

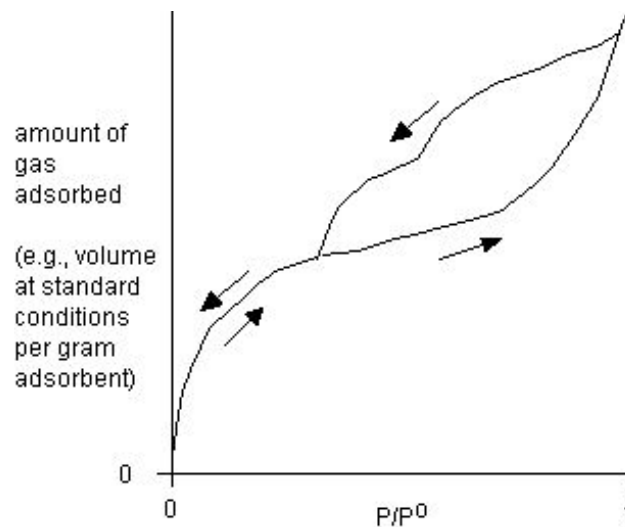
Pore size distribution

The distribution of pore volume as a function of pore radius can be used in estimating effective diffusion coefficients in porous media such as adsorbents and heterogeneous catalysts. Pore size distributions can be estimated in several ways. Here we introduce the use of condensation of liquid in pores during physisorption experiments and the intrusion of liquid mercury into pores in the mercury porosimetry method. In both methods, the surface tension of a liquid in contact with the porous solid is used in determining the distribution of pore volume vs. pore radius.

Physisorption and capillary condensation method

A multipoint BET apparatus is used for this method. The fit of the BET isotherm equation to data usually applies only in the the pressure ratio range P/P^0 from 0.05 to 0.3. One reason is that, at higher pressure ratios, filling of small pores or void spaces in the material with liquid will start to occur as the thicknesses of the adsorbed multilayers approach the radii of the pores. This phenomenon can be used to determine the distribution of pore sizes in a material.

Consider a sample over which the amount of gas adsorbed has been measured as the pressure ratio has been increased to a value near 1. Then consider that the pressure is reduced and the equilibrium amount adsorbed is measured at each pressure. We might get data like this:



The arrows show the direction in which the pressure changes were made with increasing time during the experiment. We see a hysteresis loop.

Using the thermodynamics of curved vapor-liquid interfaces, we can analyze the descending (top) branch of the loop in order to determine the pore size distribution of the material.

First, we model the porous material as having cylindrical pores. Note that the shapes of the pores or void spaces in some materials may deviate significantly from this model. The effect of a change in pressure and volume on the free energy of a pure, single-component material is given by:

$$\Delta\bar{G} = \Delta(P\bar{V})$$

where $\Delta\bar{G}$ is the molar Gibbs free energy, and \bar{V} is the molar volume. For a liquid (l) and an ideal vapor (v) in equilibrium, the chemical potentials and Gibbs free energies of the two phases are equal. If a change is made, e.g., changing the vapor-liquid interface from plane to curved, then the changes in the chemical potentials and Gibbs free energies on the two phases must be equal:

$$\Delta\bar{G}^v = \Delta\bar{G}^l$$

From determining the work required to create a curved, semi-spherical surface of radius r , we get a form of the **equation of Young and Laplace**:

$$\Delta P = \frac{2\gamma}{r}$$

where ΔP is the pressure difference across the surface, γ is the surface free energy or surface tension, and r is the radius of curvature of the surface. The change in molar volume of a liquid with pressure is negligible, thus,

$$\Delta\bar{G}^l = \bar{V}^l \Delta P^l = \frac{2\gamma\bar{V}^l}{r}$$

The change for the vapor phase is the change from vapor in equilibrium with a plane surface of the liquid to vapor in equilibrium with a curved surface of the liquid. The vapor phase can be considered an ideal gas:

$$\bar{V}^v = \frac{RT}{P^v}$$

$$\Delta\bar{G}^v = \int_{P^{v0}}^{P^v} \bar{V}^v dP^v = \int_{P^{v0}}^{P^v} \left(\frac{RT}{P^v} \right) dP^v = RT \ln \left(\frac{P^v}{P^{v0}} \right)$$

Combining the equations for the changes in Gibbs free energies, we get the **Kelvin equation**:

$$RT \ln \left(\frac{P^v}{P^{v0}} \right) = \frac{2\gamma\bar{V}^l}{r}$$

For example, for a water drop in equilibrium with a mixture of water vapor and air, the curved surface is convex such that the value of r is positive and the vapor pressure of the liquid water, P^v , is larger than the standard vapor pressure of the water, P^{v0} , over a plane surface of liquid water. This means, for the water drop and the water vapor to be in equilibrium, the partial pressure of the water vapor is equal to P^v which is greater than P^{v0} .

Because of the molar volume of the vapor phase is much larger than the molar volume of the liquid phase, the change in vapor pressure due to a curved vapor-liquid interface or meniscus is much smaller than the change in total pressure across the interface for equal changes in Gibbs free energy. For $\Delta\bar{G}^v = \Delta\bar{G}^l$, $\Delta(P^v\bar{V}^v) = \Delta(P^l\bar{V}^l)$. Since the mean $(\bar{V}^v) \gg \bar{V}^l$, $\Delta P^v \ll \Delta P^l$. For water at 298 K and 1 atm, $(\bar{V}^v / \bar{V}^l) = 1360$. For nitrogen at 77 K and 1 atm, $(\bar{V}^v / \bar{V}^l) = 167$.

A qualitative explanation: The total pressure inside of an inflated rubber balloon is higher than atmospheric pressure and the forces are balanced by the "tension" of the rubber balloon skin. The surface tension holding a water drop together is analogous to the skin of a rubber balloon, except the "skin" of the water drop is a layer of water molecules which are at a higher energy state than interior molecules because they are bonded to fewer water molecules and, since they are at a higher energy state, work must be done to increase the area of the surface of the drop. The increased total pressure of the water inside a water drop results in an increased chemical potential and, thus, an increased tendency to evaporate, i.e., an increased "vapor pressure" or pressure of vapor that would be in equilibrium with the liquid. Consider a small water drop surrounded by a mixture of air and water vapor that is in equilibrium with a large pool of liquid water with a plane surface. The vapor pressure of the water in the drop (i.e., the pressure of water vapor that would be in equilibrium with the water inside the drop) is higher than the partial pressure of water outside the drop (the standard vapor pressure of water). Thus, the liquid water in the drop will have a tendency to evaporate. The vapor pressure of the water in the drop is larger than the standard vapor pressure of water but is not nearly as much larger as the total pressure of the liquid in the drop is larger than 1 atm. This is because (a) the free energy change of water evaporation from the drop is the change in the product of the vapor pressure and the molar vapor volume, (b) which is equal to the change in the product of the total pressure and the molar liquid volume, and (c) the molar vapor volume is much larger than the molar liquid volume.

For a liquid in a cylindrical tube or pore, the radius r equals the radius of the liquid meniscus, r_m . For a liquid that "wets" the walls of the tube, the value of r_m is negative because the curved surface is concave with respect to the liquid. The vapor pressure over the meniscus of a liquid that wets the tube walls is less than the standard vapor pressure, $(P^v/P^{v0}) < 1$.

A qualitative explanation: For water wetting the inside of a small glass tube ("capillary tube"), the total pressure of the water inside the tube is less than 1 atm because the water molecules are attracted to the glass. The mechanical forces across the vapor-liquid interface or meniscus is balanced by the surface tension of the curved meniscus. Consider water in a small glass tube which the water wets and which is surrounded by a mixture of air and water vapor that is in equilibrium with a large pool of liquid water with a plane surface. Water vapor over the tube will tend to condense inside the tube because the vapor pressure of water in the tube (i.e., the pressure of water vapor that would be in equilibrium with the water inside the tube) is less than that of the surrounding water vapor, again due to the attractive forces between the water molecules and the glass. As above, because of the large differences between the molar volumes of water liquid and vapor, the reduction of the vapor pressure of water in the tube from the standard vapor pressure is much less than the reduction of the total pressure of the water in the tube from the surrounding total pressure.

The radius of a cylindrical pore in our model porous material is r_p , where the value of r_p is positive. The effective radius of the meniscus is $r_m = -r_p / \cos \theta$. The angle θ is the contact angle between the liquid-vapor interface and pore wall. The contact angle $\theta = 0^\circ$ for a liquid that completely "wets" the pore wall material and $\theta = 180^\circ$ for a liquid that does not wet the pore wall.

For water in a 2 μm -diameter tube surrounded by an air-water mixture at a total pressure of 1 atm, the vapor pressure of the water, P^v , is only 0.1% less than the standard vapor pressure, P^{v0} , a small effect. However, the capillary rise of the water in the tube due to the total pressure difference across the curved liquid interface is 14.7 m, a large effect. For this case, ΔP in the Young and Laplace equation is -144 kPa = -1.42 atm, and the total pressure in the liquid under the meniscus is -0.42 atm. Such a negative pressure implies that the liquid water is in tension rather than compression (see references at end of this document). The total pressure is 1 atm in the liquid water in the tube at the level of the liquid pool in which the lower end of the capillary tube is immersed.

The pore radii in most catalysts and adsorbents are in the range 1 nm - 100 nm (100 nm = 0.1 μm).

For liquid nitrogen in most materials, $\theta = 0^\circ$ such that $\cos\theta = 1$. However, the radius of the meniscus is smaller than the pore radius, comparing absolute values, by the thickness of the multilayer adsorption layer that is present at the pressure ratio, t . So $r_m = -(r_p - t)$. This correction for t will only be significant for very small pores. The Kelvin equation for this experiment becomes

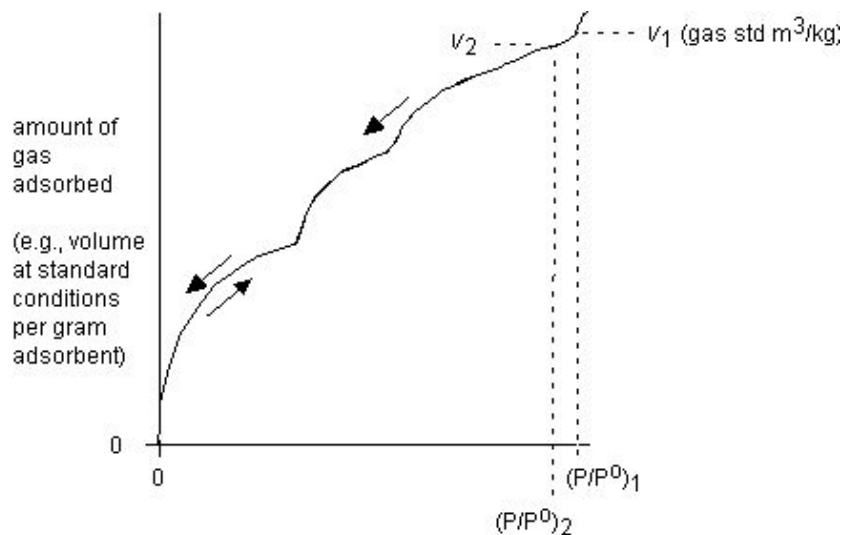
$$-RT \ln\left(\frac{P^v}{P^{v0}}\right) = \frac{2\gamma\bar{V}^l}{(r_p - t)}$$

$$r_p = \frac{2\gamma\bar{V}^l}{-RT \ln\left(\frac{P^v}{P^{v0}}\right)} + t$$

where the adsorbed layer thickness is a function of (P^v/P^{v0}) and can be computed from the molecular diameter and the BET equation using parameters determined from data at low (P^v/P^{v0}) where pores are not filled. This equation says that the vapor pressure of the liquid inside the pore, P^v , is smaller than the standard vapor pressure of over a plane surface of the liquid, P^{v0} . Thus, in order to get liquid inside the pore to evaporate, the pressure of the pure vapor outside the pore must be reduced below the pressure P^v predicted by the equation.

At a given pressure ratio (P^v/P^{v0}) , all pores of radius larger than r_p will not contain liquid, i.e., they will be empty except for the adsorbed layer. During the experiment, the change in the amount adsorbed is recorded as a function of the pressure ratio as the pressure ratio is reduced. The larger pores will empty first at high (P^v/P^{v0}) and the smallest pores will empty last at lower (P^v/P^{v0}) . At $(P^v/P^{v0}) = 0.5$, $r_p = 1.4$ nm for nitrogen at 77 K.

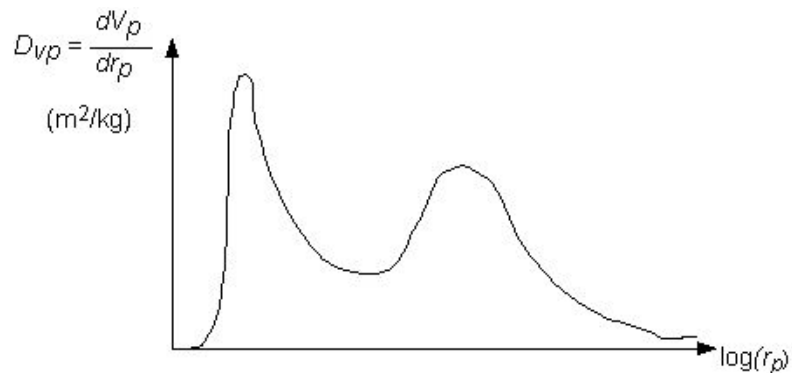
Consider the adsorption curve shown above but now we remove the lower part of the hysteresis loop from the plot.



Start at $(P^v/P^{v0})_1$ which corresponds to a pore radius r_{p1} which is the largest pore radius in the material. At this pressure ratio, all pores are filled with liquid nitrogen. The total pore volume per gram solid is the volume of liquid nitrogen that corresponds to the nitrogen gas volume at standard conditions, $v_1 = v^s_1$. From v^s_1 (standard m^3/kg), we calculate mol/kg, then use the density of liquid nitrogen to calculate liquid volume v^l_1 (m^3/kg). At this starting pressure ratio, v^l_1 equals the total pore volume, $v_{p, total}$.

Next, reduce the pressure ratio to $(P^v/P^{v0})_2$ which corresponds to a pore radius r_{p2} , equilibrate and determine the change in amount of nitrogen adsorbed, $\Delta v^s = v^s_1 - v^s_2$. Then calculate the change in pore volume Δv^l . This change in pore volume Δv^l is the volume of pores with radius $r_{p2} < r_p \leq r_{p1}$. This process is continued until all pores have emptied.

The results can be plotted as a pore volume distribution, usually vs. pore radius or diameter on a log scale, e.g.,



where

$$\int_0^{\infty} D_{v_p} dr = v_{p, total} \text{ (m}^3/\text{kg)}$$

Alternative forms of plots are "cumulative pore volume" distribution plots, e.g., plots of

$$\int_0^r D_{v_p} dr \text{ vs. } r \quad \text{or} \quad \int_r^{\infty} D_{v_p} dr \text{ vs. } r$$

Note the different integration limits on the integral symbols.

The Barret-Joyner-Halenda or BJH method is frequently used to calculate the pore volume distribution as a function of pore radius from experimental data:

Barrett, E. P., Joyner, L. G. & Halenda, P. P. "The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms," Journal of the Americal Chemical Society, vol. 73, p. 373 (1951).

Also see part II in the same journal in July 1951, p. 3155, for a comparison of pore volume distributions measured by nitrogen physisorption to those measured using mercury porosimetry. Automated physisorption instruments have this and similar calculation methods already programmed into their computers.

Mercury porosimetry

This apparatus consists of a steel chamber that contains the sample and a piston. The sample is placed in the chamber and the chamber is evacuated. Liquid mercury is introduced. The piston is used to force liquid mercury, which doesn't "wet" the material, into the pores of the material. The force applied to the piston is recorded as a function of the piston displacement. The piston displacement (m) times the cross-sectional area of the piston (m²) is the volume of mercury (m³) that is forced into the pores by that piston displacement.

By applying the equation of Young and Laplace above to the case where the pressure inside the material is near zero, the applied pressure is P , and the contact angle between the liquid and the solid is θ , we get the so-called Washburn equation:

$$r_p = -\frac{2\gamma \cos \theta}{P}$$

For mercury in common materials, the contact angle used is $\theta = 135\text{-}140^\circ$. At a pressure P , all pores with radius r_p and larger will be filled with mercury. Initially, at low applied pressure, only large pores will fill with mercury. As the pressure is increased, smaller and smaller pores will fill. Instruments are available which can attain 60,000 psi (414 MPa = 4140 bar), at which pores of radius 1.5 nm can be filled.

Constants and physical property values

$$R = 8.3143 \text{ (Pa m}^3\text{)/(mol K)} \text{ -- ideal gas constant}$$

$$g = 9.8 \text{ m/s}^2 \text{ -- gravitational acceleration}$$

Water at 298 K

$$\gamma = 7.20\text{E-}2 \text{ (N/m)}$$

$$\rho^l = 1.0\text{E}3 \text{ kg/m}^3$$

$$\bar{V}^l = 1.80\text{E-}5 \text{ m}^3\text{/mol}$$

$$\bar{V}^v = 2.2445\text{E-}2 \text{ m}^3\text{/mol}$$

Nitrogen at 77 K

$$\gamma = 9\text{E-}3 \text{ (N/m)}$$

$$\rho^l = 0.808\text{E}3 \text{ kg/m}^3$$

$$\bar{V}^l = 3.47\text{E-}5 \text{ m}^3\text{/mol}$$

$$\bar{V}^v = 0.5780\text{E-}2 \text{ m}^3\text{/mol}$$

Interestingly, at $(P^v/P^{v0}) = 0.5$, $r_p = 1.4 \text{ nm}$ for N_2 at 77 K and $r_p = 1.5 \text{ nm}$ for water at 298 K at this reduced pressure ($\gamma\bar{V}^l/T = 4.06\text{E-}9$ for N_2 at 77 K; $\gamma\bar{V}^l/T = 4.35\text{E-}9$ for water at 298 K).

Mercury at 293 K

$$\begin{aligned}\gamma &= 0.436 \text{ (N/m)} \\ \rho^l &= 1.35\text{E}4 \text{ kg/m}^3 \\ \bar{V}^l &= 1.48\text{E-}5 \text{ m}^3/\text{mol}\end{aligned}$$

References for water under tension - negative pressure:

N. R. Tas, P. Mela, T. Kramer, J.W. Berenschot and A. van den Berg, "Water plugs in nanochannels under negative pressure," 7th International Conference on Miniaturized Chemical and Biochemical Analysts Systems, <<http://www.chem.ualberta.ca/~microtas/Volume1/004-52.pdf>> accessed April 27, 2006.

References cited by Tas, et al.:

Trevena, D.H. Cavitation and tension in liquids 15 (Adam Hilger, Bristol, 1987).

Q. Zheng, D.J. Durben, G.H. Wolf and C.A. Angell, "Liquids at large negative pressures: Water at the homogeneous nucleation limit," Science 254, 829-832 (1991).

L.J. Briggs, "Limiting negative pressure of water," J. Appl. Phys. 21, 721-722 (1950).

S.J. Henderson and R.J. Speedy, "A Berthelot-Bourdon tube method for studying water under tension," J. Phys. E: Sci. Instrum. 13,778-82 (1980).