8. Pore analysis by adsorption

8.1. Kelvin equation

Adsorption data $\rightarrow$ pore size or pore size distribution

$$\ln\left(\frac{P}{P_0}\right) = -\frac{2 \gamma \bar{V}}{r \, RT} \cos \theta$$

$$\Rightarrow \ln\left(\frac{P}{P_0}\right) = -\frac{2 \gamma \bar{V}}{r \, RT} \quad \text{if } \theta = 0$$

$P$ : equilibrium $P$ in pores with a radius $r$.

$P_0$ : equilibrium $P_0$ on planar surface.

$r$ : pore radius

$\gamma$ : surface tension

$\bar{V}$ : molar volume of liquid

In a pore, the overlapping potential of the wall can overcome the translational energy of an adsorbate molecule. So that condensation will occur at a lower pressure. Thus, as the relative pressure is increased, condensation will occur first in pores of smaller radii and will progress into larger pores.
In five isotherms, Types I, IV, V are related to porosity.

Type I → microporosity
Type IV → r = 15-1000 Å
Type V → rarely observed

Complete wetting, θ=0°, cosθ=1
Incomplete wetting, θ=20°, cosθ=0.94
8.2. Adsorption hysteresis

Hysteresis:

two relative pressures corresponding to a given quantity:

\[(P/P_0)_{ads} > (P/P_0)_{des}\]

\[
\Delta G_{ads} = RT\left(\ln P_{ads} - \ln P_0\right)
\]

\[
\Delta G_{des} = RT\left(\ln P_{des} - \ln P_0\right)
\]

\[\therefore P_{des} < P_{ads} \implies \Delta G_{des} < \Delta G_{ads}\]


\[ \therefore \] desorption value corresponds to the more stable condition

→desorption isotherm should be used for pore analysis.

Theories for hysteresis:

Zsigmondy : different contact angles during adsorption and desorption.

McBain : bottle neck

Cohan : adsorption on a cylindrical meniscus desorption from a hemispherical meniscus.
8.3. Total Pore Volume

Gurvitsch rule:

At saturation \((P / P_0 \approx 1)\) the liquid volume of different adsorbates, when measured on porous adsorbents, is essentially constant and is independent of adsorbate.

This constancy of adsorbed liquid at saturation provides direct evidence that the pores are filled.

\[ \therefore \text{ at } P / P_0 \approx 1 \]

The amount of adsorption can be used to calculate total pore volume.

For example

At \(P/P_0 = 0.99\) \(W_a\) gram of \(N_2\) are adsorbed

\[ V_p = \frac{W_a}{\rho} \], \(\rho = \text{liquid density}\]
Based on Kelvin eq., the largest pore radii are given by

\[
r_k = \frac{-2\gamma \bar{V}}{RT\ln\left(\frac{P}{P_0}\right)} = \frac{-2 \left( 8.85 \text{ erg} \ cm^{-2}\right)\left(34.6 \text{ cm}^2 \text{ mol}^{-1}\right)}{8.314 \times 10^7 \ \text{erg} \ K^{-1} \text{ mol}^{-1} \times (77K) \times (\ln0.99)} = 950 \times 10^{-8} \text{ cm} = 950 \ \text{Å}
\]

\[\therefore \ V_p \text{ represents the pore volume of all the pores up to 950Å.}\]

An implicit assumption: no surface other than the inner walls of the pores exists.

\[
V_p = \pi \bar{r}_p^2 \cdot L
\]

\[
S_{BET} = 2\pi \bar{r}_p \cdot L
\]

Average pore size = \[
2 \cdot \bar{r}_p
\]

\[
\bar{r}_p = \frac{2V_p}{S_{BET}}
\]

Porous materials: most of the surface area is contributed by the pore wall
8.4. Pore Size Distribution (PSD)

PSD is usually measured using the desorption isotherm. N\textsubscript{2} as the adsorbate

\[ r_k = \frac{4.15}{\log\left(\frac{P_0}{P}\right)} \text{ [Å]} \]

\( r_k \): Kevin radius or critical radius

It is difficult to estimate film thickness over the inner walls.

Assumptions for adsorption in pores.
1. A planar surface
2. Adsorbate evenly distributed over surface.

\[ t = \left( \frac{W_a}{W_m} \right) \tau \]

\( W_a \): weight adsorbed
\( W_m \): weight for monolayer coverage.
\( \tau \): thickness of one layer
For liquid N$_2$

One mole of molecules spread on surface

\[ S = (16.2 \text{ Å}^2)(6.02 \cdot 10^{23}) = 97.5 \cdot 10^{23} \text{ Å}^2/\text{gmol} \]
\[ \bar{V} = 34.6 \cdot 10^{24} \text{ Å}^3/\text{gmol} \]

\[ \tau = \frac{\bar{V}}{S} = 3.54 \text{Å} \quad t = \left( \frac{W_a}{W_m} \right) \cdot 3.54 \text{Å} \]

On nonporous surface, it has been shown that when $W_a/W_m$ is plotted vs. $P/P_0$, the data all approximately fit a common Type II curve as $P/P_0 > 0.3$ regardless of the adsorbent used.

This is an implication of even distribution of the adsorbate.

ie. When $W_a/W_m = 3 \quad \Rightarrow \quad t = (3 \times 3.54) = 10.62 \text{Å}$

Halsey equation for N$_2$ adsorption on planar surface to predict $t$. 
Halsey equation for N\textsubscript{2} adsorption on planar surface to predict t.

\[ t = 3.54 \left( \frac{5}{2.303 \cdot \log \left( \frac{P_0}{P} \right)} \right)^{\frac{1}{3}} \]

Table 8.1 (Next page)

- consider both the layering and condensation.

◆ Similar to the BJH method (Barrett, Joyner and Halenda), only for mesopores
Table 8.1  Pore size distribution work table

<table>
<thead>
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<th></th>
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<th>3</th>
<th>4</th>
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<td>13</td>
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<td>$P/P_0$</td>
<td>$V_{gas}$ (cm$^3$g$^{-1}$)</td>
<td>$r_k$ (Å)</td>
<td>$t$ (Å)</td>
<td>$r_p$ (Å)</td>
<td>$\bar{r}_k$ (Å)</td>
<td>$\bar{r}_p$ (Å)</td>
<td>$\Delta t$ (Å)</td>
<td>$\Delta V_{gas}$ (cm$^3$g$^{-1}$)</td>
<td>$\Delta V_{liq}$ (cm$^3$g$^{-1}$)</td>
<td>$\Delta t \Sigma S$ (cm$^3$g$^{-1}$)</td>
<td>$V_p$ (cm$^3$g$^{-1}$)</td>
<td>$S$ (m$^2$)</td>
<td>$\Sigma S$ (m$^2$)</td>
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<td>28.0</td>
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<td>737</td>
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<td>9.2</td>
<td>42.4</td>
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<td>40.9</td>
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<td>3.8</td>
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<td>9.22</td>
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<td>0.58</td>
<td>12.34</td>
<td>6.97</td>
<td>26.15</td>
</tr>
</tbody>
</table>
Table 8.1 shows that: the pore volume = 0.28 cm$^3$g$^{-1}$ for $r_p > 15.1$ Å
Three conditions Kelvin eq. analysis should be terminated

1. \( \frac{P}{P_0} < 0.3 \), adsorption in micropore range
   The validity of Kelvin eq. becomes questionable, because the uncertain-ty regarding molar volume and surface tension when only one or two molecular diameters are involved.

2. When \( \Delta t \sum S \approx \Delta V_{liq} \), represents the absence of evaporation from center cores

3. Hysteresis loop closes,
   Micropore vol. = total pore vol. – \( \sum V_p \) (BJH, column 12)
   \[
   \frac{Wa}{P_{P0}} = 0.99 \\
   \sum S' = 212.1 \text{ m}^2\text{g}^{-1} \text{ (in Table 8.1) } \rightarrow \text{does not include micropore S.A.}
   \]
   (\( \therefore \sum S' \) should be smaller than BET area)

◆ BJH takes into account the film thickness change after each decrement of \( P/P_0 \).
But in some cases, you obtain $\sum S > \text{BET S.A.}$, indicating the presence of ink-bottle pores.

You use a small $r$ and a correct $\Delta V_{\text{liq}}$ to estimate the surface area, 

$$S = \frac{2 \cdot \Delta V}{r}$$

(you should use the adsorption isotherm to calculate pore size distribution)

For any distribution, the integrated area represents the volume within the pore size range.
**8.7. V-t curves**

**Adsorption on nonporous materials**

If plot $W_a/W_m$ vs. $P/P_0$

The data fit a common Type II curves, especially for $P/P_0 > 0.3$ and

t = $(W_a/W_m) \cdot 3.54\text{Å}$ is used  \( (t : \text{statistical depth}) \)

\[ t = \frac{V_{\text{liq}}}{S} \times 10^4(\text{Å}), \quad V_{\text{liq}} = [\text{cm}^3], \quad S = [\text{m}^2] \]
9. Microporosity

9.1. Introduction

Pore diameter analyzed by Kelvin eq. 15-1000 Å

Dubinin’s definition:

Pore diameter $> 1000$ Å  macropores
$15–1000$ Å  transitional (Kelvin)
$< 15$ Å  micropores
Langmuir eq. (Type I isotherm) can describe the adsorption on microporous materials, but may be only a correct mathematical description.

Micropores have high overlapping potential, so they can be filled at low $P$. 

Ads. on microporous materials
Microporosity

\[ \therefore \text{in micropore regime, pore filling starts from the pores with larger over potentials (or adsorption energy).} \]

Because the pore size is so small, once a molecule is attached to the pore wall, the pore size reduction will initiate the filling of the pore. (no layering behavior in micropores.)

9.2. Langmuir Plots for Microporous Surface Area

\[ \text{∵ adsorption in micropores belongs to Type I, Langmuir equation can describe the isotherm.} \]

\[ \frac{P}{W} = \frac{1}{KW_m} + \frac{P}{W_m} \]

\[ \frac{P}{W} \text{ vs. } P \rightarrow \frac{1}{W_m} \implies St = \frac{W_m \bar{N}A}{\bar{M}} \]
In reality, adsorption in micropores is not monolayer, and Langmuir usually over estimates the S.A.

9.3. Polanyi’s Theory for Micropore Volume and Area

\[ \Delta G = 0 \quad \text{Liq.} \quad T, P_0 \quad \text{Vapor} \]

\[ \Delta G = RT \ln \left( \frac{P_0}{P} \right) \quad \text{Vapor} \quad T, P < P_0 \]

\[ \Delta G = RT \ln \left( \frac{P_0}{P} \right) \]

Polanyi’s potential theory of adsorption

\[ P_0 \quad E_n = 0 \]

\[ P_1 \quad E_1 = -RT \ln(P_0/P_1) \]

\[ E_s = RT \ln(P_0/P) \]

Adsorption represents that adsorbates can be trapped on surfaces with energies between \( E_n \) and \( E_s \).

\[ P \uparrow \Rightarrow \text{adsorption potential required} \downarrow \]

\[ P = P_0 \Rightarrow \text{adsorption potential required} = 0 \]

\[ P \text{ is very small} \Rightarrow \text{required potential is large} \]
Let adsorption vol.  \( \tilde{V} = \frac{W}{\rho} \)

\[ W = f(P/P_0) \]

\[ E = f(P/P_0) \]

At the same value, \( \tilde{V} \) represents the relative affinity

Dubinin assumed that \( E/E_0 \) are constant at different \( \tilde{V} \) values,

\[ \frac{E}{E_0} = \beta = \text{affinity coefficient} \]
for the reference, \[ \tilde{V} = F \left( \frac{E}{\beta} \right) = F \left( E_0 \right) \]

Normally, benzene is used as the reference.

Dubinin and Radushkevich assume

\[ \tilde{V} = \tilde{V}_0 \cdot e^{-KE_0^2} \Rightarrow \tilde{V} = \tilde{V}_0 \cdot e^{-K \left( \frac{E}{\beta} \right)^2} \]

\[ \tilde{V}_0 = \text{total adsorption volume} \]

\[ \therefore E = RT \ln \left( \frac{P_0}{P} \right) \]

\[ \tilde{V} = \tilde{V}_0 \cdot \exp \left[ - \frac{K}{\beta} (RT)^2 \left( \ln \frac{P_0}{P} \right)^2 \right] \]

\[ \log W = \log(W_0) - 2.303K \left( \frac{RT}{\beta} \right)^2 \left[ \log \frac{P_0}{P} \right]^2 \]

or

\[ \log W = \log(W_0) - k \left[ \log \frac{P_0}{P} \right]^2 \ldots \text{D–R equation} \]
\[ \log(W) \text{ vs. } [\log(P_0/P)]^2 \rightarrow \log(W_0) \rightarrow \tilde{V}_0 = \frac{W_0}{\rho} \]

at \( P/P_0 = 10^{-5} \sim 10^{-1} \), give good linear fit for DR eq.

\[ \tilde{V} = \tilde{V}_0 \cdot e^{-K/E_0^2} \]

Let \( K = \left( \frac{1}{\varepsilon_0} \right)^2 \)

When \( E_0 = \varepsilon_0 \Rightarrow \tilde{V} = \tilde{V}_0 \cdot e^{-1} = 0.368 \cdot \tilde{V}_0 \)

\( \varepsilon_0 \) is called the characteristic adsorption energy.

For slit-like micropores

Stoeckli:

\[ L(nm) = \frac{10.8}{\varepsilon_0(kJ \cdot mol^{-1}) - 11.4}, \quad S_{mi}(m^2g^{-1}) = \frac{2000 \cdot \tilde{V}_0(cm^3g^{-1})}{L(nm)} \]
9.4 The t-method

de Boer et al. used microporous material isotherm and standard type II isotherm
de Boer equation

\[ t(\AA) = \left( \frac{13.99}{\log \frac{P_0}{P} + 0.034} \right)^{\frac{1}{2}} \]

\( t \): statistical thickness on nonporous materials, but with \( C \) value close to that of microporous materials

for the standard sample

\[ \text{slope} = \frac{S_t(m^2)}{10^4} \]

\[ S_t(m^2) = \frac{V_{\text{liq}}(cm^3)}{t(\AA)} \times 10^4 \]

de Boer
Microporous + standard

Slope = area of standard + external area of micropore

Micropore volume

Microporous

Micropore volume
Mesoporous + standard

Micro+Meso

Slope = total SA

Fill up of micropore

Slope = SA of meso + external surface
9.6 The micropore analysis method (MP method)

\[ S_{\text{micro}} = \left[ \left( \frac{V_{\text{liq}}}{t} \right)_{\text{lower}} - \left( \frac{V_{\text{liq}}}{t} \right)_{\text{upper}} \right] \times 10^4 \]

or

\[ S_{\text{micro}} = S_{\text{BET}} - \left( \frac{V_{\text{liq}}}{t} \right)_{\text{upper}} \times 10^4 \]
Fig. 9.5 Isotherm of N2 silica gel, Davidson 03 at 77.3°K
Fig. 9.6 V-t curve from Fig. 9.5
Slope of line 1 → $S = 792 \text{ m}^2/\text{g}$
0.0792 (>4Å)

Slope of line 2 → $S = 520 \text{ m}^2/\text{g}$
0.0520 (>4.5Å)

Slope of line 3 → $S = 360 \text{ m}^2/\text{g}$
0.0360 (>5Å)

$\Delta S = 160$, pores of 4.5~5Å are filled up

$\bar{r} = 4.75\text{Å}, \ V = \Delta S \cdot \bar{r} \times 10^4 \text{ cm}^3/\text{g} = 0.076 \text{ cm}^3/\text{g}$

The calculation is continued in this manner until there is no further decrease in the slope. $S_{\text{min}} = S_{\text{ext}}$

$\Sigma \Delta S = \text{micropore SA} \quad \Sigma V = \text{micropore vol.}$
The authors attributed the difference between the V-t and BET areas to surfaces that did not lie within pores.