An Introduction To The Physical Characterization of Materials by Mercury Intrusion Porosimetry with Emphasis On Reduction And Presentation of Experimental Data

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CONTENTS

INTRODUCTION

Mercury intrusion porosimetry is one of only a few analytical techniques that permits an analyst to acquire data over such a broad dynamic range using a single theoretical model. Mercury porosimetry routinely is applied over a capillary diameter range from 0.003 µm to 360 µm— five orders of magnitude! This is equivalent to using the same tool to measure with accuracy and precision the diameter of a grain of sand and the height of a 30-story building.

Not only is mercury porosimetry applicable over a wide range of pore sizes, but also the fundamental data it produces (the volume of mercury intruded into the sample as a function of applied pressure) is indicative of various characteristics of the pore space and is used to reveal a variety of physical properties of the solid material itself.

The information that follows falls into three main categories: I) instrument theory and its application in data collection, II) information derived from reduced data, and III) presentation of the information. A glossary of terms also is included.

Understanding how a fluid behaves under specific conditions provides insight into exactly how a mercury porosimeter probes the surface of a material and moves within the pore structure. This allows one to better understand what mercury intrusion and extrusion data mean in relation to the sample under test and allows one to understand the data outside of the bounds of the theoretical model. It also allows one to make an educated comparison between similar data obtained using other measurement techniques and theoretical models.

The information contained herein pertains for the most part to the general technique of mercury porosimetry without regard to a specific instrument manufacturer or model. However, Micromeritics' AutoPore series of porosimeters is used as a reference, particularly when examples are required and details of data reduction are presented.

SECTION I.
THEORY AND METHOD OF
MEASUREMENT

Introduction

Routine operation of an analytical instrument does not require knowledge of the fundamentals of instrument theory. However, an in-depth understanding of the relationship between the probe and the sample allows one to interpret data outside of the strict limitations of the theoretical model upon which data reduction is based. Although this may have limited relevance for day-to-day quality or process control applications, it is of extreme importance in research work and when developing analysis methods for control applications. For these reasons, this document begins with information about how a non-wetting liquid (specifically, mercury) reacts in seeking equilibrium between internal and external forces at the liquid-solid, liquid-vapor, and liquid-solid-vapor interfaces.

Fluid Dynamics and Capillary Hydrostatics

Note: Supporting information on fluid dynamics and hydrostatics can be found on the Internet at sites (1,2,3) cited in the Reference section of this document.

Consider a drop of liquid resting on a solid surface as shown in Figure 1. The underside of the liquid is in contact with the solid surface. The remainder of the surface of the liquid is in contact with some other fluid above— typically, either its own vapor or air. In this configuration, there are areas of liquid-solid, liquid-vapor, and solid-vapor interfaces. There also exists a liquid-solid-vapor boundary described by a line.
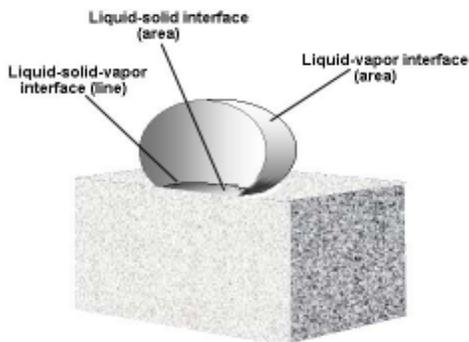
Figure 1. Cross-section of a drop of non-wetting liquid resting on a solid surface. All interfaces are shown.

There is tension in each interface. The liquid-vapor interfacial tension is symbolized g_{l-v}, the liquid-solid g_{l-s}, and the solid-vapor g_{s-v}. The liquid-vapor and solid-vapor interfacial tensions also are referred to as surface tensions. Surface tension has dimensions of force per unit length and acts tangentially to the interface.

The angle of contact of the liquid-vapor surface to the solid-vapor surface at a point on the liquid-solid-vapor interface characterizes the interfacial tension present between the solid, liquid, and vapor. Figure 2 shows five liquids of different surface tensions resting on the same surface material. Different surface energies cause the liquids to assume different contact angles relative to the solid surface. A liquid with low surface tension (low surface energy) resting on a solid surface of higher surface tension will spread out on the surface forming a contact angle less than 90°; this is referred to as wetting. If the surface energy of the liquid exceeds that of the solid, the liquid will form a bead and the angle of contact will be between 90° and 180°; this is a non-wetting liquid relative to the surface.
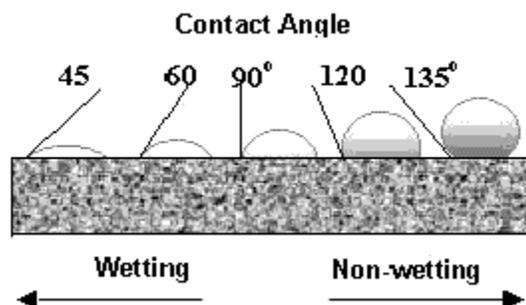
Figure 2. Various liquids resting on a solid surface. The different angles of contact are illustrated for wetting and non-wetting liquids.

Considering any point along the line that describes the liquid-solid-vapor interface and indicating all force vectors on that point results in a diagram similar to those of Figure 3. These illustrations represent a time sequence (top to bottom) showing what happens when a liquid drop first is placed on a horizontal surface until it achieves equilibrium. One can imagine the initial, somewhat spherical drop flattening and spreading over the surface prior to stabilizing. The contact angle begins at about 180°, and the liquid–vapor tension vector at the liquid-solid-vapor interface points at the angle of contact. As the contact angle decreases, the horizontal component of the liquid-vapor tension vector changes in

magnitude and, if the contact angle decreases past 90°, the horizontal component changes sign. When the sum of the solid-vapor tension vector, liquid-solid tension vector, and horizontal component of the liquid-vapor tension vector equal zero, equilibrium occurs and spreading ceases.
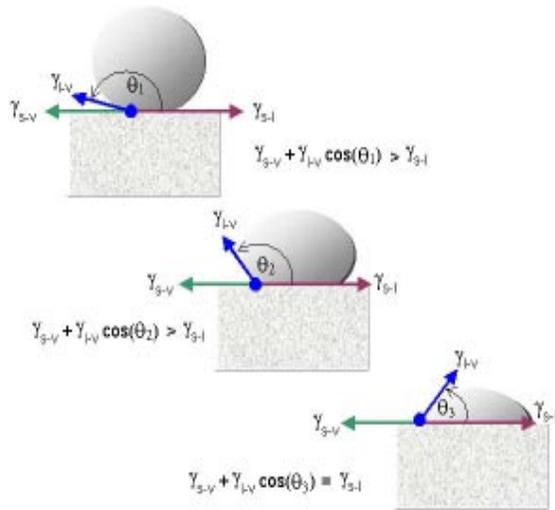
Figure 3. A droplet of liquid placed on a solid surface assumes a contact angle that balances the horizontal force components of the three tension vectors. For this example, è₃ is the angle that results in equilibrium.

The surface of the liquid at the liquid-vapor interface assumes a curvature having two radii, r_1 and r_2, one in the x-z plane, the other in the y-z plane, where the solid surface is the x-y plane. This is another effect of surface tension. The surface molecules act like an elastic membrane pulling the surface into the smallest configuration, ideally a sphere where $r_1 = r_2 = r$. Surface tension contracts the surface and volume until the internal force F_i per unit area of surface A_s is in equilibrium with the external forces on the same surface element. Since pressure, P, is force per unit area (F/A), equilibrium can be expressed in terms of internal and external pressures. From the equations of Young and Laplace for spherical surfaces, the difference in pressure across the surface is

$$P" - P' = \gamma(1/r_1 + 1/r_2) = 2\gamma/r \quad (1)$$

where P" is the pressure on the concave side, P' the pressure on the convex side, g the liquid-vapor surface tension, and, since it is a spherical surface, $r_1 = r_2$.

Interfacial tensions also cause liquids to exhibit capillarity. If one end of a capillary tube is forced to penetrate the vapor-liquid surface from the vapor side, a wetting liquid spontaneously enters the capillary and rises to a level above the external liquid-vapor interface. A non-wetting liquid resists entering the capillary and that a level always below the external liquid-vapor level. In other words, a non-wetting liquid must be forced to enter a capillary.

Why does a non-wetting liquid resist entry into a capillary? Inside the capillary and along the line describing the vapor-liquid-solid boundary, the liquid-solid interface assumes an angle that results in equilibrium of forces. The contributing forces are those of cohesion between the liquid molecules, and the force of adhesion between the liquid molecules and the walls of the capillary. The liquid-vapor interface in the capillary (the meniscus) is concave for a wetting liquid and convex for a non-wetting liquid. In summary, there are three physical parameters needed to describe the intrusion of a liquid into a capillary: a) the interfacial tension (surface tension) of the liquid-vapor interface, hereafter symbolized simply by g, b) the contact angle q, and c) the geometry of the line of contact at the solid-liquid-vapor boundary. For a circular line of contact, the geometry is described by pr², where r is the radius of the circle or capillary.

Washburn (4) in 1921 derived an equation describing the equilibrium of the internal and external forces on the liquid-solid-vapor system in terms of these three parameters. It states concisely that the pressure required to force a non-wetting liquid to enter a capillary of circular cross-section is inversely proportional to the diameter of the capillary and directly proportional to the surface tension of the liquid and the angle of contact with the solid surface. This physical principal was incorporated into an intrusion-based, pore-measuring instrument by Ritter & Drake in 1945 (5). Mercury is used almost exclusively as the liquid of choice for intrusion porosimetry because it is non-wetting to most solid materials.

Washburn's equation, upon which data reduction is based, assumes that the pore or capillary is cylindrical and the opening is circular in cross-section. As has been stated, the net force tends to resist entry of the mercury into the pore and this force is applied along the line of contact of the mercury, solid, and (mercury) vapor. The line of contact has a length of 2pr and the component of force pushing the mercury out of the capillary acts in the direction cosq (see Figure 4), where q is the liquid-solid contact angle. The magnitude of force tending to expel the mercury

5

is
$$F_E = 2\pi\, r\gamma\, \cos\theta \qquad (2)$$
where γ is the surface tension.

An external pressure on the mercury is required to force its entry into the pore. The relationship between force (F) and pressure (P) is P = F/area. Solving for force gives
$$F_I = \pi\, r^2 P \qquad (3)$$

Where $\pi\, r^2$ is the cross-sectional area of the pore opening.
Balancing the intrusion and extrusion forces results in the Washburn equation
$$-2\pi r\gamma\cos\theta = \pi r^2 P \qquad (3)$$

or, in terms of diameter D,
$$-\pi D\gamma\cos\theta = (\pi D^2 P)/4 \quad (4)$$

The relationship between applied pressure and the minimum size pore into which mercury will be forced to enter is
$$D = -4\gamma\cos\theta/P \qquad (5)$$

For a given liquid-solid system, the numerator is constant, providing the simple relationship expressing that the size of the pore into which mercury will intrude is inversely proportional to the applied pressure. In other words, mercury under external pressure P can resist entry into pores smaller than D, but cannot resist entry into pores of sizes larger than D. So, for any pressure, it can be determined which pore sizes have been invaded with mercury and which sizes have not.
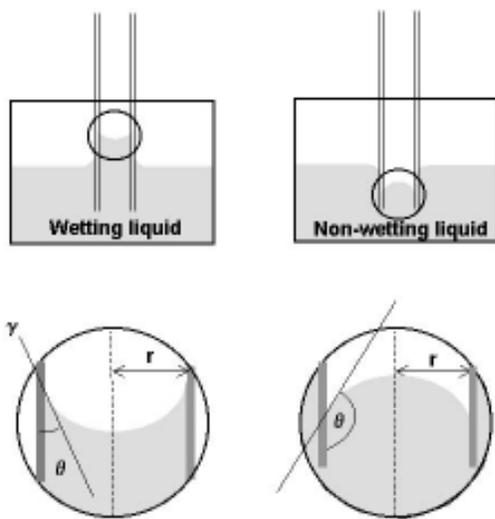
Figure 4. Capillary action of a wetting and non-wetting liquid relative to the walls of a capillary. The g indicates the direction of the interfacial tension (force) vector.

Collecting Experimental Data

A typical mercury intrusion porosimetry test involves placing a sample into a container, evacuating the container to remove contaminant gases and vapors (usually water) and, while still evacuated, allowing mercury to fill the container. This creates an environment consisting of a solid, a non-wetting liquid (mercury), and mercury vapor. Next, pressure is increased toward ambient while the volume of mercury entering larger openings in the sample bulk is monitored. When pressure has returned to ambient, pores of diameters down to about 12 mm have been filled. The sample container is then placed in a pressure vessel for the remainder of the test. A maximum pressure of about 60,000 psia (414 MPa) is typical for commercial instruments and this pressure will force mercury into pores down to about 0.003 micrometers in diameter. The volume of mercury that intrudes into the sample due to an increase in pressure from P_i to P_{i+1} is equal to the volume of the pores in the associated size range r_i to r_{i+1}, sizes being determined by substituting pressure values into Washburn's equation, Eq. 5.

The measurement of the volume of mercury moving into the sample may be accomplished in various ways. A common method that provides high sensitivity is to attach a capillary tube to the sample cup and allow the capillary tube to be the reservoir for mercury during the experiment. Only a small volume of mercury is required to produce a long 'string' of mercury in a small capillary. When external pressure changes, the variation in the length of the mercury column in the capillary indicates the volume passing into or out of the sample cup. For example, a capillary of 1 mm radius requires only 0.03 cm^3 of mercury to produce a mercury column 1 mm in length. Therefore, volume resolution of 0.003 cm^3 easily could be obtained visually from a scale etched on the capillary stem. However, electronic means of detecting the rise and fall of mercury within the capillary are much more sensitive, providing even greater volume sensitivity down to less than a microliter.

The measurement of a series of applied pressures and the cumulative volumes of mercury intruded at each pressure comprises the raw data set. A plot of these data is called the intrusion curve. When pressure is reduced, mercury leaves the pores, or extrudes. This process also is monitored and plotted and is the extrusion curve. According to the shape of the pores and other physical phenomena, the extrusion curve usually does not follow the same plotted path as the

intrusion curve. Therefore, the intrusion curve and extrusion curve contain different information about the pore network.

When to collect the data point is an important consideration when measuring intrusion and extrusion characteristics. Since the intrusion process involves moving a mass of mercury into a confined pore space, the process is not instantaneous as exemplified by the Hagen-Poiseuille law

$$Q = V/t = (\pi r^4/8\eta)(\Delta P/l) \qquad (6)$$

where Q = flow of the liquid, V the volume of liquid, t time, r the capillary radius, η the liquid viscosity and $\Delta P/l$ the pressure drop per unit length of capillary.

However, long and tortuous pore channels result in smaller Q values, therefore requiring more time to fill the same volume as would be the case for pore systems having higher Q values. To obtain highly resolved and highly accurate data, the intrusion process must be allowed to equilibrate before changing pressure and probing the next smaller-sized pore class. Expressed another way, high-resolution data collection, particularly in the small pore size range, requires a pressure step, that is, pressure is raised to the next pressure, then held until flow ceases. Scanning mode, in which pressure is continually changed, is best employed for very large pores or for screening purposes.

Measurement Transducers

From the above discussion, it is clear that a mercury porosimeter measures only applied pressure and the volume of mercury intruded into or extruded from the sample bulk. Pressure measurements are obtained by pressure transducers that produce an electrical signal (current or voltage) that is proportional to the amplitude of the pressure applied to the sensor. This analog electrical signal is converted into digital code for processing by the monitoring computer.

The transducer that detects mercury volume is integrated into the sample holder assembly as previously exemplified and shown in Figure 5.
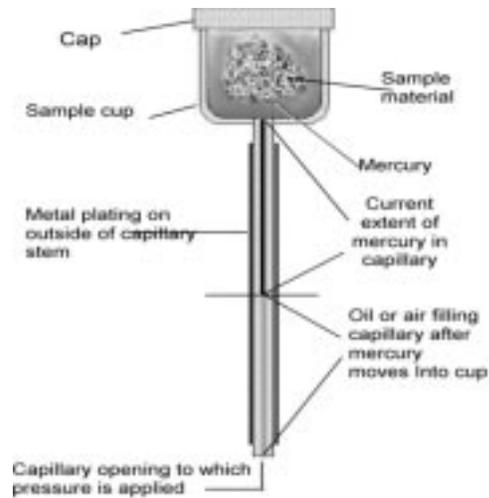
Figure 5. Cross-section of a penetrometer in which pressure has forced some mercury into the pores of the sample and about 50% of the stem capacity has been used.

The sample cup has a capillary stem attached and this capillary serves both as the mercury reservoir during analysis and as an element of the mercury volume transducer. Prior to the beginning of each analysis, the sample cup and capillary are filled with mercury. After filling, the main source of mercury is removed leaving only the mercury in the sample cup and capillary stem, the combination being referred to as the penetrometer. Pressure is applied to the mercury in the capillary either by a gas (air) or a liquid (oil). The pressure is transmitted from the far end of the capillary to the mercury surrounding the sample in the sample cup.

The capillary stem is constructed of glass (an electrical insulator), is filled with mercury (an electrical conductor), and the outer surface of the capillary stem is plated with metal (an electrical conductor). The combination of two concentric electrical conductors separated by an insulator produces a co-axial capacitor. The value of the capacitance is a function of the areas of the conductors, the dielectric constant of the insulator, and other physical parameters. In the case of this particular capacitor, the only variable is the area of the interior conductor as mercury leaves the capillary and enters the sample voids and pores, or as it moves back into the capillary when pressure is

reduced. This is mechanically analogous to a mercury thermometer in which case mercury moves in and out of a calibrated capillary from a large bulb at one end. A small volume of mercury entering or leaving a small capillary causes the length (and area) of the mercury column to change significantly, thus providing volume-measuring sensitivity and resolution. In the case of the thermometer, the change in volume is proportional to the change in temperature by the coefficient of volumetric expansion of mercury.

The capacitance value of the stem is monitored by a capacitance detector that, similar to the pressure transducer electronics, produces an electrical signal that is proportional to capacitance. Capacitance measurements are transformed into volume measurements by knowledge of the diameter of the precision capillary and the equation governing coaxial capacitors.

SECTION II.

OBTAINING INFORMATION ABOUT THE SAMPLE MATERIAL

PART A. Information Obtained Using Volume and Mass Measurements Only

Part A discusses characteristics of the sample that can be deduced directly from the intrusion volumes combined with physical properties of the sample and system. Detailed Pressure data are not required, nor is Washburn's equation.

Total Pore Volume

Total pore volume is the most direct determination of a physical property by mercury intrusion, involving only the volume of mercury entering the sample bulk and not requiring Washburn's equation or a pore model. At the lowest filling pressure, intrusion is considered nil and no pore volume of interest has been filled. Pressure is increased to maximum; at this pressure mercury has been forced into all voids of the sample accessible to the mercury at maximum pressure. The volume of mercury required to fill all accessible pores is considered the total pore volume. Dividing this value by the mass of the sample gives total specific pore volume in units of volume per unit mass.

Material Volume and Density

The concepts of volume and density seem simple at first consideration. However, they become complex when an attempt is made to rigorously define each term. The Glossary section of this document con-

tains various definitions. For a more complete discussion of density and volume, refer to Micromeritics' publication, "Volume and Density for Particle Technologists."(6)

Bulk and Envelope Volume and Density: Bulk volume (as applied to a collection of pieces) is the sum of the volumes of the solids in each piece, the voids within the pieces, and the voids among the pieces. Envelope volume (as applied to a single piece) is the volume of a particle or monolith as would be obtained by tightly shrinking a film around it. Therefore, it is the sum of the volumes of the solid components, the open and closed pores within each piece, and the voids between the surface features of the material and the close-fitting imaginary film that surrounds the piece. Bulk and skeletal densities follow from dividing the respective material mass by volume.

Mercury porosimetry tests in general incorporate the majority of steps in Archimedes' displacement method for volume determination. Including the remaining steps requires additional weights otherwise not necessary for pore characterization. Examples of density determinations are given below. Powdered and solid (monolithic) forms of sample materials are considered separately because of a slight but important difference between volumes determined for a solid object compared to that of a finely divided powder.

Assume, then, that two samples are to be analyzed, one a solid piece of irregularly shaped material, and the other a quantity of powder, both of known mass. Prior to the tests, empty sample containers are weighed, filled with mercury, and then weighed again. From these measurements and the density of mercury, the exact volume of each container is calculated. After the samples have been loaded into the containers and the containers refilled with mercury, the mercury surrounds the samples. Being a non-wetting liquid with only atmospheric pressure applied, it does not enter small indentions, cracks, and crevices on the surface nor into pores within the structure of the material. In the case of fine powders, mercury does not invade the interparticle voids.

The weight of the surrounding mercury in each case is calculated from values obtained by reweighing the filled sample container and subtracting the weight of the empty sample container and sample. Mercury volume follows from density and weight. The differ-

8

ence in volumes of mercury in the sample container before and after introducing the sample is equal to the bulk volume (in the case of the solid piece), or envelope volume (in the case of the powder). Whether the term 'bulk' or 'envelope' applies depends on the sample form (powder, single piece, granules, etc.) as well as the applications-specific definitions of these terms.

Skeletal and True Volume and Density: A pore may have access to the surface (open pores), or may be isolated from the surface (closed or blind pores). Skeletal volume, as applied to discrete pieces of solid material, is the sum of the volumes of the solid material in the pieces and the volume of closed pores within the pieces. True volume is the volume only of the solid material, excluding the volume of open pores and closed pores. Skeletal and true densities follow from dividing the respective material mass by volume.

If a sample contains both open and closed pores, at maximum applied pressure, only open pores in the sample are filled with mercury. The volume of mercury intruded into the pores subtracted from the bulk or envelope volume of the sample gives its *skeletal volume*. The volume measured is the *true volume* if the sample contains no blind pores and all pore space is filled. Finely grinding materials with closed pores (when appropriate) may allow true volume and density also to be determined. If so, then the volume measurements obtained prior to and after grinding provide a means for obtaining the total volume of closed pores by subtracting true volume from skeletal volume.

If the sample contains pores smaller than the minimum pore size into which mercury can intrude at maximum instrument pressure, then skeletal and true volumes cannot be obtained accurately. This may represent a small, perhaps insignificant, volume percent when using an instrument capable of generating 60 kpsia (414 MPa). For these samples, volumes determined by gas pycnometry are smaller than those obtained by mercury porosimetry because gases such as helium and nitrogen can penetrate into micropores where mercury cannot. The difference in skeletal density obtained by mercury porosimetry and by gas pycnometry serves as a good approximation of pore volume in the range from essentially the size of the gas molecule to the lower size represented by the highest pressure obtained by mercury porosimetry.

When measuring volume (density) by mercury porosimetry, it should be recognized that the value obtained is pressure-dependent up to the pressure at which all particle voids and pores are filled. The pressure required for total pore filling may be only several thousand psi, but may require the full pressure range of the instrument. At higher pressures, one must be aware of material compressibility, which will reduce the reported skeletal volume. More information about compressibility is presented in a subsequent section.

Interstitial Void Volume

Interstitial void volume, sometimes called inter-particle void, is the space between packed particles. Such voids were taken into consideration in the definition of envelope volume, above. These voids typically are larger than voids in the individual particles and therefore fill at lower pressure. Being larger, they also hold more mercury than particle pores. This means that the rate of intrusion of mercury with increasing pressure is greater when filling the interstitial void than when filling pores within the sample material. The completion of interparticle void volume filling is indicated by an abrupt change in filling rate observed on the intrusion curve. The total volume of the interparticle voids is the volume of mercury intruded at the inflection point.

Percent Porosity and Percent Porosity Filled

Knowing the bulk or envelope volume (V_B or V_E) of a sample and total porosity (V_{Pt}) allows percent porosity to be calculated by the simple relationship

$$P\% = (V_{Pt}/V_*) \times 100\%. \qquad (7)$$

The type of volume used in the equation for V_* determines what volumes are considered 'porosity.' Volumes associated with interstitial voids and with porosity can be differentiated as discussed previously.

In some applications, it is desired to know what percent of total porosity has been filled (or remains unfilled, or has emptied) at a certain pressure or pore size boundary. This information also is readily available from mercury porosimetry data since, once total intrusion volume (total porosity) is known, the cumulative intrusion scale can be represented in units of percent porosity.

PART B. INFORMATION OBTAINED BY APPLICATION OF WASHBURN'S EQUATION

The characteristics of a sample discussed in Part A, with the exception of percent porosity filled at a

pore size boundary, are not dependent on any geometrical pore model. When the sizes of pores are to be determined and associated with volume determinations, Washburn's equation and a pore model are required. Characteristics that require models are discussed in Part B.

Pore Volume Distribution by Pore Size
Rather than pumping the system immediately to maximum pressure as in the example of obtaining total pore volume, pore size distribution analyses achieve maximum pressure by a series of small pressure steps or by controlled-rate scanning. In step mode, pressure and volume are measured after intrusion (or extrusion) equilibration is achieved. The cumulative intrusion volume of mercury at each measured pressure is determined by subtracting the volume of mercury remaining in the stem from the original volume.

Applying Washburn's equation to each measured pressure provides the pore size associated with each pressure, that is, the pore size class interval boundaries. In the great majority of cases and in the form of Washburn's equation derived and presented as Eq. 5, the pore is considered to be a right circular cylinder.

The volume of mercury intruded as the result of each pressure step is the difference between the respective cumulative intrusion volumes. This value and the associated pressure (pore size) values yield a table of pore size intervals and incremental volumes associated with each interval. This is sufficient data for a bar graph of pore volume versus size class. For a continuous curve, only a single size value is required to represent the size class. This value may be the upper or lower size boundary or some representative size between the two boundaries (the average size, for example).

Pore Area and Number of Pores
Since the Washburn model is based on cylindrical capillaries, the pore shape is assumed to be cylindrical with a circular opening. Therefore, the equivalent cylindrical pore size is obtained from the data. In principle, any pore opening geometry (cavity cross-section) is applicable as long as the equation is known for equilibrium between the external pressure applied over the spanned area of the opening and for the resistive force produced by interfacial tension around the perimeter of the opening (the solid, liquid, vapor interface).

A cylindrical pore model is used almost exclu-

sively in practice. From this model, pore wall area is easily determined from incremental pore volume V_{Iii} by the equation

$$A_{Wi} = D_i/4V_{Ii} \qquad (8)$$

where D_i is the representative diameter for the size class (the average class diameter, for example). A certain incremental pore volume and diameter implies a pore length L since the relation between the length, diameter, and volume of a cylinder is

$$L = 4V/\pi D^2 \quad (9)$$

If a representative diameter is combined with a representative pore length (thickness of the sample, for example), then the number of pores in the size range can be calculated because each pore would have a specific volume, V_{Pi}, and the total volume of all pores in the class is known. The number of pores of a specific size, then, is

$$N = V_{Ii}/V_{Pi} \quad (10)$$

Rootare and Prenzlow (7) take a modeless approach to obtaining surface area information from mercury porosimetry curves. Their calculations begin with an expression of the reversible work required to immerse in mercury a unit area of a solid surface. That expression is simply the difference in the surface tension of the solid-vacuum interface ($\gamma_{s\text{-}v}$) and the interfacial tension of the solid-mercury interface ($\gamma_{s\text{-}l}$), which reduces to $\gamma_L \cos\theta$, where γ_L is the surface free energy of liquid mercury *in vacuo* and θ is the contact angle between the mercury and solid surface. Differentiation over area (a) gives

$$dW = \gamma_L \cos\theta \, da \quad (11)$$

In a porosimeter, the work is supplied by pressure P forcing a volume V of mercury into a pore, therefore work is PdV. Substitution into Eq. 11 and subsequent integration yields

$$a = -\int PdV \, (\gamma_L \cos\theta)^{-1} \qquad (12)$$

PART C. INFORMATION OBTAINED BY APPLICATION OF SPECIAL OR MULTIPLE MODELS
Mercury porosimetry has been employed for decades to characterize sample materials in regard to the physical parameters described in Parts A and B, above. More recently, theoretical models of mercury intrusion and extrusion mechanisms have been introduced allowing additional information about the sample material to be extracted. These methods of data reduction are the subject of this part.

Particle Size Distribution

In 1965, Mayer and Stowe (8) published a paper expanding the work of Frevel and Kressley (9) on the mercury breakthrough pressure required to penetrate a bed of packed spheres and the subsequent filling of the interstitial void. This work relates particle size to breakthrough pressure. Later work by Pospech and Schneider (10) led to a method for determining the size distribution of particles from the intrusion data in the range of interstitial filling.

This method is based on models of penetration of fluids into the void spaces of a collection of uniform solid spheres packed in a regular manner. The forces resisting penetration of mercury between particles originates from interfacial tensions just as with penetration of mercury into capillaries. However, the geometric model is considerably different and therefore is not described by the Washburn equation of equilibrium. The simplest geometry exists when the particles are monosized spheres and the shapes of the void necks and void cavities of such a system are exemplified in Figure 6. The figure shows the range of angular relationships between spheres centered at W, X, Y, and Z in a plane section.
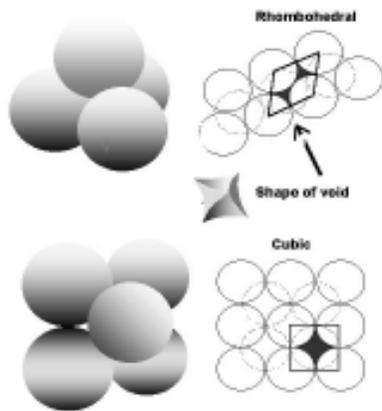
Figure 6. Ordered packing of spheres with cross-sectional view of the shapes of mercury filling the resulting voids. Also shown is the 3-dimensional shape of the void in a rhombohedral packing.

Regardless of the actual particle shape, the particle size distribution derived from this method is the size distribution of spheres that, when applied to the mathematical model, most closely reproduces the experimental penetration data. The size unit, then, is 'equivalent spherical size.' How closely the results compare to that obtained by other methods of particle sizing depends largely on how closely the sample material conforms to the model of closely packed spheres.

Pore Cavity to Pore Throat Size Ratio

For many materials, porosity is composed of a network of interconnected voids of various sizes. Small pores at the surface may connect to large pores within the material; the openings are referred to as pore throats and the spaces within the material as pore cavities. There are numerous methods for extracting pore shape information from mercury injection data. These often are based on specific pore models and may require some knowledge of the pore structure in order to select the appropriate method. A few of these methods are discussed here.

Most pore shape evaluation methods are based on the hypothesis that hysteresis in mercury porosimetry is attributable to pore shape. Indeed, if each pore were a simple, uniform cylinder and the intrusion and extrusion contact angles are known and applied, one would expect there to be no hysteresis since the intrusion and extrusion processes both are controlled by the same mechanism and known parameters. However, hysteresis loops of various shapes often are observed and many do not close when pressure is reduced from some elevated value to ambient. This is attributed to large cavities being interconnected by smaller pore throats. This applies even if the shape of the throats and cavities are cylindrical. Although large pores fill at low pressures, a large cavity connected to the surface by a small throat cannot fill until the pressure is sufficient to fill the smaller connecting throat. Upon decompression, the small throat empties at the same pressure at which it filled, but the large cavity behind the throat remains filled because the internal forces in this volume of relatively large radius is insufficient to overcome the external forces at the current pressure (see Section I). The pore will empty at the lower pressure associated with its radius, or it may not empty at all if the path to the surface is composed of pores of inappropriate sizes.

So, intrusion of mercury into a cavity is controlled by the size of the pore throat radius while the radius of the cavity and its connectivity controls extrusion of mercury from the cavity. A way to characterize the relationship between pore throat and cavity existing in a material is by the ratio of these sizes and is calculated in the following manner.

Assume that at some pressure P_x relating to pore size R_x that V_x cm³ of mercury is contained by pores in the sample. Intrusion continues to pressure P_z at which all pores are filled (V_z). Then, pressure is reduced and extrusion begins. If there is hysteresis

(as is typical), pressure must fall to a value lower than P_x, say P_w, before sufficient mercury extrudes to reduce the volume of mercury within the sample again to V_x. The pore size that relates to P_w is R_w, and this is the cavity size that is paired with throat size R_x; the pore throat to pore cavity size ratio, then, is R_x/R_w.

Intrusion volume is expressed in terms of fraction of total porosity filled in order to normalize data for sample-to-sample comparisons. The fraction of porosity filled is the ratio of the cumulative intrusion volume at any point to the total intrusion volume. The pore cavity to pore throat ratio method does not relate the cavity size to the size of the throat through which it was filled; rather it relates the fraction of porosity filled to the pore sizes that control this state during intrusion and extrusion.

The Distribution of Pore Cavity Sizes Associated With a Pore Throat Size

Reverberi and Ferraiolo (11) devised a means by which to determine the distribution of cavity sizes connected to a pore throat of a specific size. They constructed a pore model that relates hysteresis solely to the existence of inkwell- shaped pores. An inkwell-shaped pore has a cylindrical pore throat (radius R_1) that connects to a larger cylindrical pore cavity (radius R_2).

The test is performed first by allowing intrusion to occur up to maximum pressure P_z, thereby filling all throats and cavities from size R_z (at minimum pressure) to R_a (at maximum pressure) with V_z units of mercury. The intrusion curve is a record of cumulative intrusion at each point in the pressure ramp. Pressure is then lowered a few percent to some sub-maximum pressure P_y that corresponds to capillary size R_y. This empties only pores and pore cavities with diameters between R_z and R_y. The difference in the cumulative intrusion observed at P_y on the intrusion branch and P_y on the extrusion branch is the volume of cavities with sizes greater than R_y. Pressure is increased again to P_z. The intrusion curve will not take the same path as the original intrusion curve if mercury was trapped since these pores already are filled. Pressure is reduced from P_z to a pressure P_x where $P_x<P_y<P_z$. The total intruded volume remaining in the pore space is recorded. Pore throats and cavities in the size range R_x to R_z empty. The pressure is raised again to maximum. The intrusion path retraces neither path P_a to P_z nor path P_y to P_z because a different set of pores is being filled.

12

The pressure increased again to maximum, reduced to P_w, raised to maximum, reduced to P_v, and so on until the range of interest is sampled. The data thus obtained are reduced to yield a three-dimensional data set providing the distribution of pore cavity volumes versus cavity sizes behind each of a series of pore throat sizes.

Material Permeability and the Conductivity Formation Factor

Permeability is the inherent ability of a porous medium to transmit a fluid and is a property of the material. It relates to porosity in the sense that it is the "proportionality constant" linking fluid flow rate to applied pressure across a porous medium. There have been many attempts over the years to relate permeability to some relevant microstructurally-defined length scale. (12) The work of Katz and Thompson (13, 14) provides an important contribution to mass transport studies in facilitating the prediction of fluid permeability of materials from mercury injection data.

Katz and Thompson introduced two expressions for calculating absolute permeability (k) using data from a single mercury injection capillary pressure curve. The equations were derived from percolation theory. The first provided rigorous results by incorporating the measured conductivity formation factor (conductance ratio) σ/σ_0 as a parameter. Here σ is the rock conductivity at characteristic length L_c, and σ_0 the conductance of brine in the pore space. Mercury porosimetry data are used to determine the characteristic length L_c of the pore space. The equation for permeability is

$$k = 1/226(L_c)^2 \ \sigma/\sigma_0 \quad \textbf{(13)}$$

The second equation provides for an estimation of σ/σ_0 to be obtained from the same mercury intrusion data as were used to determine k. This equation, in addition to L_c requires the value of the length (pore size) at which hydraulic conductance is maximum (L_{max}), and the fraction of total porosity ϕ filled at L_{max} (symbolized by $S(L_{max})$). The equation is

$$k = (1/89)(L_{max})^2(L_{max}/L_c)\phi S(L_{max}) \quad (14)$$

Although appearing similar, the Katz-Thompson expression for conductivity formation factor is fundamentally different from the classical Archie's law. For Equations 13 and 14, k is reported in units of millidarcys and has fundamental units of area.

As pressure is increased, mercury is forced to

invade smaller and smaller pore openings in the permeable material. Ultimately, a critical pressure is reached at which the mercury spans the sample. This conduction path is composed of pores of diameter equal to and larger than the diameter calculated from the Washburn equation for the critical pressure. This diameter, L_c in equation 13, is a unique transport length scale and dominates the magnitude of the permeability.

To obtain this characteristic length L_c from the mercury intrusion data set, pressure is determined at the point of inflection in the rapidly rising range of the cumulative intrusion curve. This inflection point was determined experimentally by Katz and Thompson to correspond closely to the pressure at which mercury first spans the sample and the point at which percolation begins. This pressure point is defined as the threshold pressure (P_t). The value of L_c is the pore diameter (or length scale) calculated from the Washburn equation for P_t. Having obtained L_c is sufficient if σ/σ_0 has been measured independently and is known.

To use the second form of the equation, which estimates σ/σ_0, the cumulative intrusion volume V_t at threshold pressure (P_t) is determined. Then, the quantity V_t is subtracted from each intrusion volume value at each pressure in the data set from threshold pressure to maximum pressure. Data points prior to the threshold pressure are excluded. The net volume (V_c - V_t in cm³) times the diameter-cubed (micrometer³) for the corresponding pressure is calculated as a function of pore diameter (micrometers). This is the hydraulic conductance function, or permeability path. The pore diameter corresponding to the maximum y-value is L_{max}, the cumulative volume of mercury intruded at this diameter is V_{Lmax}. The fraction $S(L_{max})$ is calculated as the ratio of V_{Lmax}/V_t and is the fractional volume of connected pore space composed of pore width of size L_{max} and larger.

For both data reduction methods (using entered values for σ/σ_0 or calculating an estimated σ/σ_0), the equations depend on a judicious choice of the point at which inflection occurs and the resulting values of threshold pressure (P_t) and threshold volume (V_t). The computer program performs the first approximation and the initial value for permeability is reported on this basis. However, the intrusion curve should be inspected and the choice of the appropriate inflection point confirmed. There are cases in which there are multiple inflection points and a judgment is needed to determine which most likely represents the onset of percolation, or if the method is even applicable to the sample. Therefore, permeability calculations usually require a second pass through the data reduction routine using adjusted parameters. It should be noted also that a change in permeability value would affect the reported value for tortuosity.

In the literature, one frequently finds references to the K-T method, both in regard to determining permeability by mercury injection, and to their method of identifying the percolation region, the optimum path for permeability, and the threshold pressure from mercury intrusion data. These parameters are in other methods discussed in this document.

Pore Fractal Dimensions

Many natural and man-made materials have complex pore structure that changes only in size, but not in geometrical shape, over a range of pore volumes. This type of geometry has the quality of 'self-similarity' and can be described in terms of its fractal dimensions.

Angulo, Alvarado, and Gonzalez (15) published a method by which mercury porosimetry data can be reduced to extract information about the fractal characteristics of the pore space of the sample material. For their method to be applicable, there must be one or more linear regions on a log-log plot of intrusion volume versus pressure. The plot describes the volume scaling of the pore space and linearity implies that pore volume has fractal dimensions. The equation describing a linear region is determined and the value of the fractal dimension of the material in the linear range is extracted from the inverse log of the equation. Two regions of linearity are found in the data from some materials; this is attributed to there being two different processes related to pore space. The lower pressure linear region occurs during 'backbone formation' when mercury is finding a conductivity path through the pore structure. The adjacent linear region at higher pressure occurs during 'percolation' where flow through the medium is optimized.

For fractal analysis to be of value, the implications of fractal geometry must be appreciated. For anyone unfamiliar with fractal geometry, a simple, instructive exercise can be performed. First, draw a

square of dimension L, where L is any dimension. The square will be the conserved geometry, so every sub-element also will be a square, only smaller. Divide the original square into four squares of equal size (L/2 x L/2). Then, remove any one of the small squares. Divide each of the remaining three squares into four smaller squares (L/4 x L/4). From each of the three new groups, remove one square. Continue this process n times, where n is a positive integer. The result is a set of very small squares forming larger squares, all but the smallest having voids of various sizes. The dimension of the smallest square from which all other squares are composed, is called the length scale. The dimension of the smallest square is calculated using the formula $L/2^n$, where n is the number of times the original square was divided. The numerator is the original length of a side of the square, and the number 2 in the denominator is the number of equal parts into which the original length was divided. The number N of remaining squares at the end of the exercise equals 3^n, where the number 3 is derived from the number of remaining squares after each divide-and-discard step.

In general, a self-similar set of this type is expressed by the equation

$$N(\delta) = \delta^{-D} \quad (15)$$

where $N(\delta)$ is the number of elements of dimension δ, δ is the smallest dimension after n divisions, and D is the fractal dimension.

Taking the logarithm of this equation provides a solution for D, which is

$$D = \log[N(\delta)]/\log(1/\delta) \quad (16)$$

For the example given, $N(\delta) = 3^n$ and $\delta = 1/2^n$. Substituting these values into equation 10 gives

$$D = \log(3^n)/\log(2^n)$$
$$= n\log(3)/n\log(2)$$
$$= \log(3)/\log(2) = 1.58 \quad (17)$$

Note that the fractal dimension does not depend upon the number of iterations, n. Ultimately, it depends upon the fraction by which the length scale is divided and the number of remaining elements after each iteration. The total number of elements and the length scale, however, are functions of n.

Following the example above, the total area of the remaining object is equal to the number of minor elements times the area of each, or

$$A = N(\delta) \, \delta^2 \quad (18)$$

Since $N(\delta) = \delta^{-D}$,

$$A = \delta^{(2-D)} \quad (19)$$

where D in this case is the area fractional dimension.

An expression for volumetric fractal dimension is derived as above, yielding

$$V = \delta^{(3-D)} \quad (20)$$

If a sample has pore space that is fractal, then the volume of mercury intruded with increasing pressure also will scale as a fractal. Using a pressure scale rather than a length scale, and subtracting the threshold pressure Pt from the capillary pressure P, Equation 14 is expressed as

$$V = (P-Pt)^{(3-D)} \quad (21)$$

Taking the logarithm of this equation gives

$$\log(V) = (3-D)\log(P-Pt) \quad (22)$$

where (3-D) is the slope of the log(V) vs. log(P-Pt) plot. Pt is the pressure identified by Katz and Thompson (see the section on permeability) as the pressure at which mercury first percolates and spans the porous medium.

The equations developed above are based on regular geometry, as are most models, the cylindrical pore model of the Washburn equation, being an example. The application of this data reduction method indicates, by the occurrence of a linear range on the log(V) vs. log(P-Pt) plot, that pore volume filling is indicative of pores of fractal dimension. Reduction of data in that area provides the fractal dimension.

Fractal dimensions often are compared with other effects of porosity to test for correlation. For example, materials with fractal geometry often have quite different fluid transport characteristics than do materials having random geometry. Therefore, fractal dimensions can be important physical parameters when studying reservoir rocks and catalysts and other materials through which fluid must flow. The fact that the porosity has or does not have fractal geometry also may be indicative of the physical processes that formed the material.

In practice, determinations of the fractal dimensions of the backbone formation and percolation regions are accomplished after the log(V) vs. log(P-Pt) plot has been examined and the boundaries of the

linear regions identified. Another variable that may require adjustment after the analysis is Pt, the threshold pressure. Since these determinations only can be made after seeing certain reduced data, parameter adjustments and a second pass through the data reduction routine is required, this time only producing the reports on which changes are expected.

Pore Tortuosity and Tortuosity Factor

The terms tortuosity and tortuosity factor express two different characteristics of a material. Tortuosity is the ratio of actual distance traveled between two points to the minimum distance between the same two points. Tortuosity factor is commonly used in the area of heterogeneous catalysis and is the ratio of tortuosity to constriction.

The tortuosity factor characterizes the efficiency of diffusion of fluids through a porous media. Diffusion-controlled processes are of particular importance in catalysts where the solid support usually contains a pore network with pores ranging from micro- through to macropores. The manner in which pores interconnect can have a profound effect on the accessibility of reactants to the active sites and on the removal of products.

Also, characterization of the pore structure, including tortuosity, of porous filtration membranes such as microfiltration and ultrafiltration membranes is an important determination. Modeling the transport of contaminants through soil or other porous matrices also depends on knowledge of the materials tortuosity.

In 1998, Jörgen Hager (16) in his Ph. D. thesis at Lund University (Sweden) derived an expression for material permeability based on a capillary bundle model in which pores are homogeneously distributed in random directions. Using the Hagen-Poiseuille correlation for fluid flow in cylindrical geometries, making substitutions with measurable parameters, and combining with Darcy's law, he derived an expression for material permeability in terms of total pore volume, material density, pore volume distribution by pore size, and material tortuosity. All parameters but tortuosity are obtainable from mercury porosimetry tests.

As presented previously, Katz and Thompson also derived an expression for material permeability based on measurements obtainable from mercury porosimetry. Their expression does not depend on knowledge of material tortuosity. Therefore, combin-

ing the Hager and Katz-Thompson expressions provides a means for determining tortuosity from data collected by mercury porosimetry.

Obviously, if the Katz-Thompson value for permeability is used for tortuosity, permeability must first be determined appropriately. This means that the K-T point of inflection must have been accurately identified. Furthermore, for minimum error, the value of σ/σ should be known and entered as a parameter in the K-T data reduction routine. However, the K-T method can be used to estimate σ/σ but estimation diminishes the reliability of the calculated tortuosity value.

The dependency of tortuosity determinations on permeability determinations means also that any recalculation that affects the reported permeability also affects the reported value for tortuosity. Therefore, if permeability is recalculated for any reason (a better estimate of the inflection point, for example), then the system should be allowed also to recalculate and report tortuosity using the updated value of permeability.

Material Compressibility

It has long been noted that for many materials the intrusion curve at near maximum pressure takes a sudden upward swing. In some cases, the apparent uptake of mercury by the sample actually is caused by mercury filling the void in the sample cup produced by the collapse or compression of the sample material. If the extrusion curve follows the intrusion curve in this region, the material is demonstrating restitution or elasticity and returning to its original shape or volume. If the extrusion curve fails to retrace the intrusion curve, the material, to some extent, is permanently deformed. A pore filled with mercury applies pressure to the pore walls essentially with the same pressure as applied by the bulk mercury surrounding the sample. Therefore, structural collapse is not likely caused by collapse of the open pore structure, but more likely is due to voids that are inaccessible to the mercury. However, there is no way mercury porosimetry can determine whether the upward swing in the intrusion curve was caused by material compression, void collapse, filling of open pores, or a more common combination of these.

Compressibility data are more reliable when working with non-porous materials and, in this application, any apparent uptake of mercury in the high or low pressure regions may be attributed to material compression. However, before data reduc-

tion can be performed, there must be available a "blank run" file consisting (at least ideally) of a run made with the same penetrometer that is to be used in the compressibility test and on the same instrument ports as will be used in the compressibility run. The pressure range of the blank run must, at a minimum, fully encompass the planned range to be used in the compressibility measurement. This greatly improves the accuracy of the data by eliminating any deviations in the baseline caused by components in the system.

Quantifying compressibility consists of first identifying the range of data in which compressibility occurs, or in which the compressibility function is to be determined. The default range is the entire intrusion curve and this may need to be changed by having pre-knowledge of the desired range, or by inspection of the intrusion curve after the analysis. By the latter method, a second pass through the data reduction routine is required if the calculation range is changed from the pre-analysis values.

The compression function is expressed as a quadratic equation derived from the change in volume with pressure. Assume that at each experimental pressure, Pn, the corresponding blank corrected intrusion, V(Pn), can be computed using the second order polynomial expression

$$V(Pn) = Vo + B*Pn + C*Pn^2 . \qquad (23)$$

where Vo is the exact volume of the sample material computed as the ratio of the   sample weight and the sample density supplied by the user or, alternatively, supplied as the pre-measured sample volume by the user; B is the linear pressure coefficient of volumetric compressibility; and C is the quadratic pressure coefficient of volumetric compressibility.

The instrument will determine the best fit of this quadratic equation to the experimental data by adjusting the B and C appropriately. A plot of the experimental data overlaid with the predicted data can be inspected for goodness of fit. If the two plots closely agree, then the derived function expresses the compression response of the material to pressure in the range of calculation.

It is expected that the knowledgeable user will need to fully take into account various limitations in the art and technique. A blank correction run will provide a reference that will compensate for most of these variables. Perhaps the least controllable vari-

able is temperature increases which create a "thermometer effect" in the penetrometer system and are caused by compression of the hydraulic fluid as pressure is built. The amount of temperature increase depends upon the exact rate and time pattern with which the pressure is increased but can be as high as 50 C if maximally rapid pressurization of a small penetrometer is done.

Relation of Mercury Porosimetry to Other Porosimetry Techniques

Gas sorption and mercury porosimetry are complementary techniques. Physical adsorption techniques can extend the lower size measurement down to about 0.00035 mm diameter, thus probing the intraparticle microstructure. Mercury porosimetry is paired with the gas sorption technique to obtain porosity information in the large size range (greater than about 0.3 mm diameter up to about 360 mm), which is not attainable by gas sorption. When using two different techniques (two very different models), one should not expect necessarily to obtain the same results in the overlapping or common range of both instruments. However, comparable results have been reported (17) for some materials.

One potential difficulty in comparing porosity data sets obtained in the smaller size range by mercury porosimetry with data gathered in the same range by gas sorption is that sample compression is a possibility with mercury porosimetry. If sample compression occurs, an apparent uptake of mercury is superimposed on the intrusion curve leading to an erroneous indication of pore volume, and one not reproduced by the gas adsorption analysis.

As was mentioned in the sections on volume and density, mercury porosimetry data can be compared with gas pycnometry data to reveal additional porosity not detected by the mercury intrusion method alone. Indeed, comparing data obtained by different techniques for the same material characteristics can reveal information not attainable by either method alone. The requirement, of course, is that the measurement theories of both techniques be well understood.

16

GLOSSARY

Angle of contact: see *Contact Angle*

Apparent quantity: find under name of specific quantity, i.e. *Volume, Apparent*

Archie's Law: An empirical equation relating the electrical conductivity of a porous material and expressed as

$$\rho_R = \rho_F A\phi^m$$

where ρ_R is the electrical property of the rock, ρ_F the electrical property of the fluid, ϕ the porosity of the medium, and A and m depend on the geometry of the pores.

Area, Incremental Specific: The total area of pores with the size class defined by the increment boundaries. This value is calculated using incremental volume rather than cumulative volume. Therefore, the incremental pore area between the boundaries i and j is calculated by

$$A_{ij} = 4(V_j - V_i)/D_m,$$

where D_m is the mean diameter (see definition).

Area, Cumulative Pore: The summation of pore area over a range of pore sizes. Pore area is calculated from the geometry of a right circular cylinder beginning with Cumulative Volume (as measured) and equals $\pi D^2 h/4$, where D is the diameter of the pore and h is its depth. Since the area of a right circular cylinder equals πDh, the relation between the volume and area is A= 4V/D.

Backbone: That part of the spanning cluster of connected pores and voids that takes the most direct path through the medium.

Backbone Formation: Development of the main path through which the fluid will *percolate*.

Bulk quantity: find under name of specific quantity, i.e. *Volume, Bulk*

Capillarity: The action that causes the elevation or depression of a liquid surface in contact with a solid. It is caused by the relative attraction of the liquid molecules to each other and to the molecules of the solid. Same as capillary action.

Capillary Pressure: The pressure differential across the meniscus; the driving force for capillary penetration.

Characteristic Length: The pore diameter calculated from the pressure at which percolation through the porous material first occurs.

Compact: Verb form- To increase the bulk density of a granular material by the compression.

Noun form- A tablet or briquette resulting from compressing a granular or powdered material.

Conductivity Formation Factor: The ratio of the electrical conductance of a rock permeated with brine to the electrical conductance of brine. The reduction in conductivity is caused by the presence of the insulating solid phase and therefore is related the porosity. It also is affected by pore tortuosity and interconnectivity.

Connectivity: The degree to which pores, fractures, and voids are joined to form continuous paths through a medium. Directly related to *Percolation*.

Contact angle: The angle between the liquid and the solid surface at the liquid-solid-vapor interface and tangent to the curve of the droplet. The contact angle of a liquid on a smooth, homogeneous surface; depends on the surface energy of solid and liquid. The higher the surface energy of the solid substrate, the better its wettability and the smaller the contact angle. Related to the *Surface Tension* by the *Young's Law*.

Cumulative quantity: Total quantity accumulated (summation) over a range of operation (compare with *Incremental quantity*). For specific definitions, look under the name of the specific quantity, i.e. *Volume, Cumulative*.

Darcy: A unit of permeability. Equal to the flow of 1 ml of fluid of 1 centipoise viscosity in 1 second under a pressure gradient of 1 atmosphere across a $1 cm^2$ and l cm long section of porous material. Has units of area (cm^2). 1 *darcy* = $1x10^{-12}$ m^2 or $1x10^{-8}$ cm^2. *1 millidarcy* (md) = $1x10^{-15}$ m^2 or $1x10^{-11}$ cm^2.

Darcy's Law: A law describing the rate of fluid flow through a porous medium having specific physical properties. Mathematically,

$$Q = k\Delta P/\eta l$$

Where Q is the rate of flow (ml/sec), ΔP the pressure gradient, η the fluid viscosity, and l the length (thickness of sample) The material permeability (*hydraulic conductivity*) k is

$$k = r^2/8$$

where r is the radius of the pore. Darcy's Law is valid only for steady-state, laminar fluid flow. See the *Hagen-Poiseuille* equation.

Density, Apparent (or Particle Density) is the mass divided by the volume including both closed pores and open pores. This is in contrast to the mass per unit volume of the individual particles, which is a higher value.

Density, Bulk (or Packing Density) are terms used in powder technology. Bulk density or packing density is the mass of particles composing the bed divided by the bulk volume of the bed.

Density, Packing see Density, Bulk

Density The mass of a substance per unit volume (D = m/V). Volume may be defined in different ways according to how it is measured. Therefore, the definition of density is determined by the definition of volume. Definitions can vary somewhat from industry to industry.

Density, Bulk: The mass of the bulk quantity divided by the bulk volume; see *Volume, Bulk*.

Density, Envelope: The mass of the specimen divided by the envelope volume; see *Volume, Envelope*.

Density, Particle (or Envelope Density) is the mass of the particle divided by the volume of the particle including closed pores but excluding open pores.

Density, True (or Substance Density) is the mass divided by the solid volume or true skeletal volume. It is usually determined after the substance has been reduced to a particle size so small that it accommodates no internal voids.

Density, Theoretical is similar to true density except theoretical density includes the requirement that the solid material has an ideal regular arrangement at the atomic level.

Density, Skeletal is usually the mass divided by the skeletal volume remaining after the volume of all open pores larger than 0.005 micrometers have been subtracted.

Diameter / Radius: In mercury porosimetry, this is the dimension of the circular (or other) pore model. For every collected pressure point, there is a corresponding diameter obtained from the Washburn equation. Radius, when used, is obtained by dividing the calculated diameter by two.

Diameter, Mean: The average diameter within a class or data range. Over a given range of diameters (pressures) from D_i to D_j, the mean diameter is calculated as D_i-D_j/2.

Differential quantity: In general, the magnitude of the change in a quantity, or difference. Generally, the difference between two quantities, but in mercury porosimetry, the differential quantity always will be pore size (diameter or radius). It is calculated by subtracting the size of the pores corresponding to one pressure boundary of the increment from that of the other pressure boundary. For specific definitions, look under the name of the specific quantity, i.e. *Volume, Differential*.

Diffusion: As used in this document, the transport of mass by the spontaneous movement of particles (ions) through the liquid filling the pores.

Distribution (number, area, and volume): In mercury porosimetry, pore size calculated from pressure is the independent variable and this represents the distribution range. That which is distributed is the dependent variable, either the number, area, or volume of pores at each value throughout the range. For example, the pore volume distribution by pore sizes (diameter or radius).

Equilibration: The state at which mercury has ceased to flow into the pore space at the current pressure.

Fluid: A substance having no resistance to deformation when subjected to a shearing force.

Formation Factor: See *Conductivity Formation Factor:*

Fractal: A shape that is composed of smaller replicas of the same shape, that is, having *self similarity*. A simple example is a square area composed of small squares that are themselves composed of smaller squares, *ad infinitum*. Characterized by a power law distribution.

Geometric quantity: A dimension of an object of regular geometry such as a sphere or cylinder. For specific geometries (shapes), look under the name of the shape, i.e. "*Volume, Geometric*"

Greenware: Ceramic ware that has not been fired. Also applied to powdered metal compacts prior to sintering.

Hagen-Poiseuille Equation: An expression describing the laminar flow of fluid through a single cylindrical tube (capillary or pore) under the influence of a pressure gradient and as a function of fluid viscosity and density, capillary length and diameter, and flow velocity. Often expressed in terms of flow quantity, Q as

$Q = V/t = (\pi r4/8\eta)(\Delta P/l)$

Where V/t is the volume rate of flow, r the radius of the capillary (pore), η the liquid viscosity, and $\Delta P/l$ the pressure differential over a length 1 of capillary. *See Darcy's*

Law.

Hydraulic Conductivity: Permeability in relation to the fluid; unlike permeability, hydraulic conductivity takes into account the particular fluid that is present in the medium. See *Permeability*

Hydraulic Radius: The ratio of volume to surface area of a porous material. Also, the ratio of the cross-sectional area of flow to the perimeter of the channel.

Hysteresis: In mercury porosimetry, hysteresis is used to describe the failure of the extrusion curve to retrace the intrusion curve, that is, at the same pressure on the two curves, the quantity of mercury contained in the pore system differs. The extrusion curve with no hysteresis will exactly retrace the intrusion curve, and with hysteresis, will always have volume values greater than the intrusion curve at the same pressure. An error condition exists if the extrusion curve dips below the intrusion curve. The two curves seldom close to form a hysteresis loop as is required for gas adsorption -desorption curves.

Incremental quantity: A quantity summed between the two boundaries that define the increment (compare with *Cululative quantity*). For specific definitions, look under the name of the specific quantity, i.e. *Volume, Incremental.*

Interface: As used in this document, the boundary between any two phases, gas (vapor), liquid, or solid. These include, vapor-liquid, vapor-solid, liquid-liquid, liquid-solid, and solid-solid.

Interfacial Energy: The free energy of the surfaces at the interface of two phases resulting from differences in the tendencies of each phase to attract its own molecules. Also known as surface energy. See also, *Surface Tension* and *Surface Energy.*

Intergranular porosity: Void space between particles. See *Interstitial Space.*

Internal Energy (Forces): That portion of the total energy of a substance that is due to the kinetic and potential energy of the individual molecules; for example, that possessed by a compressed fluid.

Interstitial Space (Voids): The void space formed between two or more particles packed together.

Katz-Thompson Method: A method by which to determine the permeability of a porous medium using data obtained by mercury porosimetry.

Lithogenesis: The formation of rocks.

Log differential quantity: The difference between the logarithms of two quantities. In mercury porosimetry discussions, log differential quantities refer to quantities calculated using the log of the differential pore size (diameter or radius). For example, $\log(D_i) - \log(D_j)$.

Lognormal distribution: A distribution in which the log values of sizes are distributed in a normal distribution.

Macropore: Pores with diameters exceeding 0.05 μm.

Meniscus: The free surface of a liquid-vapor boundary near the walls of the containing vessel (a pore or capillary) and which assumes a curvature due to surface tension.

Mesopore: Pores with diameters between 0.002 μm and 0.05 μm.

Micropore: Pores with diameters equal to or less than 0.002 μm.

Millidarcy: 10^{-3} Darcy; see *Darcy.*

Model (Theoretical): A model, in the sense used in this document, is a mathematical or physical system that obeys specific conditions and whose behavior is used to help understand an analogous physical system. In mercury porosimetry, one theoretical model is that of system cylindrical pores.

Optimum path for Permeability: The pore size at which the product of intrusion volume and the cube of the pore size is maximum. The peak of the hydraulic conductance function in the Katz-Thompson method.

Pascal: Unit of pressure. To convert Pascals to other units, use the table below.

To convert Pascals to…	multiply by…
atmosphere	9.869×10^{-6}
bar	1×10^{-5}
dynes/cm^2	10
kg/cm^2	1.020×10^{-5}
psi or lb/in^2	1.4508×10^{-4}
torr or mm Hg	7.5028×10^{-3}

Percolate (Percolation): The movement of a fluid through a porous medium.

Penetrometer: A combination of a sample holder (cup) and the analytical mercury reservoir (stem) used in mercury porosimetry. Also called a dilatometer.

Permeability: The capacity of a material to transmit fluid. The conductance of fluid flow that a porous or fractured medium exhibits. Under special conditions, also referred to as *Hydraulic Conductivity*.

Pore Cavity: Any void laying beneath the surface and connected to the surface by a smaller void or pore.

Pore, Closed: Strictly, a pore that has no conduit to the surface. In regard to mercury porosimetry, a pore that has no conduit to the surface of sufficient size for mercury to invade at maximum pressure.

Pore, Ink Well: A pore system composed of a small cylindrical pore that opens into a larger cylindrical pore.

Pore, Open: A pore that is on the surface or has a conduit to the surface of the particle or specimen.

Pore Throat (neck): The opening at the surface (sometimes called simply 'pore'). Also, a pore through which a larger pore (cavity) is accessed.

Porosity: A dimensionless unit symbolized by ϕ and equal to the ratio of the void volume to the total volume (V_v/V_T) of the porous medium, or the fraction of the total volume of a porous medium occupied by void space. It also may be considered the storage capacity of a medium such as reservoir rock.

Power Law: A distribution of the form $y = c\, x^n$.

Pressure: In general, the force pre unit area, F/A. In mercury porosimetry, this value (measurement) is considered raw data, but actually is reduced to some extent by head pressure correction and transducer offset correction. Nevertheless, it is the most fundamental pressure data used in further data reduction. For every collected pressure point, P_i, there is a corresponding collected volume data point V_i. In certain data reduction routines, pressure data may be derived by interpolation between two measured pressure data points.

Pressure, Threshold: The pressure at which fluid first percolates through a porous medium.

PSIA: Units of absolute pressure. Pounds per Square Inch Absolute. To convert PSIA to other units, use the table below.

To convert PSIA to…. multiply by..

atmosphere   0.06805

bar 0.06893

dynes/cm^2 6.8927×10^4

kg/cm^2 7.0309×10^{-2}

mtorr or micron Hg 5.171×10^4

Pa or N/m^2 6.8927×10^3

torr or mm Hg   51.71

Radius / Diameter: In mercury porosimetry, this is the dimension of the circular (or other) pore model. For every collected pressure point, there is a corresponding diameter obtained from the Washburn equation. Radius, when used, is obtained by dividing the calculated diameter by two.

Saturation Zone (Saturated Zone): The region of pore space completely filled with fluid.

Self-similarity: Having the same properties at different size scales.

Sinter: In powder metallurgy, to form a coherent bonded mass by heat and pressure without melting.

Surface Energy: The energy per unit area of surface. Compare with definitions of *Surface Tension* and *Interfacial Energy.*

Surface Tension: The internal force acting on the surface that tends to contract the surface into a configuration of minimum surface area. It is due to an unbalance in molecular forces at the interface of two materials. The difference in molecular forces between a liquid and solid determines the contact angle. Also, the work dW necessary to increase the surface area by dA. Also known as interfacial tension or interfacial force. See also, *Surface Energy* and *Interfacial Energy.*

Tortuosity: The ratio of the length of the path described by the pore space to the length of the shortest path across a porous mass; the minimum value is 1.

Tortuosity Factor: Tortuosity factor is commonly used in the area of heterogeneous catalysis and is the ratio of tortuosity to constriction, where constriction is a function of the ratio of cross-sectional areas of the conduit.

Transport Properties: The properties of a material that are associated with the transport of mass through the material.

Unsaturated Zone: The region of the pore space that is partly filled with fluid.

Viscosity: A measure of a fluid's ability to resist deformation. High viscosity fluids flow more slowly than low viscosity fluids.

Volume: The size of a specific region in three-dimen-

sional space.

Volume, Bulk: Applied to finely divided samples and granulated solid materials. Includes all pores, open and closed, and includes interstitial space between particles. In regard to a single solid specimen, often referred to as envelope volume; see *envelope volume*.

Volume, Cumulative: In mercury porosimetry, the total volume accumulated or accounted for over the range of pressures or pore sizes. Considered raw data but may have been blank-corrected. For every cumulative volume data point (V_i) collected, there is a corresponding pressure point (P_i) collected.

Volume, Differential Specific: The *incremental* specific volume divided by the difference between the pore size at one boundary of the increment and the pore size at the other boundary. Incremental volume is used rather than cumulative because the calculation involves an incremental step in pore size and volume intruded and not the cumulative volume intruded at a specific pore size.

Volume, Envelope: The volume enclosed within a 'form fitting' surface that covers or envelops a single solid specimen of material. It includes the volume of small surface irregularities, open pores, and closed pores. Compare with *Volume, Bulk*.

Volume, Geometric is a theoretically ideal volume, derived from calculations with linear dimensions of regular shapes such as the radii (R) and heights (h) of cylinders ($V=\pi R^2 h$), the radii of spheres ($V = 4/3\,\pi\,R^3$), and the lengths (l), heights (h), and widths (w) of rectangular cubes ($V = lwh$). It does not include surface irregularities that exist on "real" objects, nor pores or voids.

Volume, Incremental: For a given range of pressure and cumulative volume data pairs, (P_i,V_i) to (P_j,V_j), incremental volume is V_i-V_j (corresponding to a pressure difference of P_i - P_j, which converts to a size range from D_i to D_j). In certain data reduction routines, incremental volume data may be calculated using values derived by interpolation between two measured volume data points.

Volume, Skeletal (or True Volume): The volume of the solid material only. Skeletal volume may be determined by mercury porosimetry or helium pycnometry and must be performed on either non-porous materials or materials with no closed pores. The skeletal volume as determined by mercury porosimetry and helium pycnometry may differ because mercury cannot intrude into small micropores, therefore including these voids

in the reported skeletal volume.

Volume, Specific: The volume (intrusion or extrusion, cumulative or incremental) divided by the sample weight. This produced units of volume per unit weight and normalizes the data for convenient comparison to similar analyses using different quantities of sample material.

Volume, True: see *Volume, Skeletal*

Washburn Equation: A mathematical expression of dynamic equilibrium between external forces tending to force a liquid into a capillary of size R and the internal forces repelling entry into the capillary. Assuming a circular cross-section for the capillary opening spanned by a non-wetting liquid such a mercury, the equation can be resolved in terms of the external pressure P and the diameter of the capillary D, the smallest size into which the liquid can be forced to enter at the prevailing pressure.

Young's law: An expression of the relationship of the solid-gas, solid-liquid, and liquid-gas interfacial tensions and the contact angle. Expressed mathematically as

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta$$

where γ_{sg} is the solid-gas interfacial tension, γ_{sl} the solid-liquid interfacial tension, γ_{lg} the liquid gas interfacial tension, and θ the contact angle

Young-Laplace Equation: An expression of the pressure differential (*capillary pressure*) across the liquid-gas interface (the *meniscus*). At equilibrium,

$$\Delta p = \gamma(1/R_1 + 1/R_2)$$

where R_1 and R_2 are the radii of curvature of the interface and γ is the surface tension of the liquid-gas interface. Within pores, the two radii are assumed to be equal to the pore size, D/2. Therefore, capillary pressure across the interface in a pore of size *D* is given by

$$\Delta p = \gamma(2/D + 2/D) = 4\gamma/D.$$

NOTE: The expression for capillary pressure is derived under the assumption that the fluids are in static equilibrium, i.e. there is no flow into or from the pore.

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