Physisorption and pore size analysis

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CV Gerhard Pirngruber

- 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 – now: hydrotreating and hydrocracking catalysts
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)
Terminology

- IUPAC distinguishes 3 categories of pore sizes
  - Micropores < 2 nm
  - Mesopores 2 – 50 nm
  - Macropores > 50 nm
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

\[ U_{LJ} = 4\epsilon \left( \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right) \]
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
- $\text{N}_2$ has a small quadrupole moment → use of Ar, Kr is preferable for precise micropore size analysis
Adsorption in micropores

- Gradual filling of pore volume starting from surfaces

- Initial slope depends on adsorbent-adsorbate interactions

- Saturation zone

- Transition zone
  - additional adsorbate-adsorbate interactions

- Adsorbed amount vs Pressure

Characterization of porous solids - Surface Science and Catalysis Course - G Pirngruber 28 October 2014
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
How to measure an adsorption isotherm?

**Volumetric method**

- **Réservoir étalon :** $V_{\text{res}}$
- **Cellule mesure :** $V_{\text{cel}}$
- **Température ambiante**
- **Température N2 liquide 77 K**

**Etat initial :** $P_{i\text{He}}, T_{i\text{He}}$
**Etat final :** $P_{f\text{He}}, T_{f\text{He}}$

**Etat initial :** $P_{i\text{N2}}, T_{i\text{N2}}$
**Etat final :** $P_{f\text{N2}}, T_{f\text{N2}}$

**Réservoir d’azote liquide à 77 K**

**Bilans Matières : He et N2**

\[
\Delta n_{\text{He}} = \frac{P_{i\text{He}}^i - P_{f\text{He}}^f}{T_{i\text{He}}^i - T_{f\text{He}}^f} \frac{V_{\text{res}}}{R}
\]

\[
\Delta n_{\text{He}} = (P_c^f - P_c^i) \frac{V_{\text{cel}}}{RT_m}
\]

\[
\Delta n_{\text{N2}} = \frac{P_{i\text{N2}}^i - P_{f\text{N2}}^f}{T_{i\text{N2}}^i - T_{f\text{N2}}^f} \frac{V_{\text{res}}}{R}
\]

\[
\Delta n_{\text{N2}} = (P_c^f - P_c^i) \frac{V_{\text{cel}}}{RT_m} + n_{\text{N2}}^{\text{ads}}
\]

**Masse d’adsorbant :** $M_{\text{sol}}$

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

- **Reservoir**: 1  
- **Sample cell**: 2

- **without adsorption (He)**, sample cell initially under vacuum

\[
\frac{p_{\text{init}}V_1}{RT_1} = \frac{p_{\text{final}}V_1}{RT_1} + \frac{p_{\text{final}}V_2}{RT_2} \quad \Rightarrow \quad \frac{V_2}{T_2} = \frac{V_1}{T_1} \cdot \frac{p_{\text{init}} - p_{\text{final}}}{p_{\text{final}}}
\]

- **with adsorption (N\textsubscript{2})**

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

determined with He
Experimental difficulties

- Precise measurement of pressure required
  - difficult at low pressure
  - difficult to measure a micropore distribution

- Isotherme !!
  - $T_2$ in principle 77 K (temperature of liquid $N_2$)
    - part of the cell is not plunged into liquid N2, 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**

after shaping with a binder
Examples - ZnO

- no micropores
- mesopores generated by stacking of individual particles

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 – $\text{Al}_2\text{O}_3$

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

The graph shows:
- Capillary condensation in mesopores
- Multilayer adsorption on the surface of particles
Comparison $\text{Al}_2\text{O}_3$

- Surface: $79999 > 61399 > 47148$
- Pore size: $47148 > 61399 > 79999$
Quantitative treatment of N\textsubscript{2} isotherms

- **Pore volume:** \( V_{\text{micro}}, V_{\text{meso}}, V_{\text{total}} \)
  - t-plot
  - Dubinin-Radushkevitch

- **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

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

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

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

- \(V_M\) = 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)

\[
S_{\text{BET}} = a \cdot \frac{p_0 V_M}{R \cdot 273K} \cdot N_A
\]

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

Recommended range of \(p/p_0\) : 0,05 - 0,35 max.
Exemple ZnO

Isothermes

BET plot

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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{BET} ) (m(^2)/g)</th>
<th>( C_{BET} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>65811</td>
<td>74</td>
<td>136</td>
</tr>
<tr>
<td>70299</td>
<td>36</td>
<td>237</td>
</tr>
</tbody>
</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

\[
S_{BET} = \frac{4.355}{0.0064 - 0.00003} = 685 m^2 / g
\]
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.

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

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

\[ V_{meso} = V_{total} - V_{micro} \]
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 g/ml

\[
V_p = \frac{m_{N_2}}{\rho_{N_2,\text{liq}}} = \frac{n_{ads} \cdot M_{N_2}}{\rho_{N_2,\text{liq}}}
\]

\[
V_p \left( \text{ml} / \text{g} \right) = 1.5468 \cdot 10^{-3} \cdot V_{ads} \left( \text{cm}^3 \text{STP} / \text{g} \right)
\]
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 $t = 3.5 – 10$ 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 $p/p^0$. $n$ is the number of moles adsorbed per gram of adsorbent and $n_m$ is the monolayer capacity, expressed in the same units. Line A: ● = silica; + = alumina. Line B: the BET isotherm (Eqn. 12.19) with $c$ values of 100–200.
Isotherm expressed as $V_{ads} = f(t)$

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

- $S = \frac{V_{ads}}{t}$
- $t =$ thickness that the adsorbed phase would have on a non-porous material

Limit of validity
Interpretation of t-plots

- **Adsorption on a non-porous solid**

- **Adsorption on a microporous solid**
  - micropores rapidly filled
  - then adsorption on external surface
Example zeolite NaX

**Isotherm**

---

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

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

<table>
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<th>( S_{t-plot} )</th>
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<td>34</td>
</tr>
</tbody>
</table>
Micro- and mesoporous solids

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

Pressions relatives \( P/P_0 \) croissantes

Solide poreux : Adsorption sur Surfaces Interne & Externe

Solide non poreux : Adsorption sur Surface Externe

Solide poreux : Adsorption sur Surfaces Interne & Externe

Vol. Ads. \( V_{\mu} + V_{m} \)

\( V_{\mu} \)

\( V_{m} \)

\( S_{B.E.T.} \)

Adsorption sur Surface Externe

Adsorption sur Surface Interne (mésopores)
t-plot may be ambiguous

- Zeolite beta with supermicropores
  - no clear linear region in the t-plot
  - micropore volume depends on the interval chosen for extrapolation
Méthode de Dubinin-Radushkevitch

- Théorie de remplissage de micropores

\[ \frac{V_{ads}}{V_{micro}} = \exp \left[ - \left( \frac{A}{E} \right)^2 \right] \quad A = -RT \ln \frac{p}{p_{vap,sat}} \]

- A = potentiel d'adsorption
- E = énergie caractéristique de l'adsorbant
- \( p_{vap,sat} \) = pression vapeur saturante
  - \( p_{vap,sat} = p_0 \) (1 atm) pour N\(_2\) à 77K

- Equation linéarisée

\[ \log V_{ads} = \log V_{micro} - D \log \left( \frac{p}{p_0} \right)^2 \]
Example NaX

-5.8 -5.7 -5.6 -5.5 -5.4 -5.3 -5.2 -5.1 0 0.5 1 1.5 2 2.5 3 3.5 4 4.5
log10(P/Po)^2
log10(Vol. liquide)

-5.1 -5.2 -5.3 -5.4 -5.5 -5.6 -5.7 -5.8

Pression élevée
Potentiel faible
Adsorption dans mesopores

Pression faible
Potentiel élevée
Début remplissage micropores

V_{micro} = 10^{-0.548} = 0.283 ml/g
Average pore size

From geometrical rules

- Cylindrical Pore:
  - \( V = \pi r^2 h \)
  - \( S = 2\pi rh \)
  - \( \frac{S}{V} = \frac{2}{r} \)
  - \( d = \frac{4V}{S} \)

- Spherical pore:
  - \( V = \frac{4}{3}\pi r^3 \)
  - \( S = 4\pi r^2 \)
  - \( \frac{S}{V} = \frac{3}{r} \)
  - \( d = \frac{6V}{S} \)

- Slit pore:
  - \( V = lhr \)
  - \( S = lh \)
  - \( \frac{S}{V} = \frac{1}{r} \)
  - \( d = \frac{2V}{S} \)
Mesopore size distribution

- via the theory of capillary condensation

![Diagram showing mesopore size distribution](image-url)
Kelvin equation

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

\[
\mu_{\text{cap}} = RT \ln \frac{p_{\text{cap}}}{p_0} \quad \mu_{\text{vap}} = RT \ln \frac{p_{\text{vap}}}{p_0}
\]

Evaporate \( n \) moles from capillary and condense on a flat surface. You have to overcome the capillary forces, i.e. 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.

\[
W = n \ln \frac{p_{\text{vap}}}{p_{\text{cap}}}
\]

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

\[ \frac{dV}{dA} = \frac{V_m \gamma \cos \theta}{RT \ln \frac{p_{\text{cap}}}{p_{\text{vap}}}} \]

\( dV/dA \) depends on the pore geometry

- **Sphere**: \( dV/dA = r/2 \)
- **Cylinder**: \( dV/dA = r \)
- **Slit**: \( dV/dA = d \)  
  distance between slits

**Relation to curvature of the pore**

\[ \frac{dV}{dA} = \frac{r_m}{2} \]

\[ \ln \frac{p_{\text{cap}}}{p_{\text{vap}}} = \frac{2}{r_m} RT \gamma \cos \theta \]
Capillary condensation

- Multilayer adsorption on the surface: layer thickness $t \uparrow$
- At a certain effective pore radius $r_p - t$, capillary condensation occurs
- Pore is filled. There is a step in the adsorption isotherm.

$p_c = p_0 \cdot \exp\left(- \frac{v_l \gamma}{RT \cdot (r_p - t)} \right)$

Where:
- $p_c$ is the condensation pressure
- $p_0$ is the initial pressure
- $v_l$ is the molar volume of the liquid
- $\gamma$ is the surface tension
- $R$ is the gas constant
- $T$ is the temperature
- $r_p$ is the effective pore radius
- $t$ is the layer thickness
Example isotherm with hysteresis

Type H1

capillary condensation

capillary evaporation
Application of the Kelvin equation

\[ \frac{p}{p_0} \]

\[ r_p = r_c + t \]

<table>
<thead>
<tr>
<th></th>
<th>( p_c/p_0 )</th>
<th>( t(p_c) )</th>
<th>( r_m )</th>
<th>( r_c )</th>
<th>( r_p = r_c + t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ads</td>
<td>0.671</td>
<td>8.2</td>
<td>23.9</td>
<td>11.9</td>
<td>20.2</td>
</tr>
<tr>
<td>Des</td>
<td>0.565</td>
<td>7.0</td>
<td>16.7</td>
<td>16.7</td>
<td>23.7</td>
</tr>
</tbody>
</table>
Origin of the hysteresis

- The lower $r_m$, the lower is the pressure of capillary condensation/evaporation
- $r_{m,\text{ads}} = 2 r_{m,\text{des}}$
- Capillary evaporation at a lower pressure than capillary condensation
  
  $\rightarrow$ Hysteresis loop in isotherm

L.H. Cohan, JACS 60 (1938)
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 size distribution – BJH model

$p_0$ – all pores filled

$p_1$ – capillary evaporation in largest pore
reduction of layer thickness

$p_2$ – capillary evaporation in 2nd largest pore
reduction of layer thickness in both pores
Mathematic description - BJH

- 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 contribute to $\Delta V_n$. 

$$\Delta V = \frac{(r_k + \Delta t)^2}{r_p^2} \cdot V_p$$
The BJH-equation

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

\[ A_p = \frac{2V_p}{r_p} \]

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: \( r_p = r_k + t \)

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

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

- \( \Delta t \) 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.
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.
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**
Ink-bottle pores

- In desorption smallest pore opening is determining.
- When pressure of capillary evaporation is reached for the smallest pore opening, whole pore is suddenly emptied.
- Sudden drop in the desorption isotherm – type H2.
Pore network effects

- 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.

$N_2$ can only desorb from pore A and C if pore B has already been emptied.

Ink-bottle type hysteresis loop

Type H2
Adsorbent: xerogel and alcogel

- 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.
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 \( T_c < 77 \) K
- No hysteresis for filling and emptying of these pores
- \( T_{c,\text{pore}} < 77 \) K for pores, which show capillary condensation at \( p/p_0 = 0.4 \) \( \rightarrow \) closure point of isotherm
- \( T_c(\text{Ar}) > T_c(\text{N}_2) \) \( \rightarrow \) Ar isotherms show hysteresis when \( \text{N}_2 \) isotherms don’t\(^2\)

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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.
Literature

- **Textbooks on adsorption**
  - D.A. Ruthven, Principles of Adsorption and Adsorption Processes, Wiley
  - D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press

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

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

**External pressure**

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

\[ p_g = p_{g0} \cdot \exp\left(\frac{v_l}{RT} \Delta p_l\right) \]
Vapour pressure of a drop of liquid

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

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

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

\[ p_l = p + \frac{2\gamma}{r} \]
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

\[ p_g = p_{g,0} \cdot \exp\left(-\frac{2v_l\gamma}{RT \cdot r}\right) \]