AutoPore® IV

Mercury Intrusion Porosimeter

micromeritics®

Calculations

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(Ver 2.x)

mi micromeritics®

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DATA REDUCTION

Data for presentation in tabular and plot form is calculated in the following manner:

P_i = head-corrected pressure as stored

V_{ri} = intrusion volume as stored

θ = user-entered contact angle

γ = user-entered surface tension

W_s = user-entered sample mass

W_p = user-entered mass for penetrometer

W_{psm} = user-entered mass for penetrometer + sample + mercury

V_p = user-entered volume for penetrometer

V_c = user-entered volume for capillary (stem)

V_{bup} = bulk volume at the filling pressure

V_{bup} = bulk volume at the user-entered pressure

ρ_{Hg} = user-entered density for mercury

$$WASHCON = Washcon\ constant = \frac{10^4\ \mu m/cm}{\left(68947.6\ \ dynes/cm^2\right)\left(psia\right)} = 0.145038$$

For all calculations requiring interpolation between collected data points, an Akima[1] method semi-spline is used.

Diameter for the ith point is:

$$D_i = \frac{WASHCON\ \ \gamma(-4\cos\theta)}{P_i}$$

Radius for the ith point is:

$$R_i = \frac{D_i}{2}$$

Cumulative specific intrusion volume for the ith point is:

$$I_i = \frac{V_i}{W_s}$$

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[1] "A New Method of Interpolation and Smooth Curve Fitting Based on Local Procedures," Journal of the Association of Computing Machinery, 17(4) 1970, 589-602.

Mean diameter for the ith point is:

$$Dm_i = \frac{D_i + D_{i-1}}{2}$$

Incremental specific intrusion volume for the th point is:

$$Ii_i = I_i - I_{i-1}$$

Incremental specific pore area for the th point is:

$$Ai_i = \frac{4 \times Ii_i}{Dm_i}$$

Cumulative specific pore area for the th point is:

$$A_i = Ai_i + Ai_i + \ldots + Ai_i$$

If more than 8 data points are available, differential and log differential specific intrusion volume are calculated as follows.

Differential and log differential data are the 1st derivative of the cumulative specific intrusion volume (all) data as a function of calculated log diameter, normalized by the diameter or log diameter interval. This derivation is comprised of four transformations.

1. Interpolation of cumulative specific intrusion volume vs. log diameter is made to get cumulative specific intrusion volume corresponding to evenly spaced log diameters.
2. The uniform cumulative specific intrusion volume data are then subjected to a 1st derivative calculation, using a 9-point smoothing method. This gives the desired differential data in terms of uniform intervals of collected data.
3. Log differential data are normalized by dividing by the log diameter interval between points. Since the points are evenly log spaced, this interval is the same for all points. Differential data are normalized by dividing by the diameter interval between points. Since the points are evenly log spaced, this interval is larger for larger diameters.
4. Interpolation of the differential or log differential data vs. log diameter is made to get data corresponding to collected data points.

If 8 or fewer data points are available, differential and log differential specific intrusion volume are calculated as:

Differential specific intrusion volume by diameter for the ith point is:

$$Id_i = \frac{-Ii_i}{D_i - D_{i-1}}$$

Log differential specific intrusion volume by diameter is:

$$I1d_i = \frac{-Ii_i}{logD_i - logD_{i-1}}$$

Differential specific intrusion volume by radius for the ith point is:

$$Ir_i = \frac{-Ii_i}{R_i - R_{i-1}}$$

Log differential specific intrusion volume by radius is:

$$I1r_i = \frac{-Ii_i}{R_i - R_{i-1}}$$

Total intrusion volume is:

$$V_{tot} = V_j$$

where the jth point is the first such that:

$$P_{j+1} \leq P_j - 10 \quad and \quad P_{j+1} \leq P_j \times 0.995$$

Total specific intrusion volume is:

$$I_{tot} = \frac{V_{tot}}{W_s}$$

Percent of total specific intrusion volume for the ith point is:

$$Ip_i = \frac{100 \times I_i}{I_{tot}}$$

Total specific pore area is:

$$A_{tot} = A_j$$

for point j as defined above.

Median diameter by volume is:

$$D_{mv} = D_k$$

where

$$l_k = \frac{I_{tot}}{2}$$

and P_k is interpolated from I_k and the collected data, and D_k is calculated from P_k

Median diameter by area is:

$$D_{ma} = D_k$$

where

$$I_k = \frac{I_{tot}}{2}$$

and P_k is interpolated from A_k and the collected data, and D_k is calculated from P_k.

Average diameter is:

$$D_{av} = \frac{4 \times I_{tot}}{A_{tot}}$$

BLANK CORRECTION BY FORMULA

For equilibration time 6 seconds: $X = log\left(\frac{T}{6}\right)$

For equilibration time < 6 seconds: $X = 0.0$

$$A_i = \left[1.23 \times 10^{-7} + 2.67 \times 10^{-7}X\right] - V_p\left[1.78 \times 10^{-7} + 1.0 \times 10^{-8}X\right]$$
$$+ V_m\left[1.64 \times 10^{-7} + 2.4 \times 10^{-8}\right]$$

For intrusion,

$$B = A_1 P_i + A_2 P_i^2$$

For extrusion points ≥ 1000 psia,

$$B = A_1 P_i + A_2 P_i^2 + 8.85 \times 10^{-3}\left(1\frac{P_i}{60000}\right)$$

For extrusion points < 1000 psia,

$$B = A_1 P_i + A_2 P_i^2 + 8.7 \times 10^{-6} P_i$$

Blank-corrected intrusion volume for the i_{th} point is:

$$V_i = Vr_i - B$$

where

T   =   equilibration time in seconds

     =   volume of mercury in penetrometer; where, volume of mercury =

V_m $\dfrac{Wpsm - Ws - Wp}{Ym}$

P_i =   pressure for this data point

V_i =   corrected intrusion volume

Blank correction by file is described in the AutoPore V Series Operator Manual (part number 962-42800-01).

Bulk volume is: $V_b = V_p - V_m$

Bulk density is: $Y_b = \dfrac{W_s}{V_{bfp} - V_{bup}}$

Skeletal volume is: $V_s = V_b - V_{tot}$

Skeletal density is: $Y_s = \dfrac{W_s}{V_s}$

Porosity % is: $P_{pc} = \dfrac{100 \times V_{tot}}{V_b}$

Percent capillary used is: $V_{pc} = \dfrac{100 \times V_{tot}}{V_c}$

COMPUTATION ALGORITHM FOR VOLUMETRIC PRESSURE COEFFICIENTS OF COMPRESSIBILITY

The data acquired during the AutoPore run is examined to determine that at least seven intrusion data points having progressively ascending pressures have been designated for use in the computation. Note that the intrusion values which will initially be referred to are not *specific* values. They are "total" values never having been divided by the sample material mass. Later, it will be necessary to shift to specific values.

The specified blank data are examined to determine that at least seven blank intrusion data points having progressively increasing pressures are available to use with the specified pressure computation range. Of the seven, the pressure values of the two blank data end points must fall within 5 % (either above or below) of the two end points of the sample material run data.

Interpolation by spline curve polynomial or other suitable technique is to be applied to the blank data to allow computation of blank intrusion volumes at pressures which exactly match those in the experimentally acquired data i.e., take a pressure from the acquired data, enter the interpolation routine and find and save the blank intrusion volume which would correspond to that exact pressure. Repeat this for each pressure value in the acquired data set.

Pointwise at each experimental pressure value, subtract the blank intrusion values as interpolated above from the experimentally acquired data intrusion values to give a "blank-corrected acquired data intrusion values set" or more simply "blank corrected data" for short.

Assume that at each experimental pressure, *Pn*, the corresponding blank corrected intrusion, *V(Pn)*, is computed using the second order polynomial expression

$$V\left(P_n\right) = V_0 + B^*P_n + C^*P_n{}^2$$

where

V_0	=	the exact volume of the sample material computed as the ratio of the sample mass and the sample density supplied by the user or, alternatively, supplied as the pre-measured sample volume by the user;
B	=	the linear pressure coefficient of volumetric compressibility must be a negative real number to avoid violation of fundamental physical laws; and
C	=	the quadratic pressure coefficient of volumetric compressibility.

Construct the summation of differences as follows and solve for the values of *B* and *C* which produce the least squared error:

$$\sum_{n=1}^{N_{max}} \left[V\left(P_n\right) - \left(V_0 + B * P_n + C * P_n^2\right)\right]^2 = minimum$$

Where N_{max} is the index of the uppermost blank corrected data point. Now it is necessary to stop using total values and change to the use of specific values; convert the total values B and C to specific values, b and c, by dividing them by the sample material volume.

The first and second order pressure coefficients of volumetric compressibility of mercury must be added to the computed first and second order coefficients yielded here. They are expressed in the same units. The resulting values are b' and c'. It is necessary to do this addition because the blank corrected experimental data actually is a measure of the sample material's differential compressibility compared to that of mercury. One may imagine that a repeat of the blank run could be considered as a test of a some unit volume of mercury itself immersed in the surrounding mercury. The result should be the same as the blank run since in reality nothing has (at least on purpose) been changed. The blank corrected data consists of all zero volume changes with pressure and the b and c computed from it will likewise both be zero.

Also one should consider the situation which we have experienced wherein a less compressible material such as stainless steel is tested. Since both mercury and glass compress more than does the steel, the mercury column actually must rise in the bore of the penetrometer as the pressure is increased. This is interpreted as a negative intrusion volume change with pressure and leads to the computation of values for b (positive) and c which are physically impossible. Only when they are interpreted as values relative to mercury can they be valid and, by addition of mercury's coefficients respectively, they can be expressed as absolute values.

The values of b' and c' produced by this calculation will likely be in units of *absolute milliliters per milliliter * psia* and *absolute milliliters per milliliter * psia squared* if internal AutoPore computations are, as expected, performed in these units. Reporting these in alternate units of measure will be required. The most useful alternate units will be *milliliters per milliliter* megaPascal* and *milliliters per milliliter* kpsia* and analogous second order units. Strictly speaking, convention requires that the duplicated fundamental units of measure in the numerator and denominator be eliminated. This results in expressing the first order coefficient as *meters squared per Newton.* This choice also is provided in spite of its less intuitive impression.

FRACTAL DIMENSIONS

Pore space in sedimentary rocks exhibit fractal characteristics. The fractal dimension of these materials has been shown to be an important petrophysical parameter partly because capillary pressure and other transport coefficients scale as power laws of fluid saturation. The scaling exponents often relate to the fractal dimension of the medium. Angulo[1], et al, show that fractal dimensions of a quantity related to pore space bulk can be determined by mercury intrusion porosimetry.

According to percolation theory (see reference to Katz and Thompson in Permeability section of this appendix), at some threshold pressure PT, the invading fluid first spans the entire sample, that is, the fluid percolates for the first time. This then produces a geometrical configuration of fluid known as the percolation backbone and pressures from the point of percolation to completion of the backbone are in the *backbone formation* region. At greater pressures, filling of pore cavities behind smaller pore throats continues but without the sudden influx of fluid as observed at the threshold pressure. The backbone is a fractal with fractal dimension DH, but at higher pressures, the geometry of the fluid cluster changes rapidly to another fractal with fractal dimension DV (>DH) of the supporting media.

MIP DATA REDUCTION

In order to calculate a fractal dimension, the threshold pressure, Pthresh, must be known. The threshold pressure is the pressure at which the intrusion volume vs.pressure curve is steepest. This is either a calculated value (if chosen) or the value entered on the Material Properties dialog if the *Use entered threshold pressure* option is selected. It is the same value used in permeability calculations.

If necessary, the value is calculated as follows. First set up an Akima spline for specific intrusion volume (Ii) vs. pressure (Pi) for all points on the first intrusion cycle. This is used to calculate the slope, (dI/dP)i, at each pressure. Use these values to set up another Akima spline for slopes vs. pressures. Finally, use the second Akima spline to find the value of pressure that gives the maximum slope. This is the threshold pressure, Pthresh. In addition, the user must specify the backbone formation and percolation pressure ranges over which calculations are to be performed.

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[1] R.F. Angulo, V. Alvarado, and H. Gonzalez, "Fractal Dimensions from Mercury Intrusion Capillary Tests," II LAPEC, Caracas, March 1992.

The equation that defines fractal dimension is:

$$I = \alpha \left(P - p^{thresh} \right)^{(3-D)}$$

I	=	specific intrusion volume
P	=	pressure
P_{thresh}	=	threshold pressure
D	=	the fractal dimension
α	=	proportionality constant

This equation is transformed to the following to make it linear in the unknown parameters.

$$log(I) = (3 - D) log(P - P_{thresh}) + log\ \alpha$$

D and α are calculated by least squares fit to this equation, using all collected points (I_i, P_i) where P_i is in the user-selected range and above the threshold pressure.

MATERIAL PERMEABILITY

BACKGROUND

Permeability is a basic permeable medium property that, unlike porosity, cannot be defined apart from fluid flow.

Permeability is the proportionality " constant" between the fluid flow rate and an applied pressure or potential gradient.

Hydrologists, petrologists, and other branches of geology need to measure the intrinsic properties of rock and soils to both store and transmit fluid. These are porosity, permeability, the hydraulic conductivity of Darcy's law, and specific storage.

BASIS OF DATA REDUCTION METHOD TO BE USED

1. A.J. Katz and A.H.Thompson, Quantitative prediction of permeability in porous rock: Physical Review, Series B, Vol. 34, pp. 8179-8191 (1986).
2. A.J. Katz and A.H. Thompson, "Prediction of Rock Electrical Conductivity From Mercury Injection Measurements," *Journal of Geophysical Research, Vol. 92*, No. B1, pp. 599-607, (1987).
3. E.J. Garboczi, "Mercury Porosimetry and Effective Networks for Permeability Calculations in Porous Materials," NIST.
4. Kelli Murbach, "Permeability in Cement Impedance Spectroscopy," Case Western Reserve University.
5. P.J. Tumidajski and B. Lin, "On the Validity of the Katz-Thompson Equation for Permeabilities in Concrete", pp. 643-647.
6. A.H. Thompson, A.J. Katz, and C.E. Krohn, "The microgeometry and transport properties of sedimentary rock," *Advances in Physics*, Vol. 36, No. 5, pp. 625-694 (1987).
7. A.H.Thompson, S.W. Sinton, S.L. Huff, A.J. Katz, R.A. Raschke, and G.A.Gist, "Deuterium magnetic resonance and permeability in porous media," *Journal of Applied Physics, Vol. 65*, pp. 3259-3263 (1989).

THEORY

In their 1986 paper, Katz and Thompson introduced a model for absolute permeability, the key relationship being

$$k = \frac{c l_c^2 \sigma}{\sigma_0}$$

where k is absolute permeability in terms of the rock conductivity σ and a characteristic length l_c. The constant c is of the order of (1/226 = 0.00442), and σ_0 is the conductivity of the brine in the pore space. The characteristic length is determined experimentally from the threshold pressure in a mercury injection experiment. The equation follows from the percolation arguments of Ambegaokar, Halperin, and Langer (1971) and pertaining specifically to electron transport in amorphous semiconductors, but which are generally applicable to systems characterized by a broad distribution of conductances.

DATA REDUCTION

In order to calculate the permeability, the characteristic length, l_c, must be determined. This is determined from the threshold pressure, P_{thresh}, using the Washburn equation. The threshold pressure is the pressure at which the intrusion volume vs. pressure curve is steepest. This is either a calculated value (if chosen) or the value entered on the Material Properties window (see ***Fractal Dimensions on page 8***). The specific volume intruded at pores larger than l_c, I_{thresh}, is also used. This is calculated by interpolating the specific intrusion volume vs. pore diameter curve at the characteristic length l_c.

If a conductivity formation factor (σ/σ_0) is entered, the permeability is calculated using the Katz Thompson expression above in which c is a user-entered permeability constant.

If the conductivity formation factor is not entered, calculations proceed using the length at which the conductance is maximum, L_{max}. The conductance is maximum when $(I-I_{thresh})D^3$ is maximum, where I is specific intrusion volume and D is diameter. To find the diameter at which this is the case, an Akima spline is created for $(I_i > I_{thresh})$. The spline is used to find the value of the diameter, L_{max}, at which this curve is maximized (not necessarily a node point). From this, the fractional volume S_{Lmax} of connected pore space involving pore widths of size L_{max} and larger, can be calculated by interpolating the specific intrusion volume vs. pore size curve to L_{max} and dividing by the total specific intrusion volume I_{tot}. With this in hand, the permeability can be calculated as:

$$k = \frac{1}{89} L_{max}^2 \left(\frac{L_{max}}{l_c} \right) \bullet I_{tot} \bullet Y_b \bullet S_{Lmax}$$

THE KATZ-THOMPSON METHOD OF DATA REDUCTION USING MERCURY POROSIMETRY

In order to calculate the permeability, the characteristic length, L_{char}, must be determined. This is determined from the threshold pressure, P_{thresh}, using the Washburn equation. The threshold pressure is the pressure at which the intrusion volume vs. pressure curve is steepest. This is either a calculated value (if chosen) or the value entered on the Material Properties window (see *Fractal Dimensions on page 8*). The specific volume intruded at pores larger than L_{char}, I_{thresh}, is also used. This is calculated by interpolating the specific intrusion volume vs. pore diameter curve at L_{char}.

If a conductivity formation factor (s/so), is entered, the permeability is calculated as:

Perm $=$ $CL^2_{char}\sigma/\sigma_o$
C $=$ user-entered permeability constant
σ/σ_o $=$ user-entered conductivity formation factor

If the conductivity formation factor was not entered, calculations proceed using the length at which the conductance is maximum, L_{max}. The conductance is maximum when $(I-I_{thresh})D^3$ is maximum, where I is specific intrusion volume and D is diameter. To find the diameter at which this is the case, an Akima spline is set up for $(I_i > I_{thresh})$. The spline is then used to find the value of the diameter, L_{max}, at which this curve is maximized (not necessarily a node point). From this, the fractional volume of connected pore space involving pore widths of size L_{max} and larger, S_{Lmax}, can be calculated by interpolating the specific intrusion volume vs. pore size curve to L_{max} and dividing by the total specific intrusion volume I_{tot}.

With this in hand, the permeability and conductivity formation factor can be calculated as:

$$Perm = \frac{1}{89}L_{max}{}^2\frac{L_{max}}{L_{char}} \cdot I_{tot} \cdot Y_b \cdot S_{Lmax}$$

where

C $=$ user-entered permeability constant
Y_b bulk density, either calculated (if chosen) or user-entered on the *Material Properties* window

TORTUOSITY

The terms tortuosity and tortuosity factor are often used interchangeably. Tortuosity is the ratio of actual distance traveled between two points to the minimum distance between two points.

$$\xi = tortuosity = \frac{Actual\ distance\ traveled}{shortest\ distance} = \frac{\ell_e}{\ell} \tag{1}$$
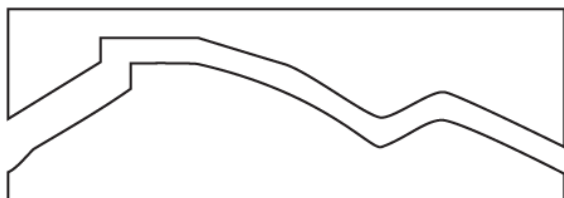
Required parameters (units specified as mass, volume, length, and area):

ρ	=	density (mass/volume) – from pycnometry
V_{tot}	=	total pore volume (volume/mass)
K	=	permeability (area)

CALCULATING TORTUOSITY

The tortuosity can be calculated from the following expression:

$$\xi = \sqrt{\frac{\rho}{24K(1 + \rho V_{tot})} \int_{\eta = r_{c, min}}^{\eta = r_{c, max}} \eta^2 f_v(\eta)d\eta} \tag{2}$$

where

$$-\int_v(r_c) = \frac{dV(r_c)}{dr_c},\ from\ MIP \tag{3}$$

In order to calculate the tortuosity, the weighted average pore size, D_{avg}, must be found. This is accomplished as:

$$D_{avg}^2 = Y_s = \left[\frac{1}{2}I_1 O_i^2 + \Sigma I_i D_i^2 + \frac{1}{2}I_n O_n^2\right]$$

Y_s =   skeletal or true density, either calculated (if chosen) or user-entered on the *Material Properties* window

D_i =   pore diameter for the ith point

I_i =   specific intrusion volume for the ith point

Given this value, the tortuosity is calculated as:

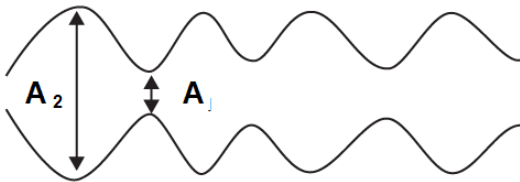$$\xi = \sqrt{\frac{D_{avg}^2}{4 \cdot 24 Perm(1 - YI_{tot})}}$$

where

Perm   =   C L^2 char s/so

I_{tot} =   total specific intrusion volume

CALCULATING TORTUOSITY FACTOR

Tortuosity factor is commonly used in the area of heterogeneous catalysis and is the ratio of tortuosity to constriction.

$$\tau = \frac{D_{eff}}{D\theta_c} \tag{4}$$

$$\tau = \frac{\xi}{\sigma} \tag{5}$$

$$\beta = \frac{A_2}{B_2}, \ area \ ratio$$

$$\sigma = f(\beta), \ constriction \ factor$$

Carniglia has derived a simple expression for calculating the Tortuosity Factor of porous media. While this expression was derived using Fick's first law of diffusion and is convenient to calculate, the use of this correlation is severely limited by the data required to calculate the tortuosity factor.

V_{tot}	=	total pore volume
ρ_b	=	bulk density
S	=	total BET surface area
ΔV_i	=	change in pore volume within a pore size interval
d_i	=	average diameter within a pore size interval

For non-intersecting cylindrical pores the following simple correlation may be used:

$$\tau = 2.23 - 1.13 V_{tot}\rho_b$$

where

$$0.05 \leq V_{tot}\rho_b \leq 0.95$$

This correlation is limited to values of τ ranging from 1 to 2.2.

A generalized correlation has also been developed, however the generalized method requires diffusivity data for the system and conditions of interest (temperature and pressure). It is worth noting that if this diffusivity data is available, tortuosity factor can be calculated directly from equation 4.

$$\tau = \left(2.23 - 1.3 V_{tot}\rho_b\right)\left(0.92\left(\frac{4}{S}\Sigma\frac{V_i}{d_i}\right)^{1+\epsilon}\right)$$

where

ε	=	pore shape exponent, Carniglia has assigned a value of 1 for cylinders.

The tortuosity factor is calculated as:

$$TF = 0.92\left[\left(\Sigma\frac{\iota_i}{D_i}\right)\frac{4}{S}\right]$$

ΔI_i	=	difference in specific intrusion volume for two adjacent points $I_i - I_{i-1}$
$\overline{D}$	=	average pore size for the interval between adjacent points 0.5 ($D_i + D_{i-1}$)
S	=	user-entered BET surface area
I_i	=	specific intrusion volume for the ith point
D_i	=	pore diameter for the ith point
I_{tot}	=	total specific intrusion volume
Y_b	=	envelope density, either calculated (if chosen) or user-entered on the *Material Properties* window

PORE SURFACE AREA COMPUTATION

It is sometimes asserted that pore wall surface area computed on the basis of the work required to immerse a surface in mercury is superior to assuming the pores are cylindrical and calculating area from geometric relationships. What those who make the assertion fail to recognize is that mathematically and in practice, the two computations are identical as shown below.

WORK

The reversible work dW required to immerse an area dA of a non-wetting object in mercury[1] is

$$dW = \gamma \cos \Theta \, dA \tag{1}$$

where γ is the surface tension of mercury and θ its contact angle with the object. In the case of mercury and pores, this work is supplied when the external pressure P forces a volume of mercury dV into pores. Equation 1, therefore, becomes

$$\gamma \cos \Theta \, dA = -P \, dV \tag{2}$$

Assuming that γ and θ do not vary with pressure, equation 2 can be written

$$A = -\frac{\int P \, dV}{\gamma \cos \theta} \tag{3}$$

which, expressed for evaluation from pressure-volume mercury penetration data, becomes

$$\Sigma \quad A = -\frac{\Sigma P \quad V}{\gamma \cos \theta} \tag{4}$$

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[1] Rootare, H.M. and Prenzlow, C.F., "Surface Areas from Mercury Porosimeter Measurements," J. Phys. Chem., 71, 2733-6 (1967).

CYLINDRICAL GEOMETRY

The basic relationship describing the penetration of mercury into a cylindrical pore of diameter *D* derived from equating the applied pressure to the resisting surface tension[1] is

$$PD = -4\gamma\cos\Theta \tag{5}$$

The relationship among wall area, diameter, and volume for a cylinder is

$$A = \frac{4V}{D} \tag{6}$$

Combining equations 5 and 6, yields

$$A = \frac{PV}{\gamma\cos\Theta} \tag{7}$$

which, as before, when written for evaluation from pressure-volume mercury penetration data, becomes

$$\Sigma \quad A = -\frac{\Sigma P \quad V}{\gamma\cos\theta} \tag{8}$$

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[1] Washburn, E.W., "Note on a Method of Determining the Distribution of Pore Sizes in a Porous Material," Proc. Nat. Acad. Sci., 7, 115-6 (1921).