Capillary Condensation

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Pore volume and pore size distribution

- The range of validity of BET equation is between 0.05 and 0.35 relative pressure.
- Adsorption beyond this range will result in filling of mesopore with adsorbate liquid through the action of capillary condensation.
- Capillary condensation and its variation with the pore size will be discussed, and how to get useful information about the mesopore size distribution from the data of volume adsorbed versus pressure.
- The range of validity for the capillary condensation is between 0.35 and 0.99 relative pressure.
Adsorption in mesoporous solids

- A typical adsorption-desorption isotherm of a practical porous solid usually exhibits a hysteresis over the pressure range where the capillary condensation phenomenon is operating.
- The onset of the hysteresis loop indicates the start of the capillary condensation mechanism.
Kelvin equation for Capillary Condensation

Due to the capillary force in small pores, the vapor pressure of a liquid inside such pores is less than that of a flat surface.

The pressure at which the liquid will condense in a pore of radius \( r \) is:

\[
\frac{P}{P_0} = \exp \left( - \frac{2\sigma \cos \theta \, v_M}{R_g T} \cdot \frac{1}{r} \right)
\]

- \( \sigma \): surface tension
- \( P_0 \): vapor pressure of the bulk phase
- \( \theta \): contact angle
- \( v_M \): liquid molar volume.
When the pore is very large, i.e.:

\[ r \gg \frac{2\sigma \cos \theta \nu_M}{R_g T} \]

the pressure at which the species condenses or evaporates is equal to the vapor pressure of the liquid, i.e. \( P/P_o = 1 \).

On the other hand, for pores of radius \( r \), the liquid will form at pressure \( P/P_o < 1 \).
Basis of the capillary condensation theory

- For gas having a pressure lower than the condensation pressure $P_k$, there is no capillary condensation except a submonolayer adsorption, while for gas having pressure equal to or greater than the condensation pressure $P_k$, the capillary of size D will be filled completely with liquid.
Evaporation of liquid from a pore of radius $r$ ($r_m$ is the radius of curvature)

Capillary pressure as a function of radius for nitrogen at 77 K

<table>
<thead>
<tr>
<th>$r$ (nm)</th>
<th>$P$ (Torr)</th>
<th>$P/P^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>297</td>
<td>0.391</td>
</tr>
<tr>
<td>2</td>
<td>475</td>
<td>0.625</td>
</tr>
<tr>
<td>5</td>
<td>630</td>
<td>0.829</td>
</tr>
<tr>
<td>10</td>
<td>691</td>
<td>0.909</td>
</tr>
<tr>
<td>20</td>
<td>725</td>
<td>0.954</td>
</tr>
<tr>
<td>25</td>
<td>732</td>
<td>0.963</td>
</tr>
</tbody>
</table>
In the region of hysteresis, there are two values of the pressure that give rise to the same amount uptake (i.e. two values of the pore size).

To properly account for this, one must investigate the way liquid is condensed or evaporated during the adsorption and desorption cycles.

We can apply the capillary condensation to adsorption and desorption cycles.

\[
\frac{P}{P_0} = \exp\left(-\frac{2\sigma v_M}{R_g T} \cdot \frac{1}{r_m}\right)
\]

$r_m$ is the mean radius of curvature
Desorption from a pore

- During evaporation (desorption) the pore is filled and the sorbate starts to evaporate from the liquid meniscus, taking the form of hemispherical shape having a contact angle of $\theta$.
- The radius of curvature of this hemispherical, $r_m$, is related to the pore radius as follows:

$$r_m = \frac{r}{\cos \theta}$$

Classical Kelvin equation

$$\frac{P}{P_0} = \exp\left(-\frac{2\sigma \cos \theta \nu_m}{R_g T} \cdot \frac{1}{r}\right)$$
Filling of a pore during the adsorption cycle

For adsorption, the radius of curvature is:

\[ \frac{P}{P_0} = \exp \left( -\frac{\sigma v M}{R g T} \cdot \frac{1}{r} \right) \]

Cohan equation
Adsorption and desorption

\[ \frac{P_{\text{ads}}}{P_0} = \exp\left( - \frac{\sigma v_M}{r R_g T} \right) \]

\[ \frac{P_{\text{des}}}{P_0} = \exp\left( - \frac{2\sigma v_M}{r' R_g T} \right) \]

where \( r' \) is the radius of curvature of the meniscus (\( r' = r/\cos\theta \), where \( \theta \) is the contact angle).

For zero contact angle, the radius of curvature is the same as the capillary radius.

\[ \left( \frac{P_{\text{ads}}}{P_0} \right)^2 = \frac{P_{\text{des}}}{P_0} \]
The reduced pressure required to empty a capillary is equal to the square of that necessary to fill it.

For example, a pore of radius $r$ which fills with liquid adsorbate at a reduced pressure $P/P_0$ of 0.7 would have its filled liquid evaporated at a reduced pressure of about 0.5.

The status of filling and emptying at two different relative pressures is the basis of hysteresis in mesoporous solids.
Pore Size Distribution

- For each pore of radius $r$, there exists a threshold pressure for condensation and a threshold pressure for evaporation.
- This can be used to determine the pore size and its distribution.
- During the adsorption cycle the filling of pore with adsorbate is in a radial fashion, and hence the rise in the amount adsorbed versus pressure is gradual.
- After the pore is filled, and when the pressure is reduced the liquid in the pore will remain until the pressure in the gas phase reaches the evaporation pressure at which the liquid will instantaneously evaporate, leaving only the adsorbed layer behind.
- As the pressure is reduced further the amount adsorbed will decrease and the relationship between the amount adsorbed and the pressure is dictated by the equilibrium between the two phases (e.g. BET equation).
Knowing this condensation pressure from the desorption branch of point A, the pore radius then can be calculated from the Kelvin equation:

\[ r = \frac{2\sigma v_M \cos \theta}{R_g T} \left[ \ln \left( \frac{P_0}{P_{des}} \right) \right]^{-1} \]

Unfortunately, this ideal situation never occurs in practice as all practical porous solids have a distribution of pore size, so there will be a gradual change in the desorption branch rather than an abrupt change as in the case of ideal solids.
Solids with no adsorbed layer (pure Condensation and Evaporation)

- Consider a porous solid having a PVD of $f(r)$, then $f(r) \, dr$ is the pore volume of pores having radii ranging between $r$ and $r + dr$.

- For a gas phase of pressure $P$, the threshold radius ($r_K$) is calculated from either equations for condensation or evaporation mechanisms.

- The amount adsorbed at a pressure $P$ is simply the fraction of pores having radii less than $r_K$, that is:

\[
V(P) = \int_0^{r_K(P)} f(r) \, dr
\]

For simplicity, the lower limit is zero.

where

\[
r_K = \begin{cases} 
\frac{2v_M \sigma \cos \theta}{R_g T \ln(P_0 / P)} & \text{for evaporation} \\
\frac{v_M \sigma}{R_g T \ln(P_0 / P)} & \text{for condensation}
\end{cases}
\]
If Maxwellian pore volume distribution

\[ f(r) = \frac{V_s}{r_0} \left(\frac{r}{r_0}\right) \exp\left(-\frac{r}{r_0}\right) \]

- where \( V_s \) is the total pore volume and \( r_0 \) is the characteristic pore radius.
- Figure shows a typical plot for \( V_s = 0.4 \text{ cc/g} \), and \( r_0 = 3 \text{ nm} \)
Then, the adsorbed volume by capillary condensation as a function of pressure is:

\[ V(P) = V_s \left[ 1 - \left( 1 + \frac{r_K}{r_0} \right) \exp \left( - \frac{r_K}{r_0} \right) \right] \]
Double Gamma PVD
If we let "t" to represent the statistical thickness of the adsorbed layer (which is a function of pressure), then the effective pore radius available for condensation is related to the true pore radius as follows:

\[ r_K = r - t \]

\( \sigma \) is the thickness of one layer, or obtain the film thickness measured for a nonporous reference material.

\[ t = \frac{V}{V_m} \sigma \]

The statistical adsorbed film thickness as a function of pressure for nitrogen adsorption at 77 K.

\[ t \text{ (nm)} = 0.354 \left[ \frac{5}{\ln(P_0 / P)} \right]^{1/3} \]

where 0.354 nm is the thickness of one nitrogen molecule.
The threshold radius corresponding to a gas phase of pressure $P$ is:

$$r(P) = \begin{cases} t + \frac{2v_M \sigma \cos \theta}{R_g T \ln(P_0 / P)} & \text{for desorption} \\ t + \frac{v_M \sigma}{R_g T \ln(P_0 / P)} & \text{for adsorption} \end{cases}$$

- The amount adsorbed at a given pressure $P$ is then:

$$V(P) = \int_{0}^{r(P)} f(r) \, dr + t \int_{r(P)}^{r_{\text{max}}} \frac{2f(r)}{r} \, dr$$

- The pores are assumed cylindrical in shape, and the film thickness is independent of the pore radius. The factor $(2/r)$ is the surface area per unit void volume. The parameter $r_{\text{max}}$ is taken as the upper limit of the mesopore range, that is 25 nm.
Surface area determination

Knowing the pore volume distribution $f(r)$, the surface area is determined from:

$$S_g = \int_0^{r_{\text{max}}} \frac{2f(r)}{r} \, dr$$
Typical surface area, pore volume and mean pore radius of some solids

<table>
<thead>
<tr>
<th>Solids</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>Mean pore radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>500-1500</td>
<td>0.6-0.8</td>
<td>10-20</td>
</tr>
<tr>
<td>Silica gel</td>
<td>200-600</td>
<td>0.4</td>
<td>15-100</td>
</tr>
<tr>
<td>Silica-alumina</td>
<td>200-500</td>
<td>0.2-0.7</td>
<td>33-150</td>
</tr>
<tr>
<td>Activated clays</td>
<td>150-225</td>
<td>0.4-0.52</td>
<td>100</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>175</td>
<td>0.39</td>
<td>45</td>
</tr>
<tr>
<td>Celite (kieselguhr)</td>
<td>4.2</td>
<td>1.1</td>
<td>11,000</td>
</tr>
</tbody>
</table>