CHAPTER 3

POROSITY ESTIMATION
3. POROSITY ESTIMATIONS

Most porous solids such as activated carbons possess micropores, mesopores and macropores. According to IUPAC classification, micropores are pores with widths not exceeding 2 nanometers (nm), mesopores have widths between 2 nm and 50 nm and in macropores the widths exceed 50 nm. Simplest methods for determining pore size and their distribution in porous solids are adsorption-desorption isotherms and mercury intrusion porosimetry. This chapter deals with two methodologies for determining pore size, its distribution, pore volume and surface area of porous polymer supports. The illustrative examples as and when required are taken from the results of the estimation of pore size etc. of the polymers synthesised in the present study.

3.1 MERCURY POROSIMETRY

Mercury porosimetry is the most extensively used tool for the characterisation of various aspects of porous media and powders. This is the simplest and most rapid technique to obtain a kind of 'fingerprint' of a porous medium. Washburn was the first to demonstrate in 1921 this methodology to obtain pore size distribution from the pressure-volume data for mercury penetration into a porous body. Ritter and Drake in 1945 were the first to describe the construction and working of the mercury porosimeter.

3.1.1 Methodology

Mercury behaves as a non-wetting liquid towards most substances. Consequently, it does not normally penetrate into openings and cracks in these substances but does so only when pressure is applied.

In this experimentation, a sample of porous solid is sealed into a vessel tapered into a capillary tube, evacuated, filled with mercury and subjected to increasing pressure. The
mercury penetrates into the pores and its level in the capillary decreases. This decrease is registered relative to the corresponding pressure. A porosimetric curve thus obtained indicates how large a volume of mercury has penetrated into the pores of the sample at a given pressure.

The experimental method of mercury porosimetry is dependent on the wetting or contact angle between mercury and the surface of the solid. This contact angle exceeds 90° for non-wetting liquids but is less than 90° for wetting liquids (Figure 3.1).

Mercury tends not to wet most surfaces because of its high surface tension and must be forced to enter a pore. For a pore of circular cross-section (assuming cylindrical pore geometry) the surface tension acts to force a non-wetting liquid out of the pore. The force $F$ developed due to interfacial tension is the product of the surface tension $\gamma$ of the liquid and the circumference of the pore, of radius ‘$r$’ that is,

$$ F = 2\pi r \gamma $$  \[6\]

Since the interfacial tension acts tangentially to the contact angle, the component of force driving mercury out of the pore becomes

$$ F_{out} = 2\pi r \gamma \cos \theta $$  \[7\]

where $\theta$ is the contact angle. The force driving mercury into the pore can be expressed as the product of the applied pressure $P$ and the cross-sectional area of the pore directed opposite to $F_{OUT}$, ie.,

$$ -F = P \pi r^2 $$  \[8\]

At equilibrium equations [7] and [8] are combined to give
\[ \theta = \text{Contact angle} \]

**FIGURE 3.1:** CONTACT ANGLE IN WETTING AND NON-WETTING LIQUIDS
This is the Washburn equation, the operating equation in mercury porosimetry. The product ‘Pr’ is a constant, assuming constancy of γ and θ. This implies that pressure is inversely proportional to radius. Thus, mercury will intrude progressively into narrower pores with increase in pressure. Ritter and Drake developed one of the earliest high pressure porosimeters and measured the contact angle between mercury and a variety of materials. This was estimated to be between 135 and 142°, with an average value of 140°. Using this value for θ and 0.480 N/m (480 dynes/cm) for γ at room temperature, the Washburn equation is

$$Pr = 2γ\cosθ$$  \[9\]

$$r = \frac{0.736}{P}$$  \[10\]

where P is in Mpa and r in cm and

$$r = \frac{1530}{P}$$  \[11\]

where P is in kg cm\(^{-2}\), r in μm.

3.1.2 Apparatus

The first mercury high pressure porosimeter (1945) made it possible to determine the pore size distribution by measuring the volume of mercury pressed into the pores as a function of the pressure employed. A large variety of designs have been described since then. However, the concepts of the first instrument have been preserved despite various modifications and perfections. The mercury porosimeter consists of three essential components: a) sample container; b) pressure source and c) equipment to monitor the progress of penetration of mercury.
FIGURE 3.2: INTRUSION-EXTRUSION CURVE FOR GMA-DVB COPOLYMER 3-1
The dilatometer, the container wherein mercury is pressed into the sample, is made of glass. Mercury porosimeters are classified into low and high pressure instruments. Low pressure porosimeters operate from zero to atmospheric pressure while high pressure porosimeters work above the atmospheric pressure.

3.1.3 Interpretation

Mercury porosimetry data are obtained as volume of mercury penetrated as a function of the applied pressure. A plot of intruded (or extruded) volume of mercury versus pressure is called a porogram. In routine applications an assumption is made that pores are of cylindrical shapes to transform \( P \) into \( r \) according to equation [10]/[11]. A cumulative or distributive pore size distribution is then obtained.

An intrusion-extrusion curve for a typical polymer examined in the present investigation is shown in Figure 3.2. The output (data and calculations) obtained in a typical mercury porosimetry run consists of the pore size/pore size distribution/pore volume and surface area values, as presented in Table 3.1. Further interpretation is not required.

As seen in Figure 3.2, initial intrusion at very low pressure is due to the penetration into large inter-particle voids. Additional intrusions, which occur at higher pressures, are into the pores within the particles. All porosimetry curves exhibit hysteresis. Thus, the path followed by the extrusion curve on release of pressure does not mirror the intrusion path. At a given pressure, the volume indicated on the extrusion curve is greater than that on the intrusion curve. Thus, at a given volume, the pressure indicated on the intrusion curve is greater than that on the extrusion curve. The hysteresis loop is never closed. The intrusion-extrusion hysteresis is due to two factors: (a) entrapment of mercury after a pressurisation-depressurisation cycle and (b) change in the contact angle of mercury, between the intrusion and extrusion processes. Some mercury is always partially retained by the sample on completion of a first intrusion-extrusion cycle. The subsequent intrusion-extrusion cycles
TABLE 3.1

Mercury Porosimetry Data Sheet

Date: 0-12-72  

Table 3.1

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**BRIEF STATISTICS**

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<td></td>
</tr>
<tr>
<td>4.33E-03 cu-cm/(A-gm)</td>
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<td></td>
</tr>
<tr>
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**MIN.**  

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**MAX.**
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<th>Pressure (Pa)</th>
<th>Volume (m³)</th>
<th>Mass (kg)</th>
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The table above shows the relationship between surface area, pressure, volume, mass, and compression ratio for a given set of conditions.
would continue to show hysteresis, but eventually the entrapment of mercury would cease and
the hysteresis loop would close. The phenomenon of contact angle hysteresis is well docu­
mented. This indicates that the advancing (intrusion) contact angle differs from the
receding (extrusion) angle. It has been seen that hysteresis between the intrusion and extrusion
curves can be altered if adjustments are made to the intrusion and extrusion contact angles.
The intrusion and extrusion curves cannot be brought into coincidence along the entire path
by means of contact angle adjustments since some mercury is permanently retained after the
first depressurisation. However, the effect of mercury entrapment can be eliminated by using
second or subsequent scans wherein the hysteresis loop closes.

In the present study, the pore size/pore size distribution, pore volume etc. of the series
of copolymers synthesised such as GMA-DVB, GMA-PETA, GMA-TMPTA AND GMA-
TRIM were studied by mercury intrusion porosimetry using Autoscan 60 mercury porosimeter
from Quantachrome, U.S.A. The cumulative pressure versus volume data was stored in a
microcomputer and recalled as continuous curves of different functions. The following
quantities were computed from the stored data for each run: (1) Intruded volume, (2) Percent
maximum intruded volume, (3) dV/dP, (4) Dv(r) (volume distribution function), (5) Ds(r)
(surface area distribution function), (6) Surface area.

In addition, (i) Mode and corresponding radius; (ii) Mean pore radius and (iii) Median
pore radius for volume distribution, surface area distribution and pore population distribution
were also obtained. These quantities could be documented either in tabular form or plotted
against pressure/radius.

3.1.3.1 Volume

A plot of the volume of mercury intruded and extruded vs pressure is the only function
output by the computer during a scan. All other functions are available in recall mode after
the completion of a scan.
FIGURE 3.3: PLOT OF PERCENT VOLUME VERSUS RADIUS FOR GMA-DVB COPOLYMER 3-1
3.1.3.2 Percent Volume

Volume is normalised such that the maximum intruded volume is set to 100 percent. A plot of percent volume versus radius noted for GMA-DVB polymer 3-1 is shown in Figure 3.3.

3.1.3.3 \( \frac{dV}{dP} \)

This is the first derivative of the volume vs pressure data. Plots of the derivative of the cumulative curves, \( \frac{dV}{dP} \) vs pressure or radius are often useful for the determination of the radius or pressure at which the maximum volume intrudes or extrudes. A typical curve observed for GMA-DVB copolymer 3-1 is shown in Figure 3.4. This curve is also useful for comparative purposes.

3.1.3.4 \( D_v(r) \)

This volume distribution function is the change in volume per unit interval pore radius. If \( dV \) is the volume of all the pores with radii between \( r \) and \( r + dr \) then

\[
dV = D_v(r) dr \tag{12}
\]

Differentiating the Washburn equation \( Pr = \text{constant} \) we get

\[
P dr + r dP = 0 \tag{13}
\]

Combining equations [12] and [13],

\[
-dV = D_v(r) \frac{r}{P} dP \tag{14}
\]

\[
D_v(r) = \frac{P dV}{r dP} \tag{15}
\]
FIGURE 3.4: PLOT OF $dV/dP$ VERSUS RADIUS FOR GMA-DVB COPOLYMER 3-1
This equation is a convenient means to reduce the cumulative curve to the distributive curve to obtain the pore volume within unit radius interval.

A series of $\frac{dV}{dP}$ values were taken from the cumulative $V$ vs $P$ plot or from raw data. Each $\frac{dV}{dP}$ value was then multiplied by the pressure at the upper end of the interval and divided by the corresponding radius. The resulting value of $D_v(r)$ was plotted against the pore radius for GMA-DVB polymer 3-1 seen in Figure 3.5.

### 3.1.3.5 $D_s(r)$

This surface area distribution function, is the change in surface area per unit interval pore radius.

$$D_s(r) = \frac{dS}{dr}$$

By chain differentiation

$$D_s(r) = \frac{dS}{dV} \frac{dV}{dr}$$  \[17\]

Assuming cylindrical pores

$$\frac{dS}{dV} = \frac{2}{r}$$

$$D_s(r) = \frac{2}{r} \frac{dV}{dr}$$  \[18\]

$$D_s(r) = \frac{2}{r} D_v(r)$$  \[19\]

The plot of $D_s$ against radius is shown in Figure 3.6 for GMA-DVB polymer 3-1.

### 3.1.3.6 Surface area

The surface area is obtained by
FIGURE 3.5: VOLUME DISTRIBUTION FUNCTION FOR COPOLYMER 3-1
FIGURE 3.6: SURFACE AREA DISTRIBUTION FUNCTION FOR GMA-DVB COPOLYMER 3-1
The total pore surface area ‘S’ plotted against radius is seen in Figure 3.7 for GMA-DVB polymer 3-1.

3.1.3.7 Volume Distribution, Surface Area Distribution and Pore Population Distribution Functions

(a) Mode and corresponding radius of the distribution functions: The maximum value of $D_V(r)$ is the mode of the volume distribution function and the corresponding radius is the radius at which it occurs. Similarly, the maximum value of $D_S(r)$ is the mode of the surface area distribution function and the mode of the pore population distribution is the maximum value of the pore population distribution function.

(b) Mean pore radii: These are the arithmetic average pore radii of the distribution functions.

(c) Median pore radii: The median pore radii of the volume distribution, surface area distribution and pore population distribution function are the radii at which there are an equal volume, surface area and equal number respectively, contributed by larger and smaller pores. This is the 50 percent value from the cumulative curve of volume and surface area distribution functions.

3.2 ADSORPTION STUDIES

Although the role of modern techniques in characterising adsorbents and catalysis is ever increasing, classical measurements of adsorption on solids are still very popular and well utilised in surface chemistry. The classical measurements provide information about properties of a solid with respect to the adsorbing species. The classical and still most pertinent measurement in adsorption studies is the adsorption-desorption isotherm,\textsuperscript{99,105} used in the calculation of the surface area of adsorbents.\textsuperscript{105-108}
FIGURE 3.7: PLOT OF TOTAL SURFACE AREA VERSUS RADIUS (GMA-DVB COPOLYMER 3-1)
As indicated, pores are classified as micro, meso and macropores. This classification is somewhat variable because the pore filling mechanisms depend not only on pore shape and size but also on size and structure of the adsorbate molecules.

Adsorption studies aimed at measurements of pore size and distributions generally make use of Kelvin equation.\(^{109}\) This equation relates the equilibrium vapour of a curved surface, such as that of a liquid in a capillary or pore, to the equilibrium pressure of the same liquid on a plane surface. A convenient form of the Kelvin equation is

\[
\ln \frac{P}{P_o} = \frac{2\gamma V}{rRT} \cos \theta
\]

where \(P\) is the equilibrium vapour pressure of the liquid contained in a narrow pore of radius \(r\) and \(P_o\) is the equilibrium pressure of the liquid exhibiting a plane surface. \(\gamma\) and \(V\) are surface tension and molar volume of the liquid respectively and \(\theta\) is the contact angle with which the liquid meets the pore wall.

In the adsorption process the walls of mesopores and macropores are covered layer by layer. Hence, the adsorption process in mesopores and macropores are analogous to that occurring on a non-porous solid surface. In micropores, the entire accessible volume may be regarded as adsorption space so the process is micropore filling.\(^{100}\) In an adsorbent the presence of micropores changes its sorption properties substantially. The superposition of the adsorption forces generated by the opposite walls of the micropores causes an increase in the adsorption potential inside the micropores.\(^{110}\) Consequently, there is an increase in the amount adsorbed in micropores relative to that adsorbed on the mesopore surface.\(^{111}\) The overlapping potentials of the walls in a pore overcome the translational energy of an adsorbate molecule more readily. As a consequence, condensation will occur in a pore at lower pressures than that required normally for an open or plane surface. Thus, condensation will occur first in pores of smaller radii and will progress sequentially into the larger pores as relative pressure
is increased. Finally, at a relative pressure of unity, condensation will occur on surfaces with radius of curvature tending to infinity. Conversely, as the relative pressure is decreased, evaporation will occur progressively out of pores with of radii.

Pore size distributions are generally measured from the desorption isotherm. For nitrogen as the adsorbate at its normal boiling point of 77°K, the Kelvin equation can be written as

$$r_k = \frac{4.15}{\log \frac{r}{r'}}$$

where $\gamma = 8.85 \text{ erg cm}^{-2}$, $V = 34.6 \text{ cm}^3$ for liquid nitrogen

The term $r_k$ is the radius into which condensation occurs at the required relative pressure. This radius, termed as Kelvin radius or the critical radius, is not the actual pore radius since some adsorption would have already occurred on the pore wall prior to condensation, leaving a central core of radius $r_k$. Alternatively, during desorption, an adsorbed film would remain on the pore wall after the evaporation from the central core.

Then, at a thickness $t$ for the adsorbed film during condensation/evaporation, the actual pore radius $r_p$ is

$$r_p = r_k + t$$

Assuming that at a specific value of relative pressure the depth of adsorbed film in a pore is the same as that on a plane surface, one can write

$$t = \left( \frac{V_a}{V_m} \right) \tau$$
where, \( w_a \) and \( w_m \) are the quantity adsorbed and weight corresponding to the BET monolayer.

The above equation indicates that the thickness of the adsorbed film is simply the multiple of the number of layers and the thickness \( \tau \), of one layer regardless of whether the film is in a pore or on a plane surface. The value of \( \tau \) can be calculated by considering the area \( S \) and volume \( V \) occupied by one mole of liquid nitrogen if it were spread over a surface to the depth of one molecular layer. Then,

\[
\tau = \frac{V}{S} = 3.54 \text{ Å}
\]  

[25]

where, \( S = (16.2) (6.023 \times 10^{23}) \text{ Å}^2 \) and \( V = (34.6 \times 10^{24}) \text{ Å}^3 \). Therefore

\[
t = \left( \frac{w_a}{w_m} \right) 3.54 \text{ Å}
\]  

[26]

According to Halsey equation,\(^{14}\) for nitrogen as adsorbate, 't' is given by:

\[
t = 3.54 \left( \frac{5}{2.303 \log \frac{r}{r_c}} \right)^{\frac{1}{3}}
\]  

[27]

The method in Table 3.2 uses data from either the adsorption or desorption isotherm to calculate the pore size distribution. The desorption curve is usually employed excepting when the adsorption curve corresponds to the thermodynamically more stable condition.

Columns 1 and 2 of Table 3.2 encompass data obtained directly from the isotherm. The volumes are normalised for one gram of adsorbent. Column 3, the Kelvin radius, is calculated from the Kelvin equation assuming a zero wetting angle. When nitrogen is used as the
### Table 3.2

**Pore Size Distribution work-sheet**

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<th>11</th>
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<td>P/Po</td>
<td>Vgas (STP) cm³/g</td>
<td>rK</td>
<td>t</td>
<td>rP</td>
<td>Δt</td>
<td>Vgas</td>
<td>ΔVliq</td>
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<td>Vp x 10⁻³ cm³/g</td>
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</table>

Vp = 0.205

SA = 80.6
adsorbate, calculation is made on the basis of equation 22. Column 4, the film depth $t$, is calculated using equation 27, the Halsey equation. Column 5 gives the pore radius $r_p$ obtained from equation 23.

Column 6 and 7, $r_k$ and $r_p$ values are compiled by calculating the mean value in each decrement from successive entries. Column 8, the change in film depth, is calculated by taking the difference between successive values of $t$.

Column 9, $\Delta V_{gas}$, is the change in the adsorbed volume between successive $P/P_o$ values and is the difference between two successive values in column 2. Column 10, $\Delta V_{lq}$, is the volume of liquid corresponding to $\Delta V_{gas}$. The direct conversion of $\Delta V_{gas}$ to $\Delta V_{lq}$ is by calculating the moles of gas, and multiplying this with molar volume of the liquid. At standard temperature and pressure, for nitrogen, this is given by

$$\Delta V_{lq} = \frac{\Delta V_{gas}}{22.4 \times 10^3} \times 34.6 = \Delta V_{gas} (1.54 \times 10^{-3}) \text{ cm}^3$$  \[28\]

Column 11 represents the change in volume of the adsorbed film remaining on the walls of the pores from which the central core has previously evaporated. This volume is the product of the film area $\sum S$ and the decrease in the film depth $\Delta t$. By assuming absence of pores with radii exceeding 950 Å ($P/P_o = 0.99$), the first entry in column is zero (since there is no film area corresponding to previously emptied pores). Subsequent entries in column 11 are calculated as the product of $\Delta t$ for a decrement and $\sum S$ from the row above corresponding to the adsorbed film area exposed by evaporation of the centre cores during all previous decrements.

Column 12, the actual pore volume, is evaluated by recalling that the volume of the liquid (column 10) is composed of the volume evaporated out of the centre cores plus the volume desorbed from the film left on the pore walls. Then,
\[ \Delta V_{\text{liq}} = \pi r_p^{-2} l + \Delta t \sum S \]  

and since

\[ V_p = \pi r_p^{-2} l \]

where \( l \) is the pore length; By combining equations 29 and 30,

\[ V_p = \left( \frac{r_p}{r_k} \right)^2 \left( \Delta V_{\text{liq}} - (\Delta t \sum S)(10^{-4}) \right) \text{cm}^3 \]

Column 13 is the surface area of the pore walls calculated from the pore volume by

\[ S = \frac{2 V_p}{r_p} \times 10^4 (\text{m}^2) \]

with \( V_p \) in cubic centimetres and \( r_p \) in angstroms. This value of \( S \) is summed in column 14. The summation is multiplied by \( \Delta t \) from the following decrement to calculate the film volume decrease in column 11.

The pore size distribution curve is then prepared from the above data for GMA-DVB polymer 3-7 (Figure 3.8). The values \( \Delta V_p, \Delta r_p, \) and \( r_p \) are taken from columns 12, 5 and 7 respectively. The plot of amount gas adsorbed/desorbed for the same polymer versus \( P/P_0 \) (Figure 3.9) shows the closed hysteresis loop.
FIGURE 3.8: PORE SIZE DISTRIBUTION FOR GMA-DVB COPOLYMER 3-7
FIGURE 3.9: PLOT OF VOLUME OF GAS ADSORBED/DESORBED AGAINST P/P₀ (CO PolyMER 3.7)
3.3 POROSIMETRY Vs GAS ADSORPTION

Pore size distribution measurements by nitrogen adsorption, based on the Kelvin equation, are limited to pore radii not exceeding 1000 Å. The measurement of pore size distribution with radii larger than 1000 Å would require accurate determination of relative pressures very close to but less than unity. Mercury porosimetry, with the capability of measuring pore distributions with radii as large as several hundred micrometres, is often employed when it is necessary to exceed the limits of vapour adsorption.

It can be shown thermodynamically that vapour condensation-evaporation and mercury extrusion-intrusion into and out of pores are similar processes operating in the two diametrically opposite extreme ends of pore size. Progressively smaller pores are filled as hydraulic pressure is increased in mercury penetration while progressively larger pores are filled as the adsorbate pressure is increased in vapour adsorption. The two processes occur in reverse since nitrogen and mercury are wetting and non-wetting liquids respectively on most surfaces.

In contrast to gas adsorption-desorption, the isotherms derived from mercury porosimetry data describe only condensation and evaporation processes and not the adsorption. As a result, porosimetry isotherms resemble the upper portion of the gas adsorption-desorption isotherm where the hysteresis loop remains open.

According to the Kelvin equation, a vapour will condense into pores of radius \( r \) when the equality expressed in the equation is realised. Since the wetting angle of nitrogen is at or near zero, the vapour will condense at relative pressures \( P/P_0 \) often substantially below unity.

The molar free energy change \( \Delta G \) associated with the isothermal vapour pressure change from \( P_0 \) to \( P \) is given by

\[
\Delta G = RT \ln \frac{P}{P_0} = \frac{-2yV \cos \theta}{r} \tag{33}
\]
The process of mercury intrusion requires the application of hydraulic pressure $P_h$ to force mercury into the pores for which the molar free energy change is given by

$$
\Delta G = V dP_h = VP_h
$$

Combining equations [33] and [34] results in the Washburn equation

$$
P_h r = -2 \gamma \cos \theta
$$

Equation 30, the governing equation for mercury porosimetry, establishes the pressure required to intrude into a pore of radius $r$

$$
P_h = RT \ln \frac{P}{P_0}
$$

Equation (36), also derived from equation (33) and (34), relates the hydraulic pressure $P_h$ required to force mercury into the pores to the relative pressure $P/P_0$ exerted by the liquid with radius of curvature ‘$r’$, presumed equal to the pore radius. For example, if $\gamma$ and $\theta$ are taken as 480 ergs cm$^{-2}$ and 140° respectively, mercury will intrude into pores with radii 18 Å at a hydraulic pressure $P_h$ of 60,000 psia and the corresponding relative pressure of mercury will be 11.49.

At relative pressures of unity both nitrogen and mercury will penetrate pores of $r$ equal to $\infty$. In case of nitrogen adsorption all pores with $r \leq \infty$ will be filled. In contrast, all pores with $r \leq \infty$ will remain empty in mercury porosimetry.

The two methods generally show reasonable agreement.$^{113,114}$ The most definitive surface area measurements are probably those made by nitrogen adsorption. Comparisons have been made between surface areas measured by porosimetry and gas adsorption$^{115}$ with results ranging from poor to excellent. When the two methods do not agree, it does not imply
the theoretical failure of either one. The difference between the two methods can be used to deduce meaningful information not obtainable by either method. For example, when the surface area calculated from adsorption data is large compared to the area measured by porosimetry, it implies that substantial volume is contributed by pores smaller than those penetrated by mercury at maximum pressure. Pore wall roughness is another factor which leads to slightly larger adsorption areas than those from porosimetry. Slight surface roughness will not alter the porosimetry surface area since it is calculated from the pore volume while the same roughness will be measured by gas adsorption. Ink-bottle shaped pores with a narrow entrance into a wide inner body generate larger surface areas in porosimetry than those from nitrogen adsorption. Intrusion into the wide inner body will not occur until sufficient pressure is applied to force the mercury into the narrow entrance. It will, therefore, appear as if a large volume intruded into narrow pores, generating an excessively high calculated surface area.

It is seen that the condensation-evaporation isotherms from mercury porosimetry are strikingly similar to adsorption-desorption isotherms for porous materials, excepting that the portion below the region of the hysteresis loop is absent. This difference is anticipatable since the two processes occur through differing mechanisms. The pore volume in mercury porosimetry is associated with mass transfer as a liquid or vapour into the pore while in gas isotherms adsorption occurs first on the pore walls.