption portion of the isotherm. Analysts should measure at least 20 points on both the adsorption and desorption segments, covering a relative pressure ($p/p_0$) range of approximately 0.05−0.99. The $p/p_0$ values can be distributed to achieve the best resolution of the pore size distribution. If only the desorption segment is being used to calculate the pore size distribution, fewer points can be used on the adsorption segment.

## DATA ANALYSIS

### Examination of the Isotherm

The isotherm is depicted as a plot of quantity of nitrogen adsorbed (as volume, $V_a$, or moles, $n_a$) vs. $p/p_0$. The isotherm data also can be presented in tabular form. From the graph, determine the isotherm and hysteresis types by comparison to the examples in *Figures 1* and *2*. A type I isotherm is common for microporous materials. A type IV isotherm usually is exhibited by materials that contain mesopores or small macropores.
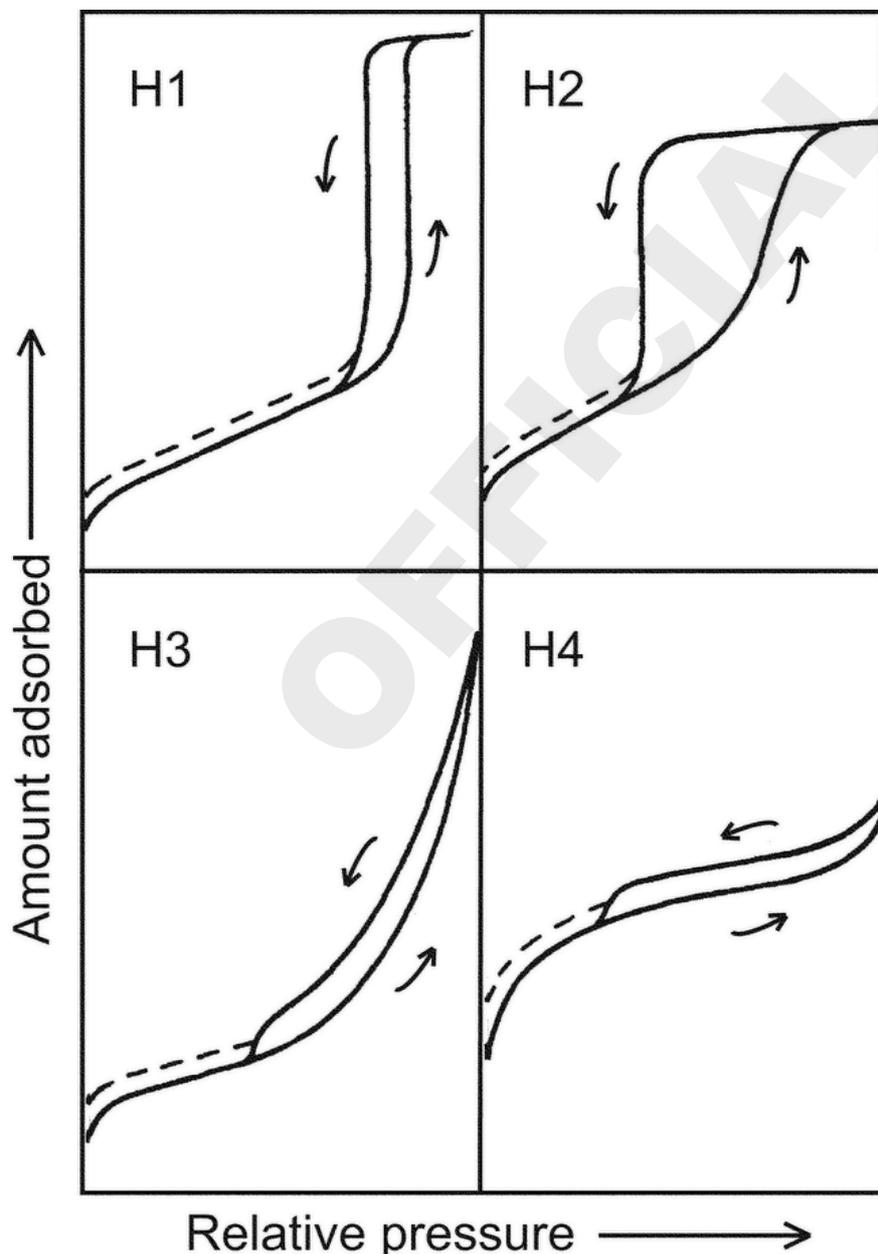
Figure 2. Hysteresis Loop Types. [Reproduced with permission and modification from: Sing KSW, Everett DH, Haul RAW, et al. Reporting physisorption for gas/solid systems with special reference to the determination of surface area and porosity (recommendations 1984). *Pure Appl Chem*. 1985;57(4):603–619, *Figure 3*.]

Constructing a *t*-plot or $\alpha_S$-plot to compare the isotherm of the test sample to that of a reference isotherm also helps to illustrate the presence of micro- and mesoporosity. The reference isotherm may be calculated using a mathematical expression, but it is recommended that an experimentally determined reference isotherm be used when the adsorbent has chemical properties that are similar to those of the test sample.

The *t*-plot method is based on the *t*-curve, which is a plot of the amount of nitrogen adsorbed on the nonporous solid as a function of *t*, the statistical thickness of the adsorbed layer. The *t* value is calculated:

$$t = \frac{n_a \times \delta_a}{n_m}$$

$n_m$ = monolayer amount

$\delta_a$ = thickness of a single molecular layer, usually taken as 0.354 nm for nitrogen

In the $\alpha_S$-plot method, the amount of nitrogen adsorbed by the reference nonporous solid is normalized by using the amount adsorbed at some fixed relative pressure ($n'_{a,x}$), often taken as 0.4. The normalized adsorption $\alpha_S$ (equal to $n_a/n'_{a,x}$) then is plotted against $p/p_0$ to obtain an $\alpha_S$-curve.

The *t*-plot or $\alpha_S$-plot is constructed by plotting the amount of nitrogen adsorbed by the test sample against *t* or $\alpha_S$ for the reference material, rather than $p/p_0$. The conversion of $p/p_0$ to *t* or $\alpha_S$ is carried out by reference to the *t*-curve or $\alpha_S$-curve. The shape of the plot depends on the nature of the porosity present in the test sample, as follows:

1. if the *t*- or $\alpha_S$-plot is linear and passes through the origin, the test sample is nonporous or macroporous
2. if the test sample contains mesopores, the plot shows an upward deviation at the relative pressure corresponding to the onset of capillary condensation in the smallest mesopores
3. if the test sample contains micropores, the plot exhibits a downward deviation because multilayers cannot fully develop within the constricted space inside the micropores.

Some materials contain combinations of pores, which may result in a complex plot that is difficult to interpret. In such cases analysts should be cautious when they analyze the isotherm.

### Calculation of Pore Size Distribution

This analysis is valid only for calculations of the size distributions of mesopores.

Calculation of the pore size distribution is based on the Kelvin equation:

$$r_k = \frac{2 \times \sigma_l \times v_l \times \cos(\theta) \times 10^3}{R \times T \times \ln(p/p_0)}$$

$r_K$ = core radius of the pore (or Kelvin radius) (nm)

$\sigma_l$ = adsorbate (nitrogen) liquid surface tension (N/m)

$v_l$ = molar volume of the condensed adsorbate (nitrogen) (cm$^3$/mol)

$R$ = universal gas constant, 8.3144 $(J \cdot K^{-1} \cdot mol^{-1})$

$T$ = temperature (K)

$\theta$ = adsorbate contact angle (0 for a wetted surface)

For nitrogen, equation 2 reduces to:

$$r_k = \frac{-0.953}{\ln(p/p_0)}$$

The actual pore radius, $r_p$, is calculated from the Kelvin radius by correcting for the thickness, *t*, of the adsorbate on the pore walls. For cylindrical pores, $r_p = r_k + t$, and the pore diameter, $d_p$, is given by $d_p = 2(r_k + t)$. Because of the different geometry of parallel-sided slit-shaped pores, the slit width is given by $r_k + 2t$.

Analysts can calculate the volume pore size distribution using the method of Barrett, Joyner, and Halenda. This model assumes that the pores are rigid and of regular shape (e.g., cylindrical or slit-shaped), micropores are absent, and the pore size distribution does not extend continuously above the largest pores measurable by this procedure, which implies that all of the pores evaluated are filled at the highest relative pressure.

Porosity and pore size distribution calculations that employ the Kelvin equation must be performed using the desorption isotherm. The Kelvin equation was derived for macroscopic systems and is not strictly valid at the molecular scale. Thus, the Kelvin equation relies on an intact meniscus in order to accurately describe experimental phenomena. For the systems discussed in this chapter, this is achieved only for the desorption isotherm. However, for desorption the application of the Kelvin equation at lower pore sizes is limited by the surface tension of the adsorbate. The limit is illustrated by the point of closure of the hysteresis loop in the isotherm. For nitrogen, this point occurs at a

relative pressure of about 0.45, corresponding to a limiting cylindrical pore radius of about 2 nm. Thus the Kelvin equation is not applicable for micropores.

## Calculation of Micropore Volume

If the $t$- or $\alpha_S$-plot indicates the presence of micropores, the micropore volume can be obtained from the intercept of the extrapolated linear portion of the curve.

## Reported Results

Typically reported results may include total pore volume or porosity, micropore volume, median or mean pore diameter, pore size distribution, and pore surface area.

## CALIBRATION AND VERIFICATION OF SYSTEM PERFORMANCE

Analysts should carry out calibration of individual components in accordance with the manufacturer's recommendations. Calibration of pressure transducers and temperature sensors is accomplished with reference to standard pressure- and temperature-measuring devices that have calibrations traceable to national standards. Manifold volume calibration is achieved by appropriate pressure and temperature measurements using constant-temperature volumetric spaces or solids of known, traceable volume.

A certified reference material or locally defined reference material that is traceable to a certified reference material should be tested on a regular basis in order to monitor instrument calibration and performance.

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