Physisorption and pore size analysis

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- **1995 – 1999** PhD in heterogeneous catalysis
  - Universiteit Twente (NL)

- **2000 – 2005** Oberassistent
  - ETH Zurich, Inst of Chemical and Bioengineering
  - Research activity
    - zeolites
    - mesoporous silica

- **2005 – now** R&D Scientist, project leader
  - IFP Energies nouvelles, Catalysis and Separation Division
  - Research activity
    - 2005 – 2012: CO2 capture, separation of hydrocarbons
    - 2012 – 2018: hydrotreating and hydrocracking catalysts
    - 2018 – now: zeolites, oxide supports
Porous solids in catalysis

- **Supported catalysts**
  - e.g. noble metals, transition metal sulfides
  - Porous support
    - provides surface for dispersing the catalyst
    - provides mechanical stability
    - has an influence on diffusion of reactants and products
    - has an influence on adsorption of reactants and products
    - determines reactor volume

- **Porous catalysts**
  - Zeolites
  - Oxydes

Optimising porosity is often the key to improving catalytic performance.
Types of porosity

- Porous crystalline structures
  - Zeolites,
  - Metal Organic Frameworks

- Ordered or disordered stacking of small particles generates an interparticles porosity
  - oxides (silica, alumina, etc.)
  - activated carbon
Characterisation of porosity

- Physisorption ($N_2$, $Ar$, $Kr$)
  - surface area
  - pore volume
  - pore size distribution

- Hg intrusion
  - pore volume
  - pore size distribution
  - surface area

- Imaging methods
  - Transmission Electron Microscopy
  - Secondary Electron Microscopy
Terminology

- Adsorption is a surface phenomenon.
- Adsorbent = solid that provides a surface for adsorption.
- Adsorbate = molecule adsorbed on the surface.
- Adsorptive = molecule susceptible of being adsorbed.

- Physisorption: no formation of chemical bonds, no transfer of electron density
- Chemisorption: formation of a chemical bond (exchange of electrons)
Forces involved in physisorption

- **van der Waals forces**
  - amplified by multiple interactions with atoms or pore wall (i)
  - maximal when size of adsorbate (j) close to pore size
Forces involved in physisorption

**Electrostatic forces**

- Any non-symmetric charge distribution in the adsorbent generates an electric field.
- Adsorbates with an electric moment (dipole, quadrupole) interact with the electric field.
- Undesirable in analysis of porosity/pores size because surface chemistry/chemical composition enter into the game.
- $N_2$ has a small quadrupole moment → use of Ar, Kr is preferable for precise micropore size analysis.
Terminology

IUPAC distinguishes 3 categories of pore sizes

- Micropores < 2 nm
- Mesopores 2 – 50 nm
- Macropores > 50 nm
Adsorption in micropores

- Due to the strong interactions with the pore wall, micropores are filled at very low $p/p_0$ values.

**Initial slope depends on adsorbent-adsorbate interactions**

- Saturation zone
- Transition zone
- Additional adsorbate-adsorbate interactions

**Graphical representation:**

- Axes: Adsorbed amount vs. Pressure

© IFP
Adsorption in mesopores

- Monolayer adsorption
- Multilayer adsorption
- Onset of capillary condensation
- Pore filled by capillary condensation
Adsorption in macropores

- Opposite pore wall is too far away to influence adsorption and provoke capillary condensation
- First monolayer, then multilayer adsorption, like on an external surface
- Macropore volume not measurable via physisorption.
Questions

- Capillary condensation is the important adsorption mechanism in
  - Micropores
  - Mesopores
  - Macropores

- In adsorption experiments aiming at characterizing porosity we want to look at
  - Electrostatic adsorption forces
  - Covalent bonding to the surface
  - Van de Waals forces
How to measure an adsorption isotherm?

- **Volumetric method**

  - **Réservoir étalon :** $V_{res}$
  - **Hélium**
    - Etat initial : $P_{iHe}$, $T_{iHe}$
    - Etat final : $P_{fHe}$, $T_{fHe}$
  - **Azote**
    - Etat initial : $P_{iN2}$, $T_{iN2}$
    - Etat final : $P_{fN2}$, $T_{fN2}$
  - **Etat initial :** $P_{ciN2}$, $T_{ciN2}$
  - **Etat final :** $P_{cfN2}$, $T_{cfN2}$

  **Bilans Matières :** He et N$_2$

  - $\Delta n_{He} = \left( \frac{P_{iHe}}{T_{iHe}} - \frac{P_{fHe}}{T_{fHe}} \right) V_{res} R$
  - $\Delta n_{He} = (P_c^f - P_c^i) \frac{V_{cel}}{RT_m}$
  - $\Delta n_{N2} = \left( \frac{P_{iN2}}{T_{iN2}} - \frac{P_{fN2}}{T_{fN2}} \right) V_{res} R$
  - $\Delta n_{N2} = (P_c^f - P_c^i) \frac{V_{cel}}{RT_m} + n_{ads}^{N2}$

  **Température ambiante**
  - **Cellule mesure :** $V_{cel}$
  - **Température N$_2$ liquide 77 K**

  **Réservoir d'azote liquide à 77 K**

  **Masse d'adsorbant :** $M_{sol}$

  **Quantité adsorbée :** $Q_{ads} = n_{N2}^{ads}/M_{sol}$
Material balance

- Reservoir: 1  Sample cell: 2
- Without adsorption (He), sample cell initially under vacuum

\[
\frac{p_{\text{init}} V_1}{RT_1} = \frac{p_{\text{final}} V_1}{RT_1} + \frac{p_{\text{final}} V_2}{RT_2}
\]

\[
\frac{V_2}{T_2} = \frac{V_1}{T_1} \cdot \frac{p_{\text{init}} - p_{\text{final}}}{p_{\text{final}}}
\]

- With adsorption (N\textsubscript{2})

\[
n_{\text{tot}} = \frac{pV_1}{RT_1} + \frac{pV_2}{RT_2} + n_{\text{ads}}
\]

determined with He

Quantity initially present in the reservoir
Experimental difficulties

- Precise measurement of pressure required
  - difficult at low pressure
  - difficult to measure a micropore distribution
- Isotherm !!
  - $T_2$ in principle 77 K (temperature of liquid N$_2$)
    - part of the cell is not plunged into liquid N$_2$, but is at ambient temperature
    - temperature gradient must be the same as during the initial calibration of the volume with He
- pay attention to the level of liquid N$_2$
Example zeolite NaX

- Micropores are entirely filled at very low pressure.
- Isotherm is totally flat once micropores are filled.
  - saturation zone

powder after shaping with a binder
Examples - ZnO

- **no micropores**
- **mesopores generated by stacking of inindividual particles**

**Graphical Representation:**

- **Quantité adsorbée (cm³ STP/g)**
- **p/p₀**

Legend:

- Capillary condensation in the mesopores
- Multilayer adsorption on the surface of the particles
Comparison of two ZnO samples

- Surface: 65811 > 70299
- Pore size: 70299 > 65811
Example – Al₂O₃

- no micropores
- high surface area, broad pore size distribution

- capillary condensation in mesopores
- multilayer adsorption on surface of particles
Comparison Al₂O₃

- **Surface**: 79999 > 61399 > 47148
- **Pore size**: 47148 > 61399 > 79999
Quantitative treatment of $N_2$ isotherms

- **Pore volume**: $V_{\text{micro}}$, $V_{\text{meso}}$, $V_{\text{total}}$
  - t-plot

- **Surface area**
  - BET (Brunauer-Emerett-Teller)
  - Langmuir

- **Pore size distribution**
  - *Micropores*
    - Horwath-Kawazoe, Saito-Foley
  - *Mesopores*
    - BJH (Brunauer-Joyner-Halenda)
    - DFT (Density Functional Theory)
Determination of the surface area

BET (Brunauer Emmet Teller): multilayer adsorption

- first layer: adsorption on the surface
- all the other layers are considered like a condensed liquid

\[ n_m = \text{number of surface adsorption sites (monolayer)} \]
\[ n_{ads} = \text{total number of adsorbed molecules} \]
BET equation

- BET equation
  
  \[
  \frac{P}{V_{ads}(P_0 - P)} = \frac{1}{V_M C} + \frac{C-1}{V_M C} \left( \frac{P}{P_0} \right)
  \]

  \[C = \frac{K_{surface}}{K_{condensation}}\]

  - \(V_M\) = monolayer volume
  - \(V_{ads}\) = adsorbed volume
  - Plot \(p/V_{ads}(p_0-p)\) vs. \(p/p_0\)
  - Calculation of surface area:
    - \(N_A\) : Avogadro number
    - \(a\) : area of \(N_2\) molecule (16.2 Å²)

- \(S_{BET} = a \cdot \frac{p_0 V_M}{R \cdot 273 K} \cdot N_A\)

  \[S_{BET} (m^2 / g) = 4.355 \cdot V_m (cm^3 STP / g)\]

Recommended range of \(p/p_0\) : 0.05 - 0.35 max.
Exemple ZnO

Isothermes

\[ y = 0.0594x + 0.0003 \]
\[ y = 0.1196x + 0.0005 \]

BET plot

\[ S_{BET} = \frac{4.355}{\text{slope} + \text{intercept}} \]
\[ C_{BET} = \frac{\text{slope}}{\text{intercept}} + 1 \]

<table>
<thead>
<tr>
<th></th>
<th>( S_{BET} ) (m(^2)/g)</th>
<th>( C_{BET} )</th>
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</thead>
<tbody>
<tr>
<td>65811</td>
<td>74</td>
<td>136</td>
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<td>70299</td>
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</table>
Example NaX

- The multilayer adsorption model does not apply well to microporous solids when the pores are filled.
- Choose a lower pressure range for microporous solids.
  - $p/p_0 = 0.05 - 0.10$
- $C$ constant may be negative. Does not make physical sense
  - lower the pressure range further

$$y = 0.0064x - 3E-05$$

$$S_{BET} = \frac{4.355}{0.0064 - 0.00003} = 685m^2/g$$
Langmuir Surface Area

- **Langmuir theory**
  - is a model of monolayer adsorption
  - this hypothesis is never fulfilled

- Do not use Langmuir surface areas !!

- $S_{\text{Langmuir}}$ is always $> S_{\text{BET}}$ because multilayer adsorption is treated like monolayer adsorption.
Determination of the pore volume

In some cases possible without using any model.

\[ V_{\text{ads}} = 178 \text{ cm}^3 \text{ STP/g} \rightarrow V_{\text{micro}} \]

\[ V_{\text{ads}} = 240 \text{ cm}^3 \text{ STP/g} \rightarrow V_{\text{total}} \]

\[ V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}} \]
Conversion gas volume – pore volume

- Volume of adsorbed gas corresponds to a certain number of moles
  - STP = Standard Temperature Pressure
    - $T = 273\text{ K}$, $p = 1\text{ bar} = 100\text{ kPa}$
  - The adsorbed phase is considered like a liquid phase
    - Density of liquid $N_2$ at $77\text{ K}$: $0.807\text{ g/ml}$

$$n_{ads} = \frac{V_{ads}p}{RT}$$

$$V_p = \frac{m_{N_2}}{\rho_{N_2,liq}} = \frac{n_{ads} \cdot M_{N_2}}{\rho_{N_2,liq}}$$

$$V_p (ml / g) = 1.5468 \cdot 10^{-3} \cdot V_{ads} (cm^3 \text{STP} / g)$$
t-plot

- Transform adsorbed amount in an average thickness ($t$) of the adsorbed layer
- For multilayer adsorption on a flat surface

$$ t = \frac{V_{ads}}{S} $$
Universal curve $t$ vs. $p/p_0$

- The isotherms ($V_{ads}/S_{BET}$) of many low surface area oxides ($\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{TiO}_2$, $\text{MgO}$) form a universal curve $t = f(p/p_0)$.

- Numerical description of that curve
  - valid for $t = 3.5 – 10 \text{ Å}$
  - and $p/p_0 = 0.1 – 0.8$

Harkins Jura

$$ t = \left( \frac{13.99}{- \log \frac{p}{p_0} + 0.034} \right)^{1/2} $$

Halsey

$$ t = 3.54 \left[ \frac{5}{\ln\left(\frac{P_0}{P}\right)} \right]^{1/3} $$

Fig. 12.3. The adsorption of nitrogen on nonporous samples of silica and alumina, the surface areas ranging from 2.6–11.5 m$^2$ g$^{-1}$ for silica and from 58–153 m$^2$ g$^{-1}$ for alumina. $n/n_m$ is plotted against $p/p^2$. $n$ is the number of moles adsorbed per gram of adsorbent and $n_m$ is the monolayer capacity, expressed in the same units. Line A: $\bullet$ = silica; $\times$ = alumina. Line B: the BET isotherm (Eqn. 12.19) with $c$ values of 100–200.
Isotherm expressed as $V_{\text{ads}} = f(t)$

$$t = \left( \frac{13.99}{-\log \frac{p}{p_0} + 0.034} \right)^{1/2}$$

$t$ = thickness that the adsorbed phase would have on a non-porous material
Interpretation of t-plots

- **Adsorption on a non-porous solid**
  - Equations: $V_{ads} = \frac{p}{p_0}$

- **Adsorption on a microporous solid**
  - Equations: $S = \frac{V_{ads}}{t}$
  - Steps:
    - Micropores rapidly filled
    - Then adsorption on external surface
**Example zeolite NaX**

- **Isotherm**
- **t-plot**

- $V_{micro} = 175 \text{ cm}^3 \text{ STP/g} = 0.271 \text{ ml/g}$
**Surface BET vs. Surface t-plot**

\[ S_{t-plot} (m^2 g^{-1}) = 1.5468 \cdot PNT (cm^3 g^{-1} nm^{-1}) \]

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Micro- and mesoporous solids

Solide non poreux : Adsorption sur Surface Externe - Courbe $t = t(P/P_0)$

Solide poreux : Adsorption sur Surfaces Interne & Externe

Pressions relatives $P/P_0$ croissantes

Solide non poreux : Adsorption sur Surface Externe

Solide μ et m-Poreux

Solide μ et m-Poreux

$V_{\mu P} + V_{mP}$

$V_{\mu P}$

Adsorption sur Surface Externe (mésopores) $\Rightarrow S_{B.E.T.}$

Adsorption sur Surface Externe
t-plot of micro/mesoporous zeolites

- **Dealuminated USY zeolites**

  - Intercept gives micropore volume
  - Slope gives surface area of mesopores
  - Hard to define a second slope for the external surface

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Increase due to capillary condensation

\( V_{\text{micro}} \)
Average pore size

From geometrical rules

- Cylindrical Pore:
  - $V = \pi r^2 h$
  - $S = 2\pi rh$

- Spherical pore:
  - $V = \frac{4}{3}\pi r^3$
  - $S = 4\pi r^2$

- Slit pore:
  - $V = lhr$
  - $S = lh$

\[
\begin{align*}
\frac{S}{V} &= \frac{2}{r} & d &= \frac{4V}{S} \\
\frac{S}{V} &= \frac{3}{r} & d &= \frac{6V}{S} \\
\frac{S}{V} &= \frac{1}{r} & d &= \frac{2V}{S}
\end{align*}
\]
Micropore size distribution

- Based on the relation between adsorption strength and the ratio between adsorbate size and pore size
  - condition: adsorption controlled by van der Waals interactions only

- Mathematical models
  - Horvath-Kawazoe: slit-shaped pores
  - Saito-Foley: cylinder pores  
    
- Input parameters
  - pore geometry: slit-shaped, cylinder, sphere
  - parameters of the Lennard-Jones potential well: $\varepsilon$ and $\sigma_{ij}$
    - not always well known for atypical solids

- Input data
  - high precision isotherm at very low pressure!
Example of micropore size distribution

- **Importance of geometry!**
- **Improved model assumes**
  Langmuir isotherm instead of linear isotherm.

*Cheng, Yang, Chem. Eng. Sci. 1994, 4*

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**Spherical pore model:** 1.3 nm

**Slit pore model:** 0.8 nm

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**Fig. 4.** Adsorption isotherms of argon on 5A (Venero and Chiu, 1988) and faujasite zeolites (Borghard et al., 1991) at 87 K: (○) 5A zeolite; (□) faujasite.

**Fig. 6.** Micropore size distributions of faujasite zeolite calculated from slit pore models: (●) improved model; (◇) H–K model.

**Fig. 11.** Micropore size distribution of faujasite zeolite calculated from spherical pores models: (●) improved model; (◇) H–K model.
Mesopore size distribution

- via the theory of capillary condensation
Kelvin equation

- Capillary forces in the pore lower the vapor pressure of the condensed liquid
  - Pressure at the concave side of an interface is higher than at the convex side.
    - Overpressure counteracts the surface tension, which tries to collapse the interface area
  - Application to interface between gas and adsorbed liquid film in a pore
    - Pressure in liquid is lower than gas pressure.
    - Means that chemical potential in liquid is lower, in other words that the equilibrium vapor pressure is lower.
    - Capillary condensation occurs at a lower pressure than condensation.
Kelvin equation

**Mathematic formalism**

- Work against interfacial tension = change in free enthalpy

\[
dA \cdot \gamma = d\Omega_{\text{cap, liq}} \cdot \mu_{\text{cap, liq}} + d\Omega_{\text{liq}} \cdot \mu_{\text{liq}}
\]

\[
d\Omega_{\text{cap, liq}} = -d\Omega_{\text{liq}} = \frac{dV_{\text{cap, liq}}}{V_m}
\]

\[
dA \cdot \gamma = \frac{dV_{\text{cap, liq}}}{V_m} \cdot \mu_{\text{cap, liq}} - \frac{dV_{\text{cap, liq}}}{V_m} \cdot \mu_{\text{liq}}
\]

\[
dA \cdot V_m \cdot \gamma = dV_{\text{cap, liq}} \left( \mu_{\text{cap, liq}} - \mu_{\text{liq}} \right)
\]

\[
(\mu_{\text{cap, liq}} - \mu_{\text{liq}}) = -\frac{dA}{dV_{\text{cap, g}}} \cdot V_m \cdot \gamma
\]

\[
RT \ln \frac{p_{\text{cap}}}{p_{\text{sat}}} = -\frac{dA}{dV_{\text{cap, g}}} V_m \gamma
\]

\[
\mu_{\text{cap, liq}} = \mu_0 + RT \ln \frac{p_{\text{cap}}}{p_0}
\]

\[
\mu_{\text{liq}} = \mu_0 + RT \ln \frac{p_{\text{sat}}}{p_0}
\]
Generalized Kelvin equation

Relation to curvature of the pore

\[ \ln \frac{P_{cap}}{P_{sat}} = -\frac{V_m \gamma}{RT} \cdot \frac{dA}{dV} \]

- \( \frac{dV}{dA} \) = change in volume per change in interface area
- \( V_m = \) molar volume

Inverse relationship with curvature radius.

Curvature depends on the pore geometry

- Sphere: \( \frac{dV}{dA} = \frac{r}{2} \)
- Cylinder: \( \frac{dV}{dA} = r \)
- Slit: \( \frac{dV}{dA} = d \) (distance between slits)
Capillary condensation associated with hysteresis

Type H1

capillary condensation
capillary evaporation

Vol$_{ads}$ (cm$^3$/g)

$p/p_0$

0 0.2 0.4 0.6 0.8 1.0

0 200 400 600 800 1000 1200
Origin of the hysteresis – Cohan's theory

The lower $r_m$, the lower is the pressure of capillary condensation/evaporation

$\text{Adsorption:}
\begin{align*}
&\text{cylindrical meniscus} \\
r_{\text{curv}} = r_{\text{eff}}
\end{align*}
$

$\text{Desorption:}
\begin{align*}
&\text{hemispherical meniscus} \\
r_{\text{curv}} = r_{\text{eff}} / 2
\end{align*}
$

- $r_{\text{curv,ads}} = 2 \times r_{\text{curv,des}}$
- Capillary evaporation at a lower pressure than capillary condensation

→ Hysteresis loop in isotherm

L.H. Cohan, JACS 60 (1938)
Application of Cohan's theory

Harkins-Jura t-plot equation

\[
\log \frac{p}{p_0} = 0.034 - \frac{13.99}{t^2}
\]

Kelvin equation

\[
\log \frac{p}{p_0} = -\frac{4.14}{r_m}
\]

<table>
<thead>
<tr>
<th></th>
<th>(p_c/p_0)</th>
<th>(t(p_c))</th>
<th>(r_{\text{curvature}})</th>
<th>(R_c)</th>
<th>(r_p = r_c + t)</th>
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</thead>
<tbody>
<tr>
<td>Ads</td>
<td>0.671</td>
<td>8.2</td>
<td>11.9</td>
<td>11.9</td>
<td>20.2</td>
</tr>
<tr>
<td>Des</td>
<td>0.565</td>
<td>7.0</td>
<td>8.35 \times 2</td>
<td>16.7</td>
<td>23.7</td>
</tr>
</tbody>
</table>

Cylinder !!

Sphere !!
Origin of the hysteresis

- Truth seems to be complicated than in Cohan’s theory.
- Cohan’s theory, based on the shape of meniscus, theory suggests that different vapor liquid equilibria exist in a spherical or cylindrical meniscus, which leads to hysteresis => is an equilibrium picture.
- Molecular simulations (DFT) suggest that adsorption branch is not in thermodynamic equilibrium, but is a metastable state.
Hysteresis and metastability

- Adsorption branch comprises metastable states. Grand free energy of filled pore is lower than that of the empty pore in the hysteresis.
- Desorption branch is in thermodynamic equilibrium.
- Reason for metastability in adsorption branch:
  - barrier of nucleation by formation of a liquid bridge across the pore.
  - condensation occurs when limit of metastability is reached.

Monson, MMM, 2012.

Peterson, JCS Farad 2, 1986.
Pore network effects

Order of capillary evaporation: C before B and A, but N$_2$ can only desorb from pore C if pore B has already been emptied.


- Desorption branch of isotherm not in thermodynamic equilibrium any more, due to pore blocking.
- Desorption is controlled by a percolation process.
  - probability that the pore is connected to the outer surface.
Ink-bottle pores

- In desorption the evaporation from the pore neck is determining.
- Whole pore will only be emptied, when the capillary evaporation pressure for the pore neck is reached.
- Sudden drop in the desorption isotherm – type H2
Ink-bottle type hysteresis loop

- If pore size distribution is calculated from desorption branch, an artificially narrow pore size distribution is obtained.
- The adsorption branch has to be used to calculate the pore size distribution.

Type H2

Adsorbent: xerogel and alcogel
Adsorption vs. desorption isotherm

- **Adsorption isotherm – Pros and cons**
  - Condensation can be delayed – not in thermodynamic equilibrium
  - Cylindrical meniscus not stable – not advisable to use adsorption branch for cylindrical pores

- **Desorption branch – Pros and cons**
  - Evaporation not delayed, in thermodynamic equilibrium – generally preferred
  - Ink-bottle type pores: smallest opening determines the desorption
  - In a network of interconnected pores: percolation (transport) effects determine the desorption

- **Conclusion:** look at both and compare them
Use of Kelvin equation for Pore size distribution analysis – BJH model

\[ p_0 \] – all pores filled

\[ p_1 \] – capillary evaporation in largest pore
reduction of layer thickness

\[ p_2 \] – capillary evaporation in 2\(^{nd}\) largest pore
reduction of layer thickness in both pores
In each desorption step \( p_{n-1} \rightarrow p_n \), capillary evaporation occurs from a pore of size \( r_{pn} \).

The volume desorbed in that step \( (\Delta V_n) \) can be related to the pore volume by the geometrical relation given above.

Complication: Reduction in layer thickness in the pores, which were already emptied, also contributes to \( \Delta V_n \).
The BJH-equation

E.P. Barret, L.G. Joyner, P.P. Halenda, JACS 73 (1951) 373.

$$V_{pn} = \frac{r_{pn}^2}{(r_{kn} + \Delta t_n)^2} \cdot \Delta V_n - \frac{r_{pn}^2}{(r_{kn} + \Delta t_n)^2} \cdot \Delta t_n \cdot \sum_{j=1}^{n-1} \frac{r_{pj} - t_j}{r_{pj}} A_{pj}$$

$$A_p = \frac{2V_p}{r_p}$$

capillary evaporation
correction term

For each desorption step the average diameter of the pore, which undergoes capillary evaporation is calculated from the Kelvin equation and the t-plot equation: $r_p = r_k + \Delta t$

$$\log \frac{p}{p_0} = 0.034 - \frac{13.99}{t^2}$$

$$\log \frac{p}{p_0} = \frac{-4.14}{r_k}$$

$\Delta t$ is the change in layer thickness in each desorption step

$\Delta V_n$ is the volume desorbed in each step

→ A plot of pore volume vs. pore radius is obtained.
Example of pore size distribution

- Alumina supports
  - Significant differences between PSD from adsorption and desorption
Limits of the BJH-model

- BJH underestimates the pore size below 7.5 nm – WHY?
  - Model separates the adsorbed film and the capillary condensate – not a realistic picture
  - Fluid-wall interactions are neglected
  - Kelvin equation may not be valid in very narrow pores
    - Surface tension might increase with curvature

- One should speak about a BJH-value rather than pore diameter.
Ink-bottle type hysteresis loop

- Narrow peak in the pore size distribution of the adsorption branch is an artefact caused by the forced closure of the isotherm at $p/p_0 = 0.43$
Isotherm without hysteresis loop
Closure point of the isotherm

- Critical temperature inside a pore lower than in bulk:
  \[ T_{c,\text{pore}} < T_{c, \text{bulk}} \]
- \( T_{c,\text{pore}} \) decreases with decreasing pore diameter\(^1\)
- Above \( T_c \) no condensate-vapour meniscus
- For narrow pores \( T_c < 77 \text{ K} \)
- No hysteresis for filling and emptying of these pores
- \( T_{c,\text{pore}} < 77 \text{ K} \) for pores, which show capillary condensation at \( p/p_0 = 0.4 \) → closure point of isotherm
- \( T_c(\text{Ar}) > T_c(\text{N}_2) \) → Ar isotherms show hysteresis when \( \text{N}_2 \) isotherms don‘t\(^2\)

Summary – Pore size analysis

- BJH relies on Kelvin equation and the universal t-curve for determining pore size distribution
  - both concepts have weaknesses
- Alternative methods exist
  - Density Functional Theory
  - Broekhoff de Boer – improvement of BJH
  - Derjaguin – concept of disjoining pressure
    - surface tension concept that takes interaction with solid into account
- Every model assumes a certain pore geometry (cylindrical, spherical, slit-shaped) – influences the results!!
- The adsorption and the desorption branch contain different information – look at both.
DFT is becoming state of the art

- Express the Grand Potential as a function of the fluid density distribution in space

\[
\Omega[\rho] = F[\rho] + \int \rho(r)V(r)dr - \mu \int \rho(r)dr
\]

- \(\rho(r)\) = fluid density at position \(r\)
- \(F(\rho)\) = Helmholtz energy of the system due to fluid-fluid interactions, in the absence of an external field
- \(V(r)\) = external potential at position \(r\)
- \(\mu\) = chemical potential
Expression for the grand potential

\[ \Omega[\rho(r)] = k_B T \int \rho(r) \left[ \ln \left( \Lambda^3(r) \right) - 1 \right] dr + k_B T \int dr \Phi \left( \{ \bar{n}_\alpha \}(r) \right) + \frac{1}{2} \int dr \int \rho(r) \rho(r') \phi_{\text{att}}(|r - r'|) dr' - \int \rho(r) \left[ \mu - \phi_{\text{ext}}(r) \right] dr \]

- Ideal gas
- Excess energy (non-ideality)
- Fluid-fluid interaction
- External potential

- Everything is in the expression of \( \Phi_{\text{ext}} \)
  - Solid-fluid interaction
  - Effect of pore size and pore geometry (confinement)
    - Similar to the HK, SF models of micropore size analysis
Pore size analysis with DFT

- Kernel of adsorption isotherms (= integrated fluid density) is calculated as function of pore size
- Experimental adsorption isotherm is fitted by a weighted sum of the kernel isotherms
- The weights give the pore size distribution.

**Recommended method:**

- Use DFT to extract pore size distribution from adsorption branch.
- Use desorption branch to analyze percolation phenomena
Be careful when using DFT

- Modern commercial equipment has DFT analysis integrated in the software
  - Is a press-button, black-box method
  - Depending on the solid-fluid interaction parameters and the pore geometry that the DFT method relies on you will get different results
    - You should know what you are doing
- Like BJH analysis, DFT produces an artifact: peak in pore size distribution at 1 nm
  - Due to formation of an ordered layer on the surface
Questions

- When you analyse the pore size distribution for a given isotherm with a cylindrical model or with a spherical model, what will be the ratio between the pore size?

- The analysis of the desorption branch of the adsorption isotherm gives the
  - Pore size distribution
  - Neck size distribution
  - None of them
Literature

- **Textbooks on adsorption**

- **Review articles discussing a more moderne view of hysteresis effects and pore size analysis**
Alternative explanations of the Kelvin equation
Physical principles of capillary condensation

- **Vapour pressure of a liquid under external pressure**

  **External pressure**

  \[
  p_g = \text{new vapour pressure of } H_2O \\
  p_{g0} = \text{original vapour pressure of } H_2O \\
  \Delta p_l = \text{external pressure on liquid (} H_2O), \text{ which induces the change in vapour pressure} \\
  v_l = \text{molar volume of liquid (} H_2O) \\
  \]

  \[
  \begin{align*}
  \Delta \mu_l &= v_l dp_l = v_g dp_g \\
  v_l \Delta p_l &= RT/p_g \cdot dp_g \\
  v_l \Delta p_l &= RT \ln (p_g/p_{g0}) \\
  p_g &= p_{g0} \cdot \exp \left( \frac{v_l}{RT} \Delta p_l \right)
  \end{align*}
  \]
Vapour pressure of a drop of liquid

\[ p_{in} - p_{out} = \frac{2\gamma}{r} \]

\( \gamma = \) surface tension
\( r = \) radius of curvature

\[ p_l - p_{out} = \frac{2\gamma}{r} \]

\( p_l = p + \frac{2\gamma}{r} \)

overpressure inside the drop holds against

surface tension tries to contract the drop
Vapour pressure of a liquid void

\[ p_{\text{in}} - p_{\text{out}} = \frac{2\gamma}{r} \]

\[ p_{\text{in}} - p_{l} = \frac{2\gamma}{r} \]

\[ p_{l} = p - \frac{2\gamma}{r} \]

Kelvin equation: vapour pressure inside a void is lowered

[\[ p_{g} = p_{g,0} \cdot \exp(-\frac{2v_{l}\gamma}{RT \cdot r}) \]
 Kelvin equation

Capillary forces in the pore lower the vapor pressure of the condensed liquid

\[ \mu_{\text{cap}} = \mu_0 + RT \ln \frac{p_{\text{cap}}}{p_0} \]

\[ \mu_{\text{liq}} = \mu_0 + RT \ln \frac{p_{\text{sat}}}{p_0} \]

Evaporate \( n \) moles from capillary and condense on a flat surface. You have to work against the surface tension \( \gamma \).

\[ W = \Delta A \gamma \cos \theta = 2\pi r \Delta l \gamma \cos \theta \]

The work done to overcome the surface tension is equal to change in chemical potential.

\[ n \cdot \Delta \mu = \frac{\Delta V}{V_m} RT \ln \frac{p_{\text{sat}}}{p_{\text{cap}}} \]

Explains why vapor pressure of the unconfined liquid is higher than in the capillary.