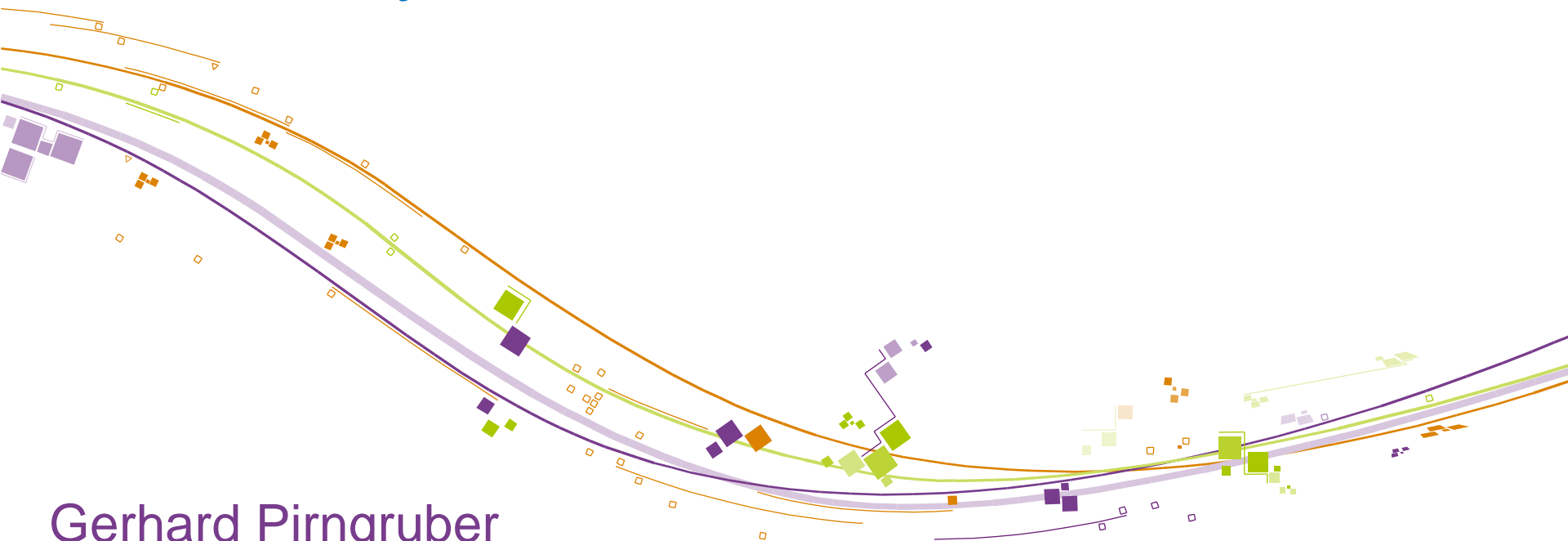


Physisorption and pore size analysis



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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

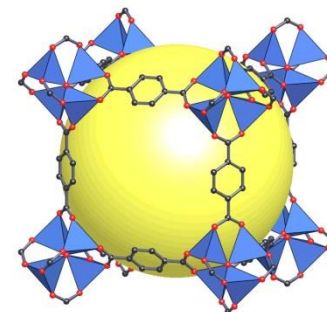
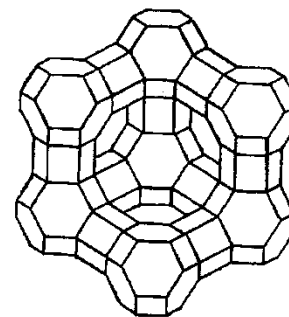
- Zeolites
- Oxides

Optimising porosity is often the key to improving catalytic performance.

Types of porosity

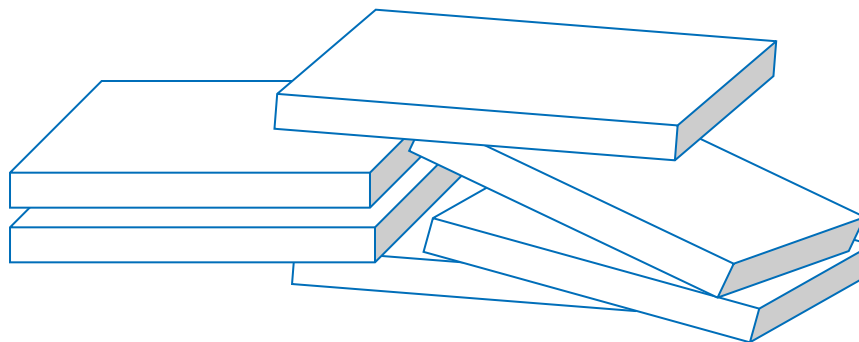
- **Porous crystalline structures**

- 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)

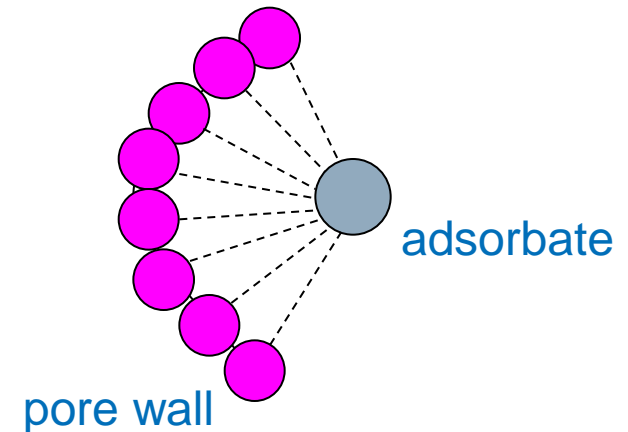
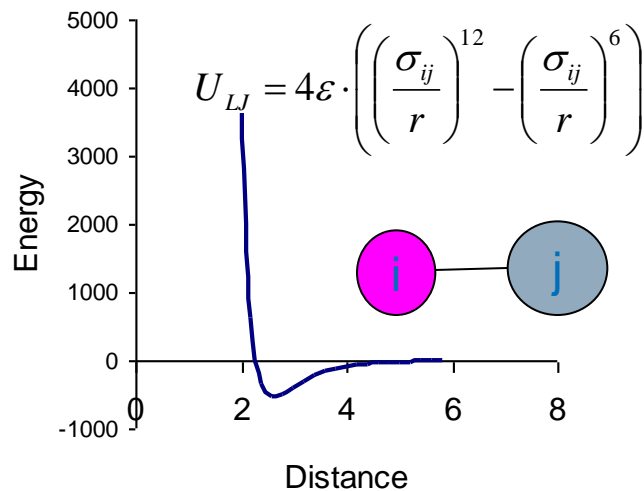
Terminology

- 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





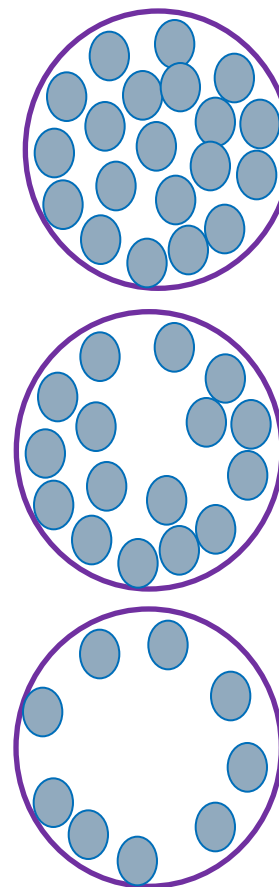
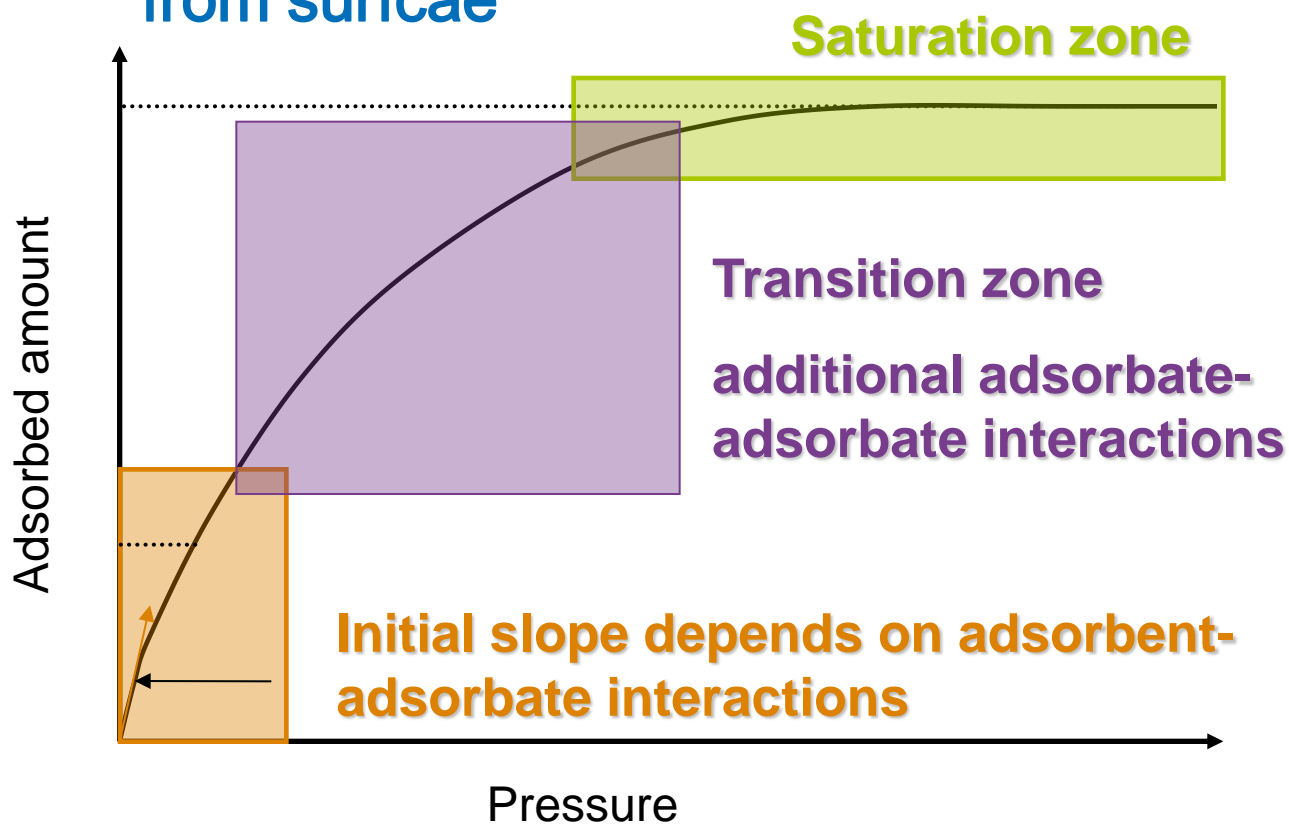
Forces involved in physisorption

■ Electrostatic forces

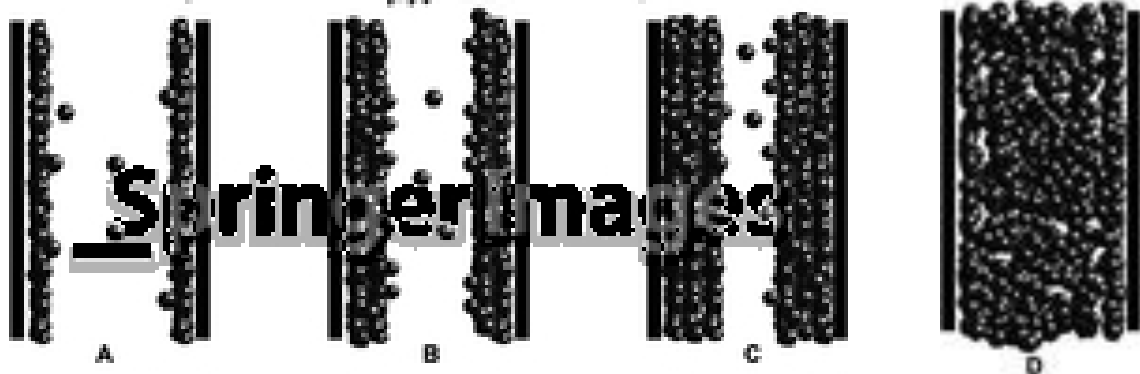
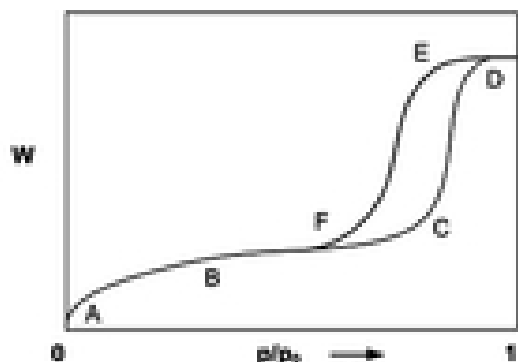
- Any non-symmetric charge distribution in the adsorbent generates an electric field
- adsorbates with an electric moment (dipole, quadrupole) interact with the electric field
- undesirable in analysis of porosity/pores size because surface chemistry/chemical composition enter into the game
- N_2 has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

Adsorption in micropores

- Gradual filling of pore volume starting from surface



Adsorption in mesopores



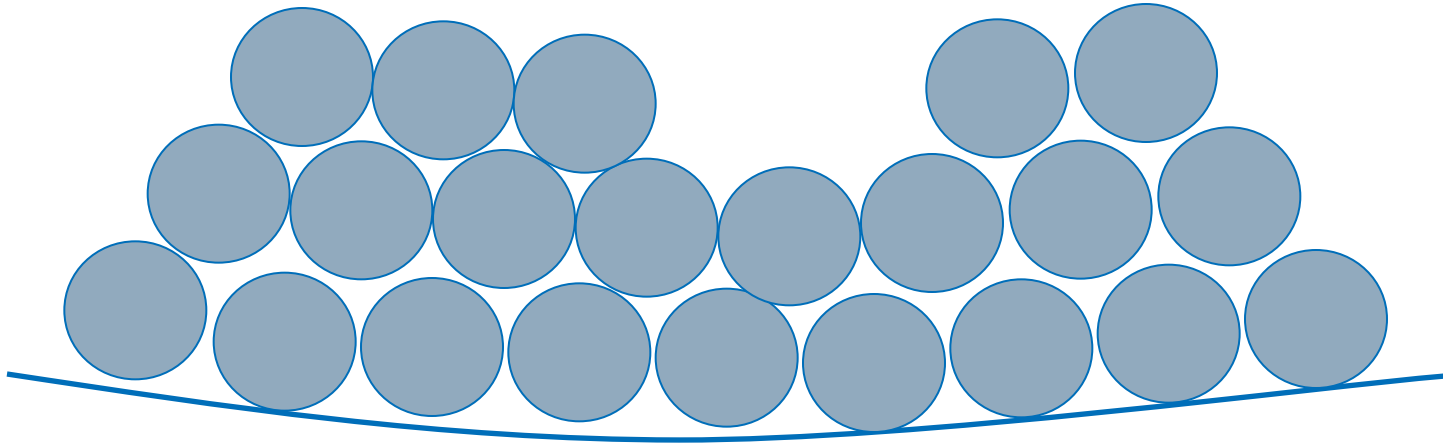
monolayer
adsorption

multilayer
adsorption

onset of
capillary
condensation

pore filled by
capillary
condensation

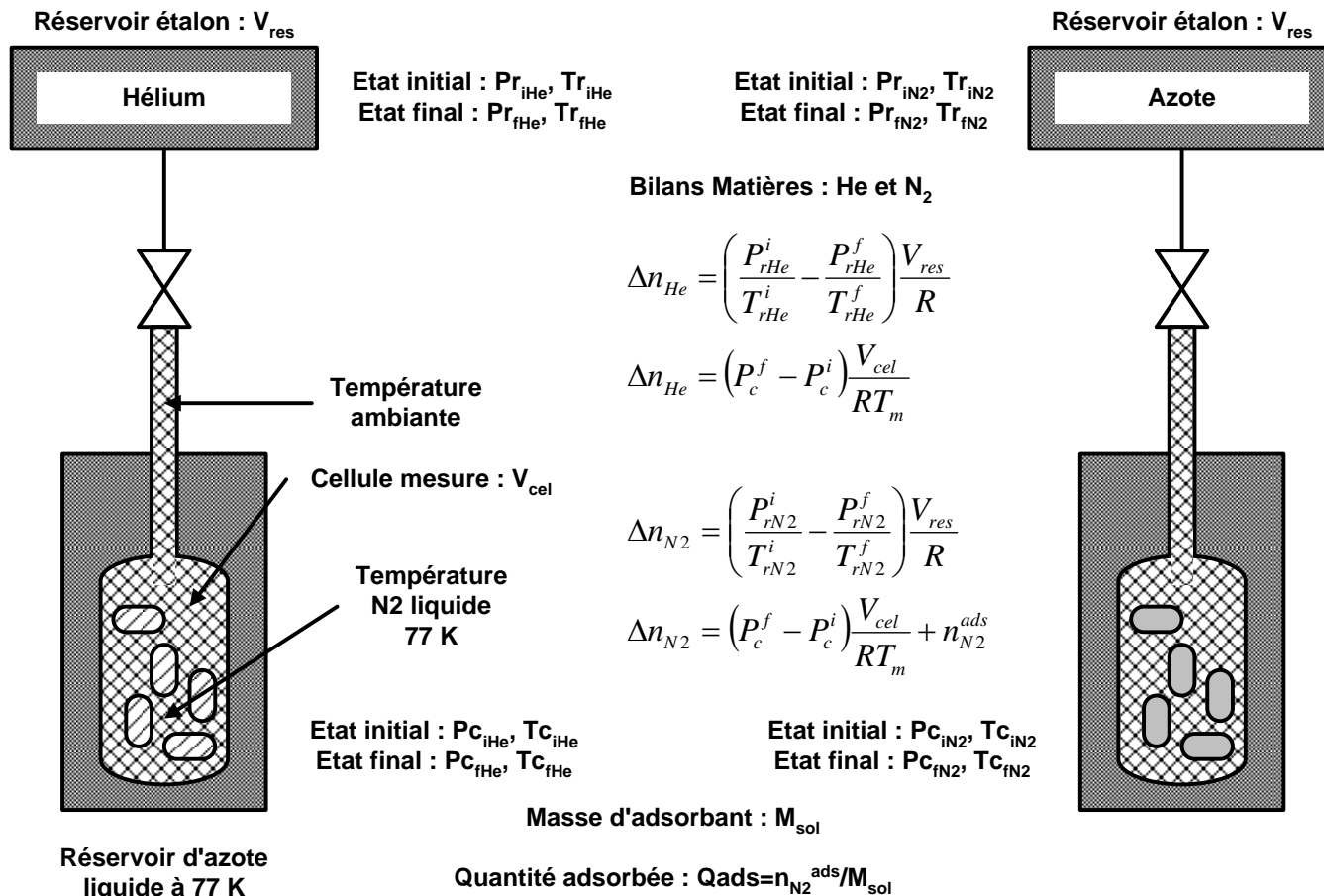
Adsorption in macropores



- 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



Material balance

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

$$\frac{p_{init}V_1}{RT_1} = \frac{p_{final}V_1}{RT_1} + \frac{p_{final}V_2}{RT_2} \quad \longrightarrow \quad \frac{V_2}{T_2} = \frac{V_1}{T_1} \cdot \frac{p_{init} - p_{final}}{p_{final}}$$

- with adsorption (N₂) determined with He

quantity initially present in the reservoir

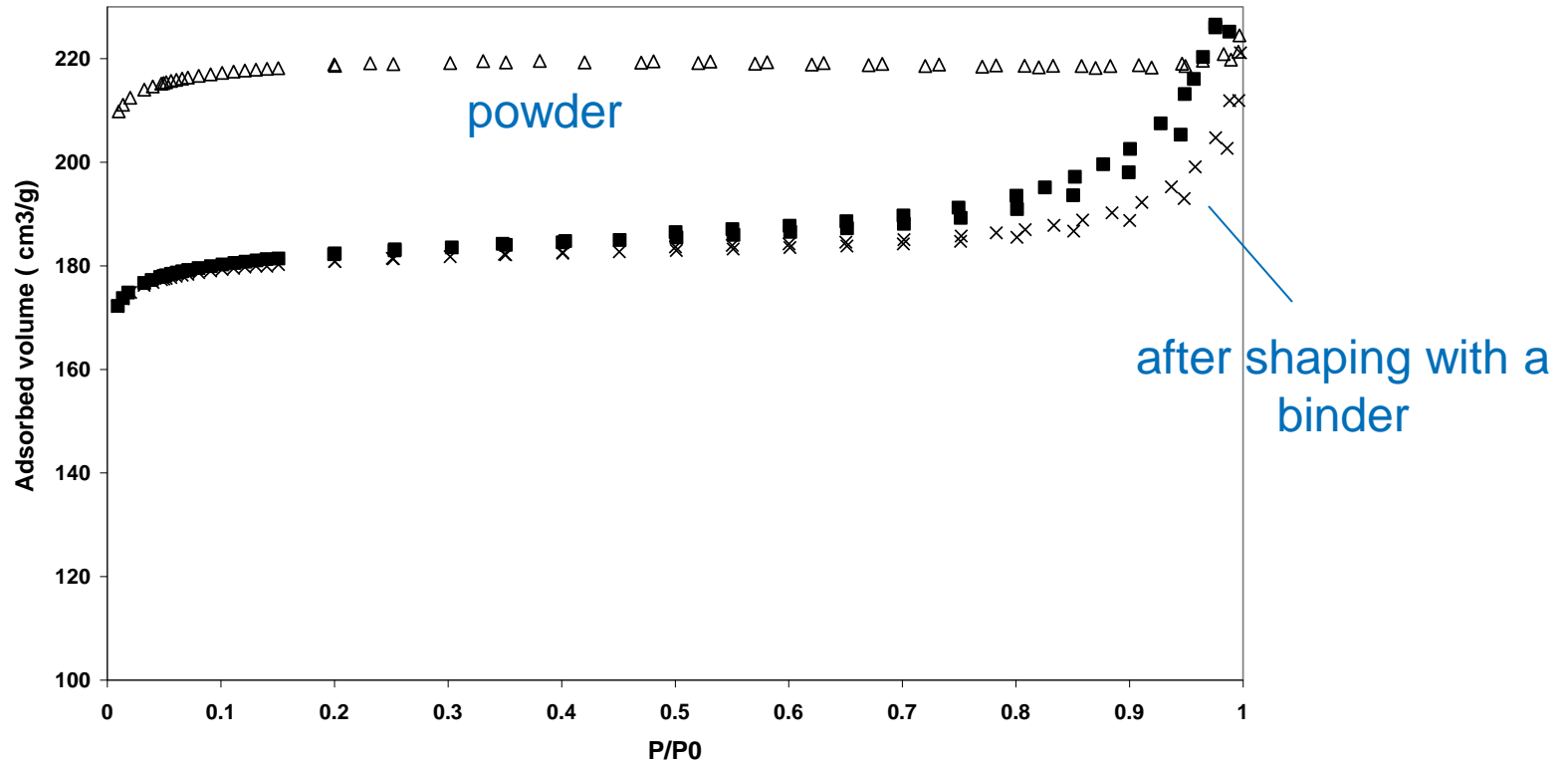
$$n_{tot} = \frac{pV_1}{RT_1} + \frac{pV_2}{RT_2} + n_{ads}$$



Experimental difficulties

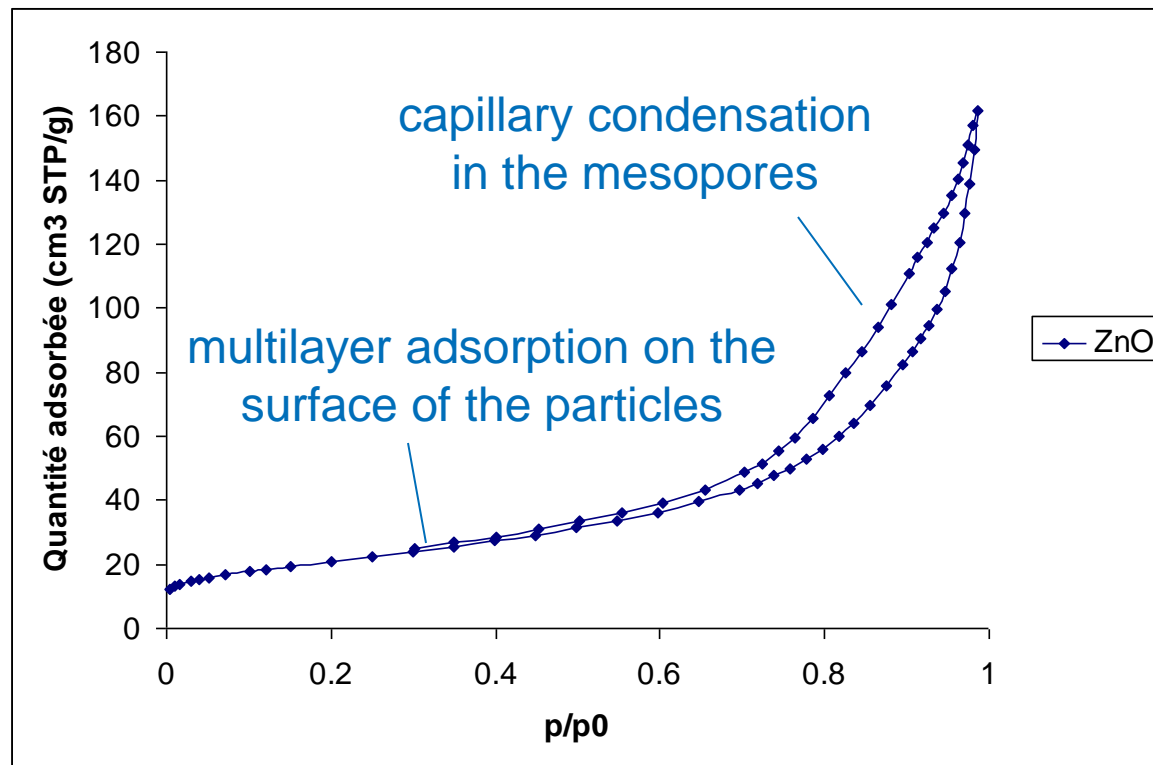
- **Precise measurement of pressure required**
 - difficult at low pressure
 - difficult to measure a micropore distribution
- **Isotherm !!**
 - T_2 in principle 77 K (temperature of liquid N_2)
 - part of the cell is not plunged into liquid N_2 , but is at ambient temperature
 - temperature gradient 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



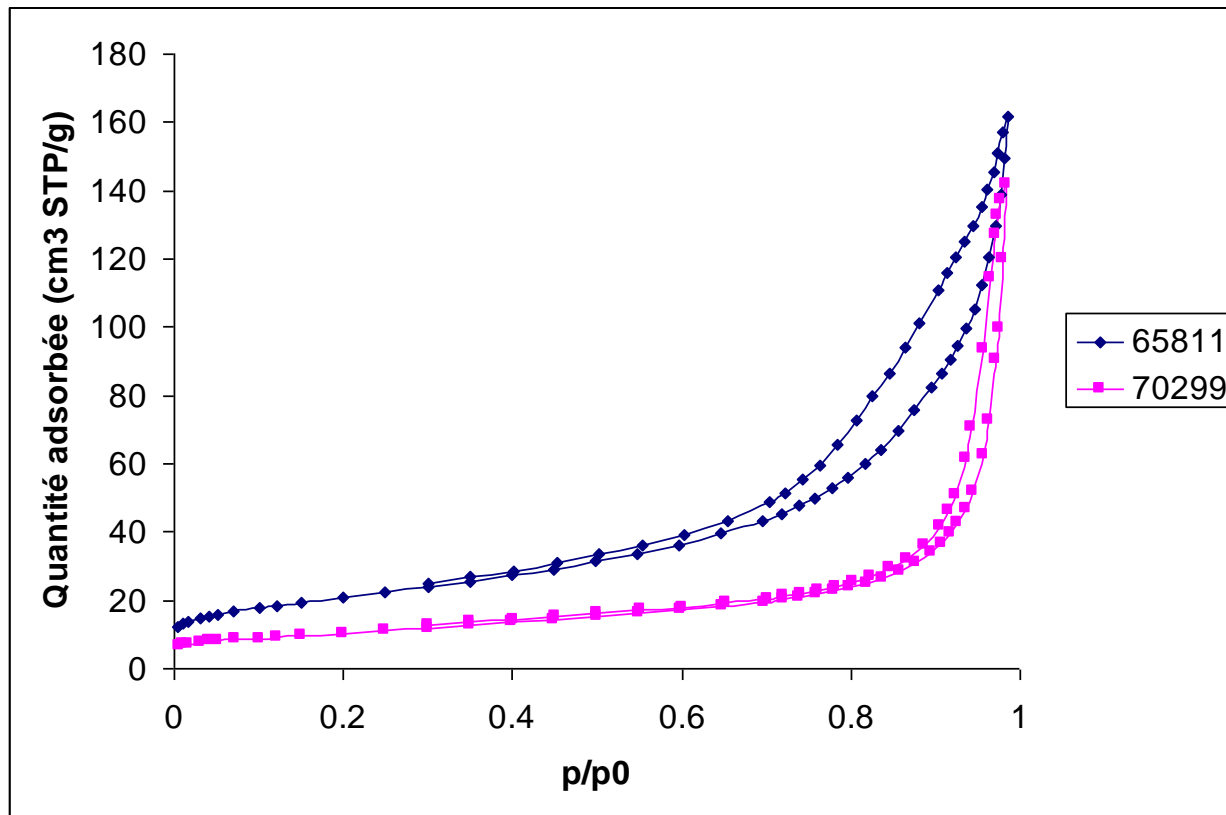
- Micropores are entirely filled at very low pressure.
- Isotherm is totally flat once micropores are filled.
- saturation zone

Examples - ZnO



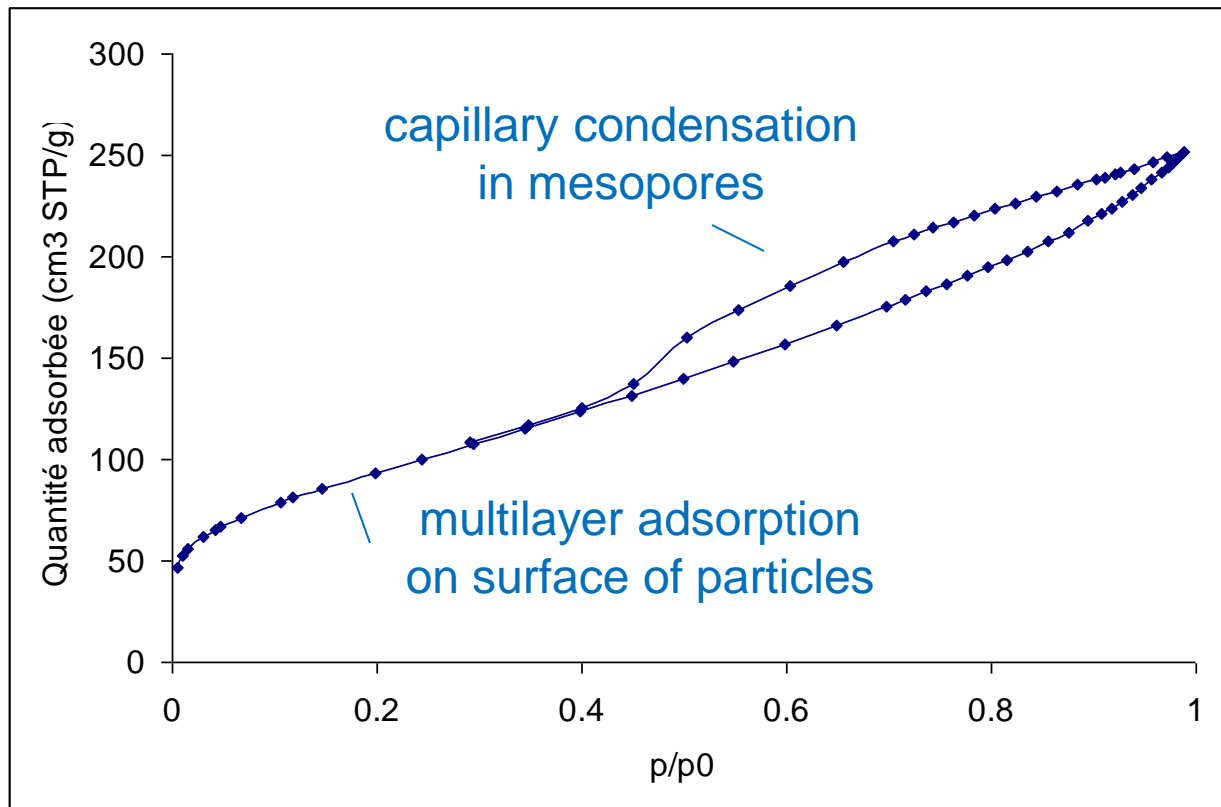
- no micropores
- mesopores generated by stacking of individual particles

Comparison of two ZnO samples



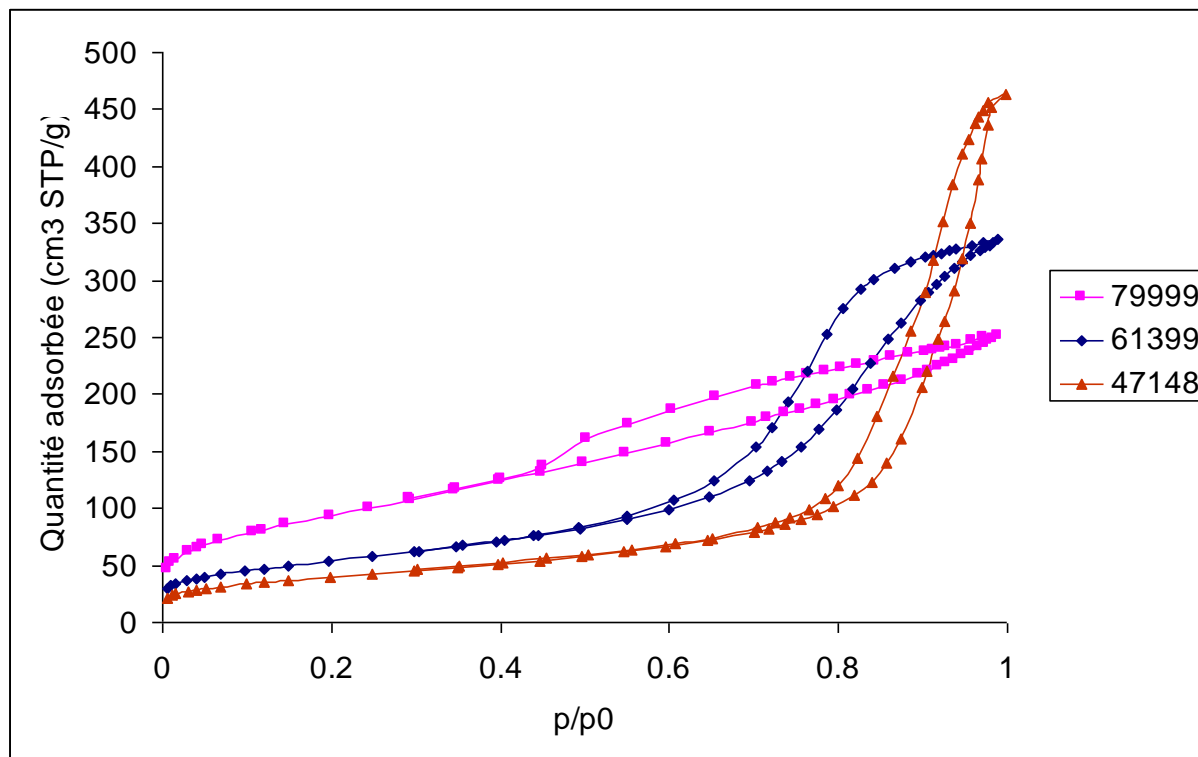
- Surface : 65811 > 70299
- Pore size : 70299 > 65811

Example – Al₂O₃



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

Comparison Al_2O_3



- Surface : 79999 > 61399 > 47148
- Pore size : 47148 > 61399 > 79999

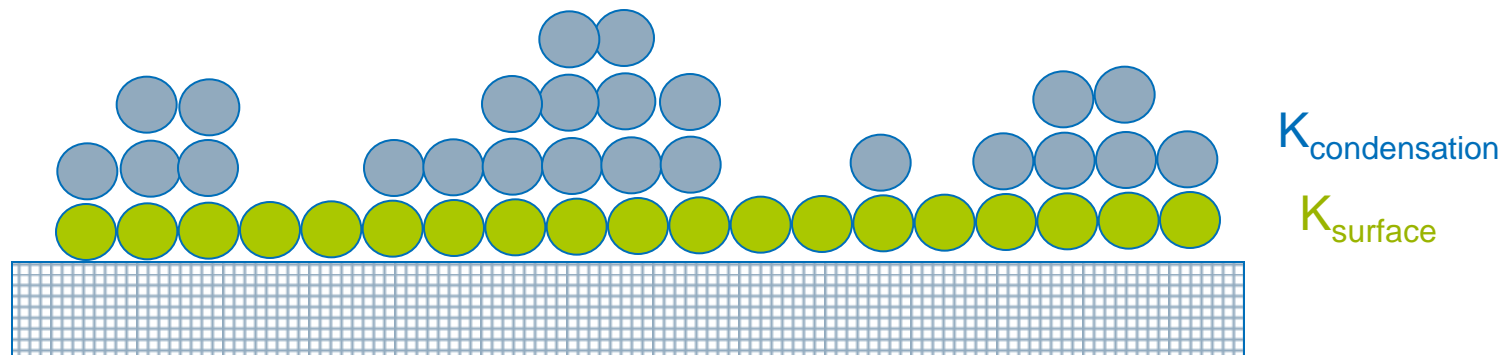


Quantitative treatment of N₂ isotherms

- **Pore volume:** V_{micro} , V_{meso} , V_{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 = number of surface adsorption sites (monolayer)

n_{ads} = total number of adsorbed molecules

BET equation

■ BET equation

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

$$C = \frac{K_{surface}}{K_{condensation}}$$

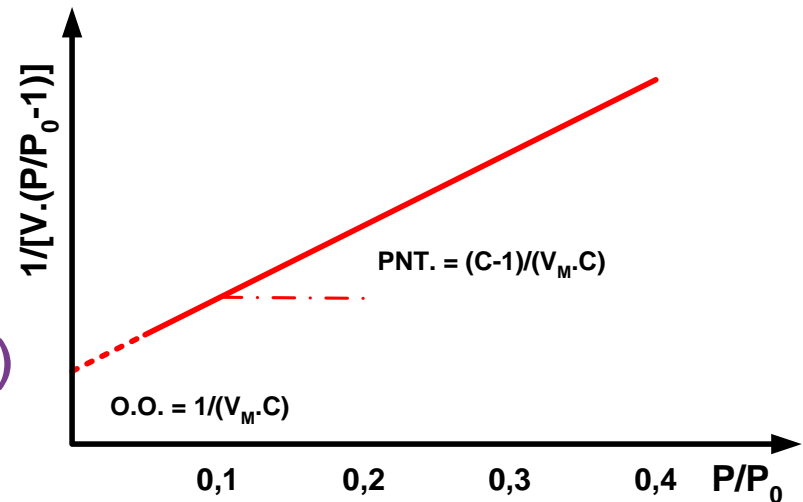
- V_M = monolayer volume
- V_{ads} = adsorbed volume

■ Plot $p/V_{ads}(p_0-p)$ vs. p/p_0

■ Calculation of surface area:

- N_{Av} : Avogadro number
- a : area of N_2 molecule ($16,2 \text{ \AA}^2$)

Recommended range of p/p_0 : 0,05 - 0,35 max.

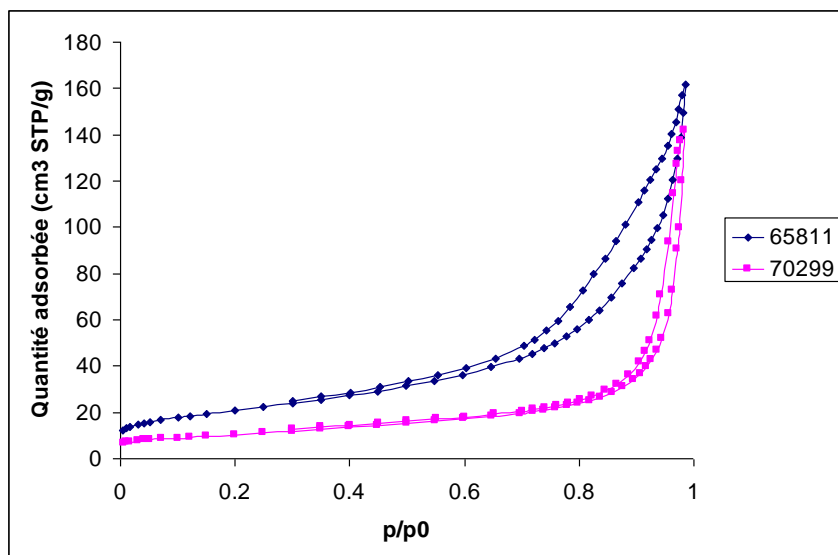


$$S_{BET} = a \cdot \frac{p_0 V_M}{R \cdot 273K} \cdot N_A$$

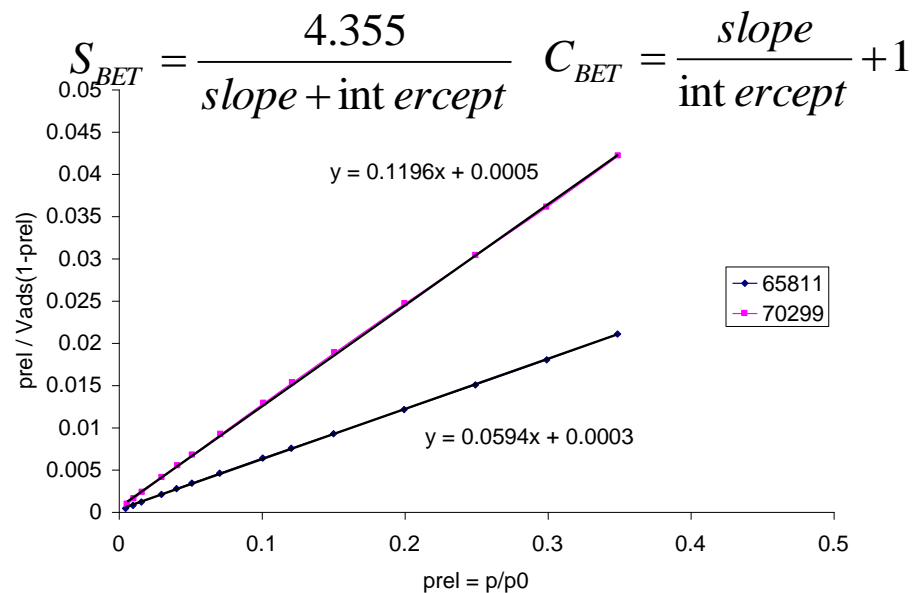
$$S_{BET} (m^2 / g) = 4.355 \cdot V_m (cm^3 STP / g)$$

Exemple ZnO

Isothermes



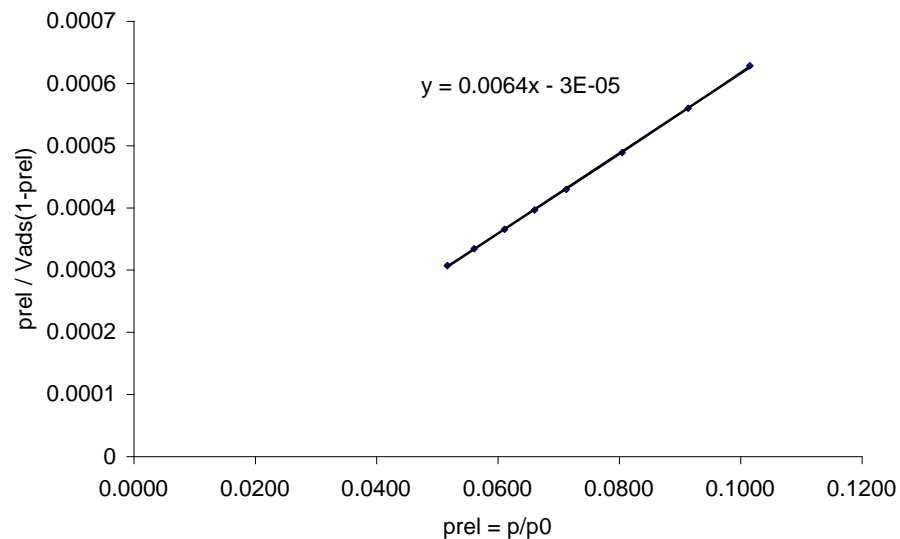
BET plot



	S_{BET} (m ² /g)	C_{BET}
65811	74	136
70299	36	237

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



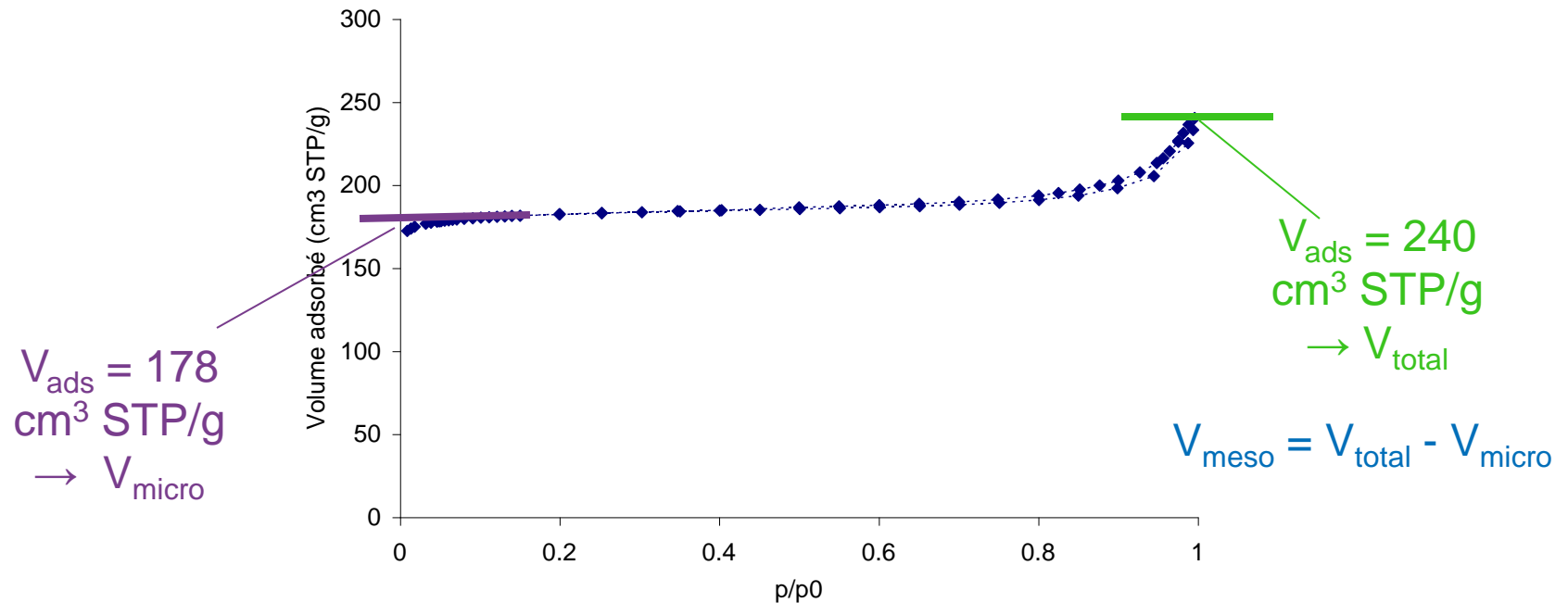
$$S_{BET} = \frac{4.355}{0.0064 - 0.00003} = 685 \text{ m}^2 / \text{g}$$



Langmuir Surface Area

- Langmuir theory
 - is a model of monolayer adsorption
 - this hypothesis is never fulfilled
- Do not use Langmuir surface areas !!
- S_{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.

Conversion gas volume – pore volume

- Volume of adsorbed gas corresponds to a certain number of moles

- STP = Standard Temperature Pressure

- T = 273 K, p = 1 bar = 100 kPa

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

- The adsorbed phase is considered like a liquid phase

- Density of liquid N₂ at 77 K : 0.807 g/ml

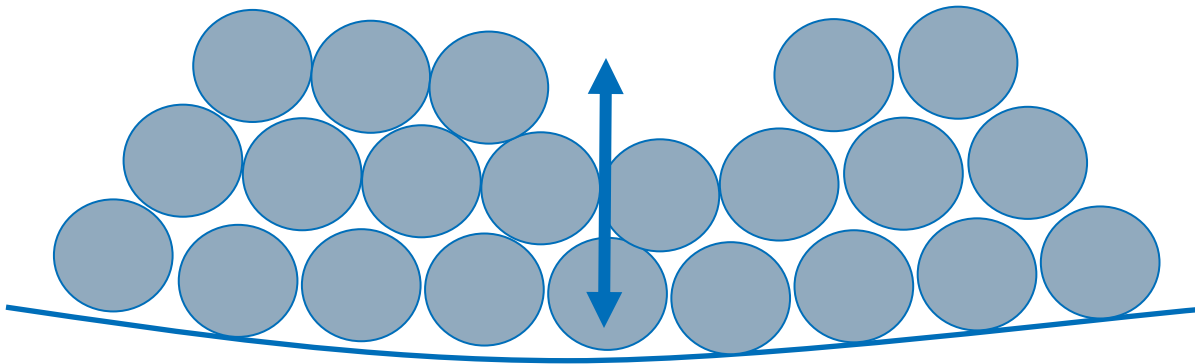
$$V_p = \frac{m_{N_2}}{\rho_{N_2,liq}} = \frac{n_{ads} \cdot M_{N_2}}{\rho_{N_2,liq}}$$

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

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 (SiO_2 , Al_2O_3 , ZrO_2 , TiO_2 , MgO) form a universal curve $t = f(p/p_0)$.
- Numerical description of that curve
 - valid for $t = 3.5 - 10 \text{ \AA}$
 - 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

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

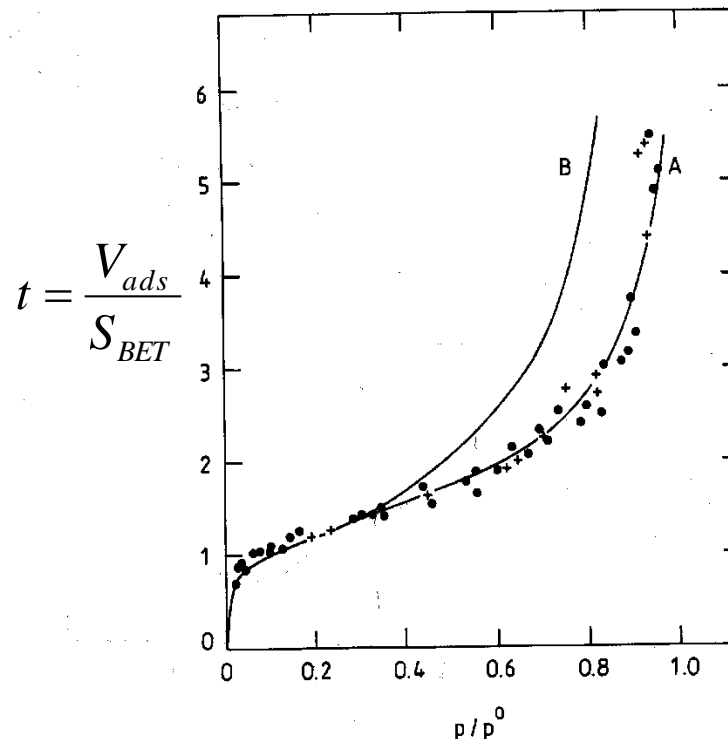
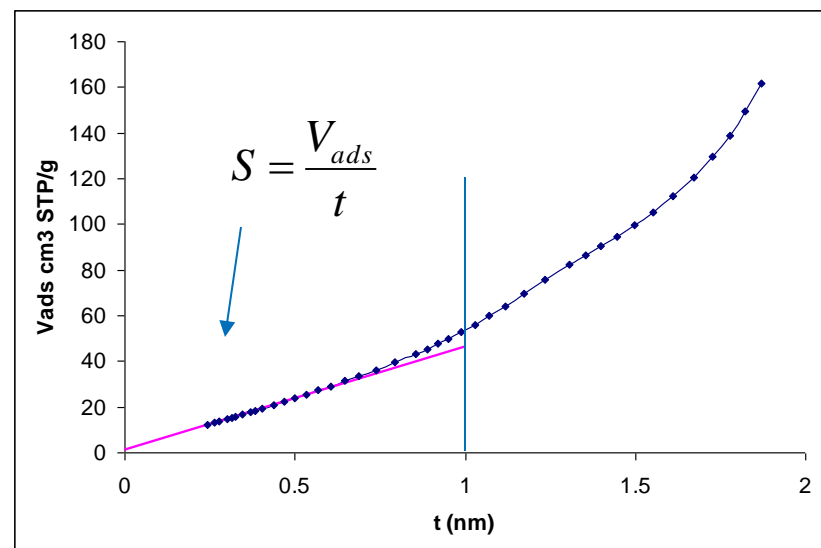
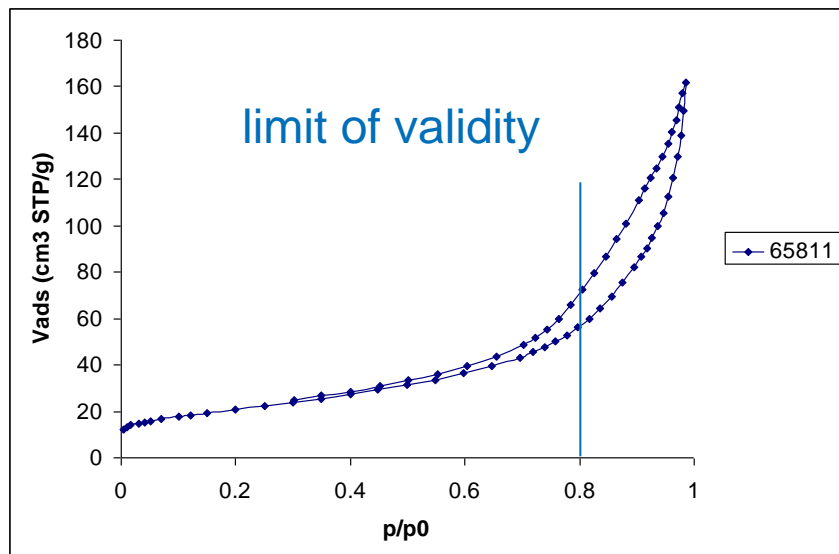


Fig. 12.3. The adsorption of nitrogen on nonporous samples of silica and alumina, the surface areas ranging from 2.6–11.5 $\text{m}^2 \text{g}^{-1}$ for silica and from 58–153 $\text{m}^2 \text{g}^{-1}$ for alumina. n/n_m is plotted against p/p_0 . n is the number of moles adsorbed per gram of adsorbent 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 $V_{ads} = f(t)$

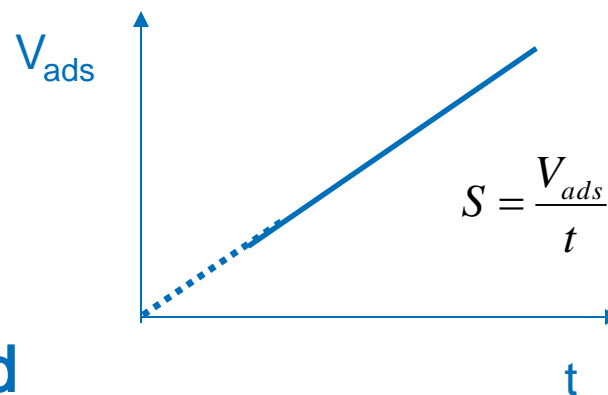
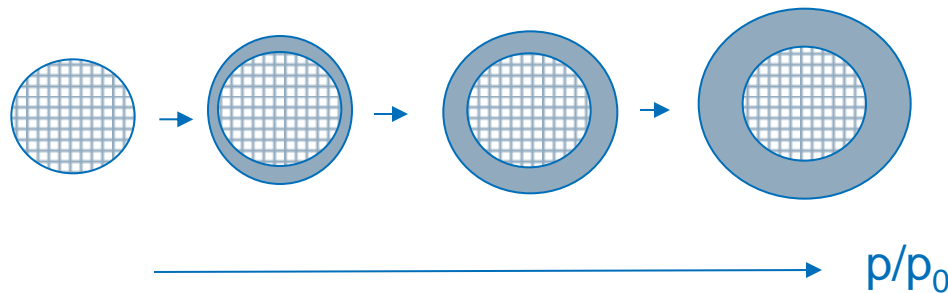


$$t = \left(\frac{13.99}{-\log \frac{p}{p_0} + 0.034} \right)^{1/2}$$

t = thickness that the adsorbed phase would have on a non-porous material

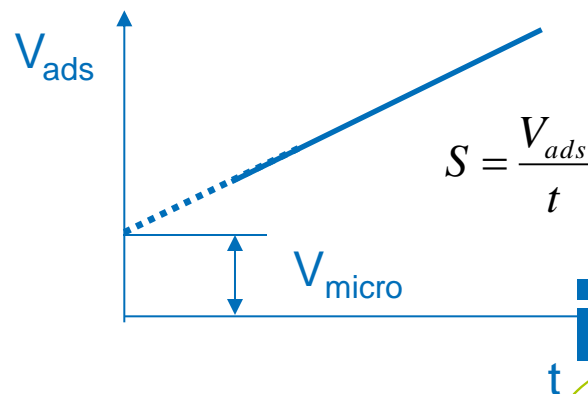
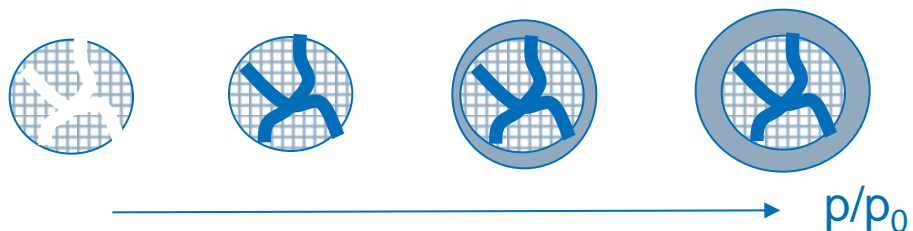
Interpretation of t-plots

■ Adsorption on a non-porous solid



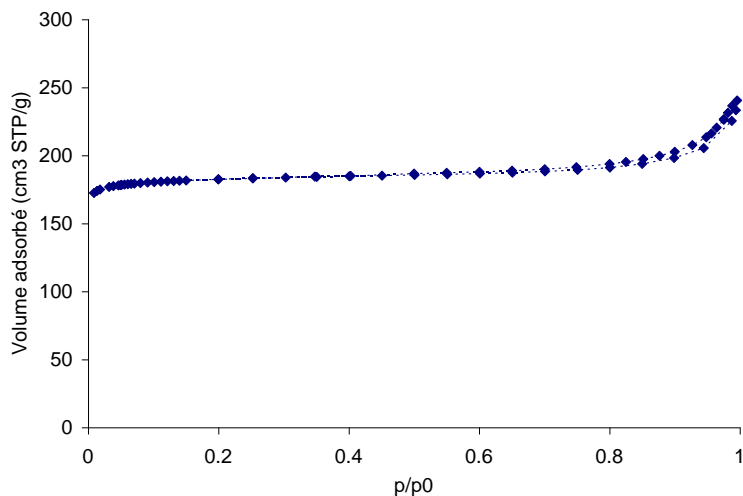
■ Adsorption on a microporous solid

- micropores rapidly filled
- then adsorption on external surface

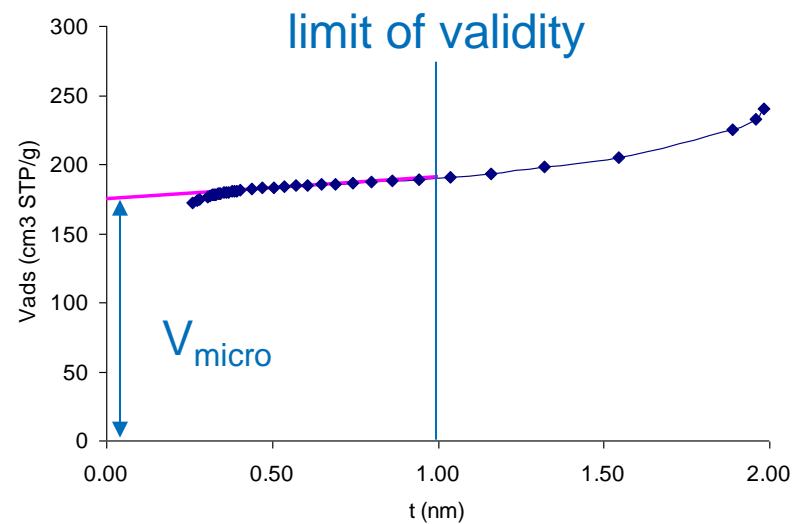


Example zeolite NaX

Isotherm

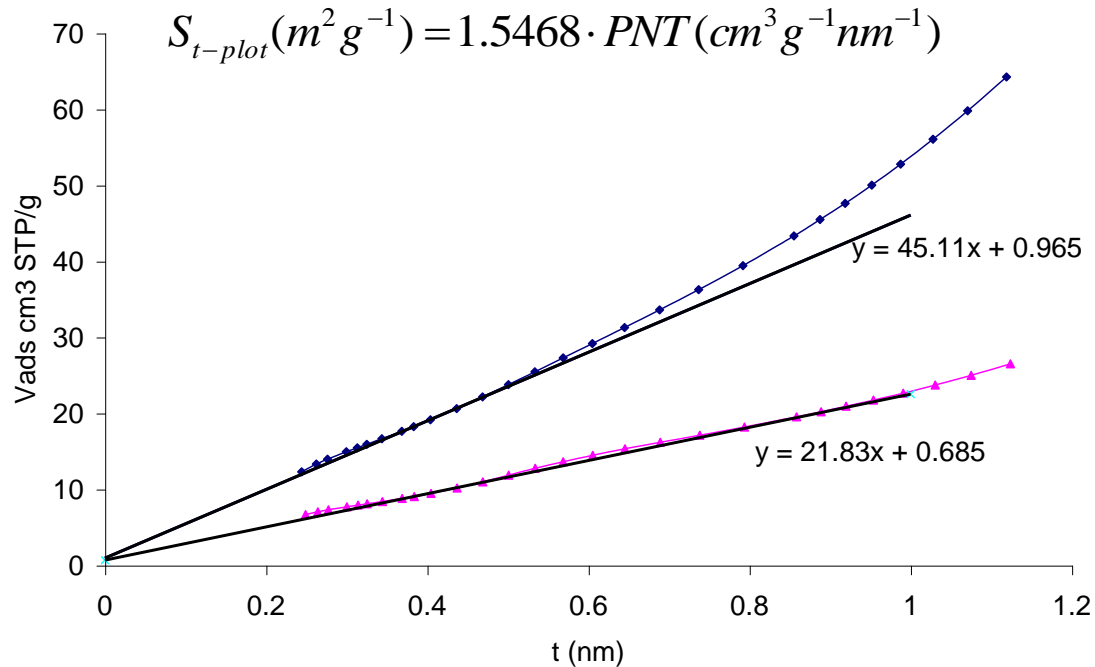


t-plot



■ $V_{\text{micro}} = 175 \text{ cm}^3 \text{ STP/g} = 0.271 \text{ ml/g}$

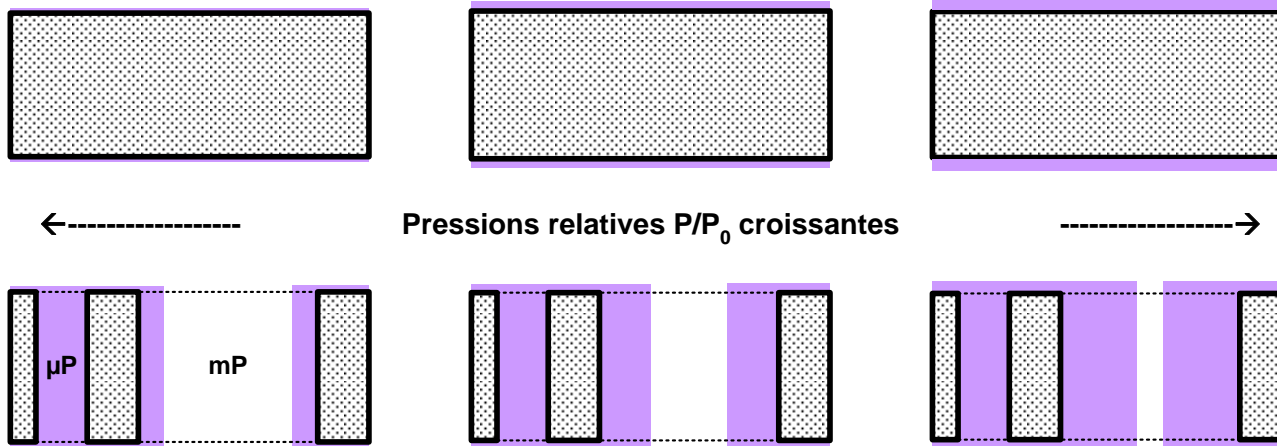
Surface BET vs. Surface t-plot



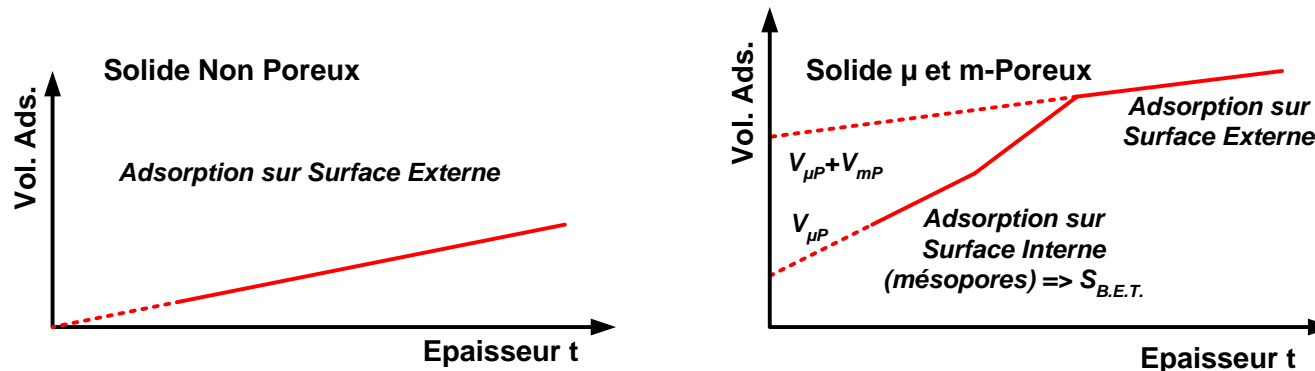
	$S_{BET} (m^2/g)$	$S_{t\text{-plot}}$
65811	74	70
70299	36	34

Micro- and mesoporous solids

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



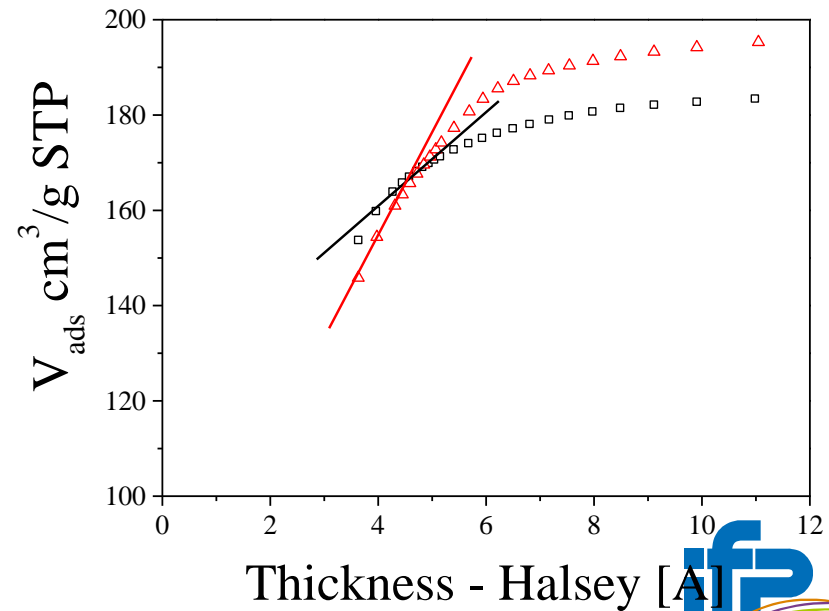
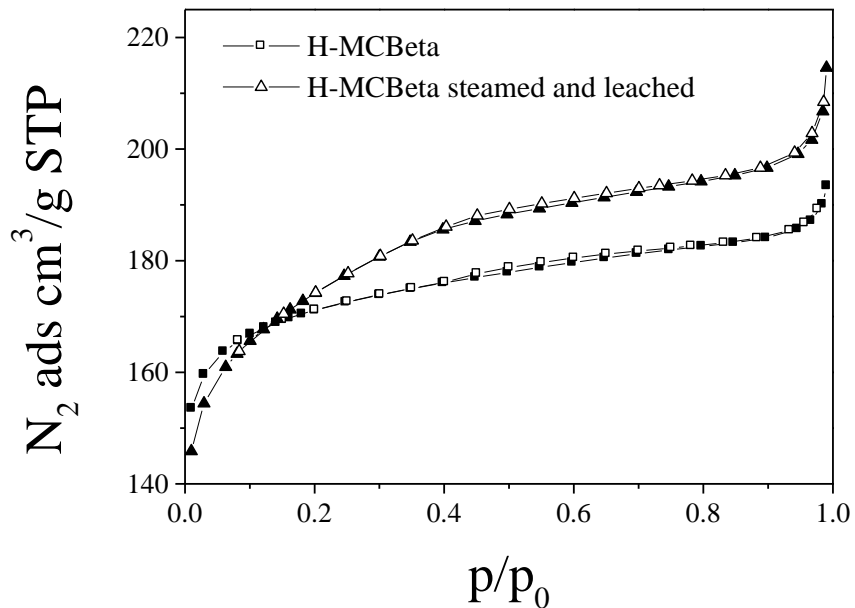
Solide poreux : Adsorption sur Surfaces Interne & Externe



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

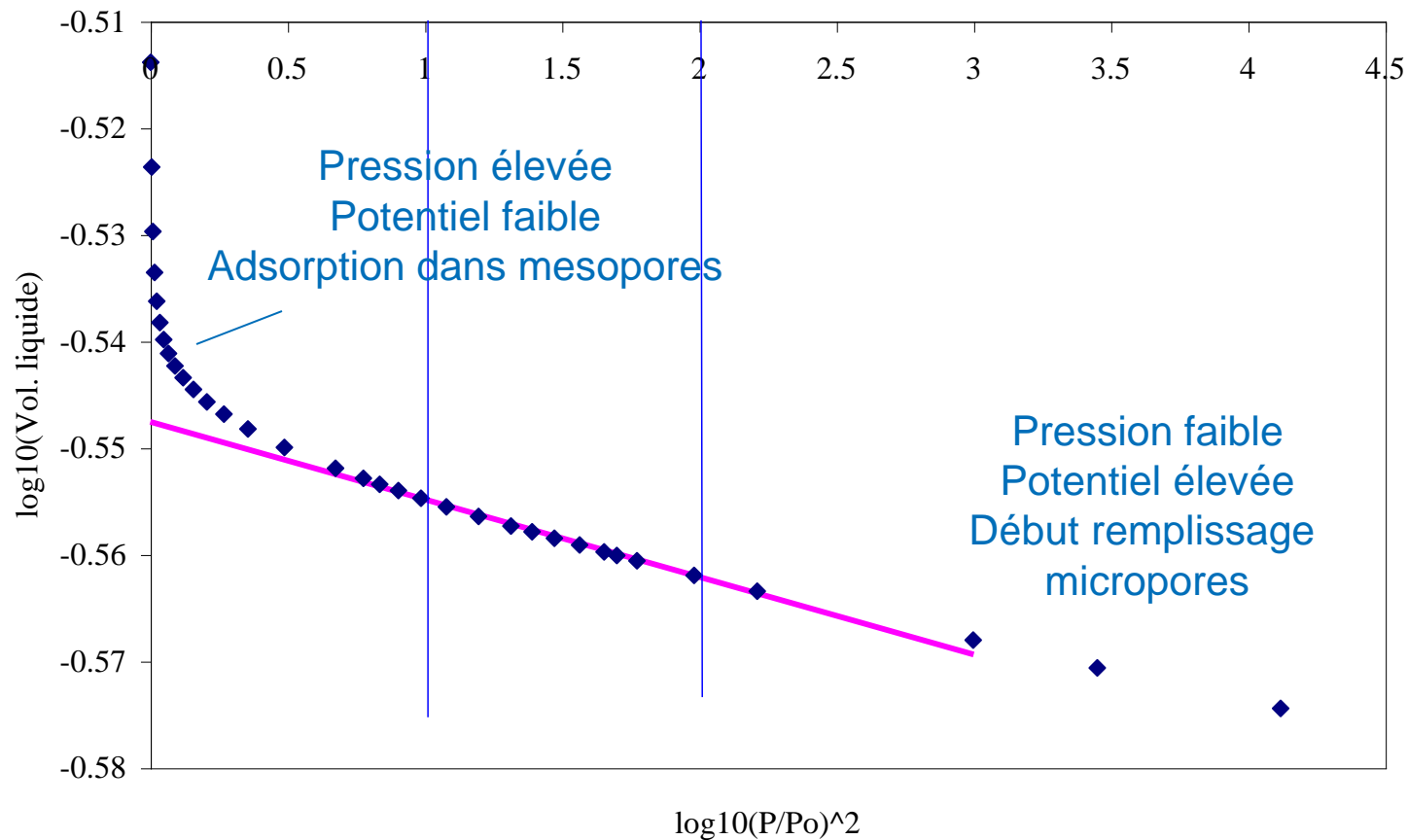
$$\frac{V_{ads}}{V_{micro}} = \exp\left[-(A/E)^2\right] \quad A = -RT \ln \frac{p}{p_{vap,sat}}$$

- A = potentiel d'adsorption
- E = energie caracteristique de l'adsorbant
- $p_{vap,sat}$ = pression vapeur saturante
 - $p_{vap,sat} = p_0$ (1 atm) pour N₂ à 77K

■ Equation linéarisée

$$\log V_{ads} = \log V_{micro} - D \log\left(\frac{p}{p_0}\right)^2$$

Example NaX



$$\blacksquare V_{\text{micro}} = 10^{(-0.548)} = 0.283 \text{ ml/g}$$

Average pore size

■ From geometrical rules

■ Cylindrical Pore:

- V = pore volume
- S = surface

$$\begin{cases} V = \pi r^2 h \\ S = 2\pi r h \end{cases} \quad \frac{S}{V} = \frac{2}{r} \quad d = \frac{4V}{S}$$

■ Spherical pore :

$$\begin{cases} V = \frac{4}{3} \pi r^3 \\ S = 4\pi r^2 \end{cases} \quad \frac{S}{V} = \frac{3}{r} \quad d = \frac{6V}{S}$$

■ Slit pore :

$$\begin{cases} V = lhr \\ S = lh \end{cases} \quad \frac{S}{V} = \frac{1}{r} \quad d = \frac{2V}{S}$$

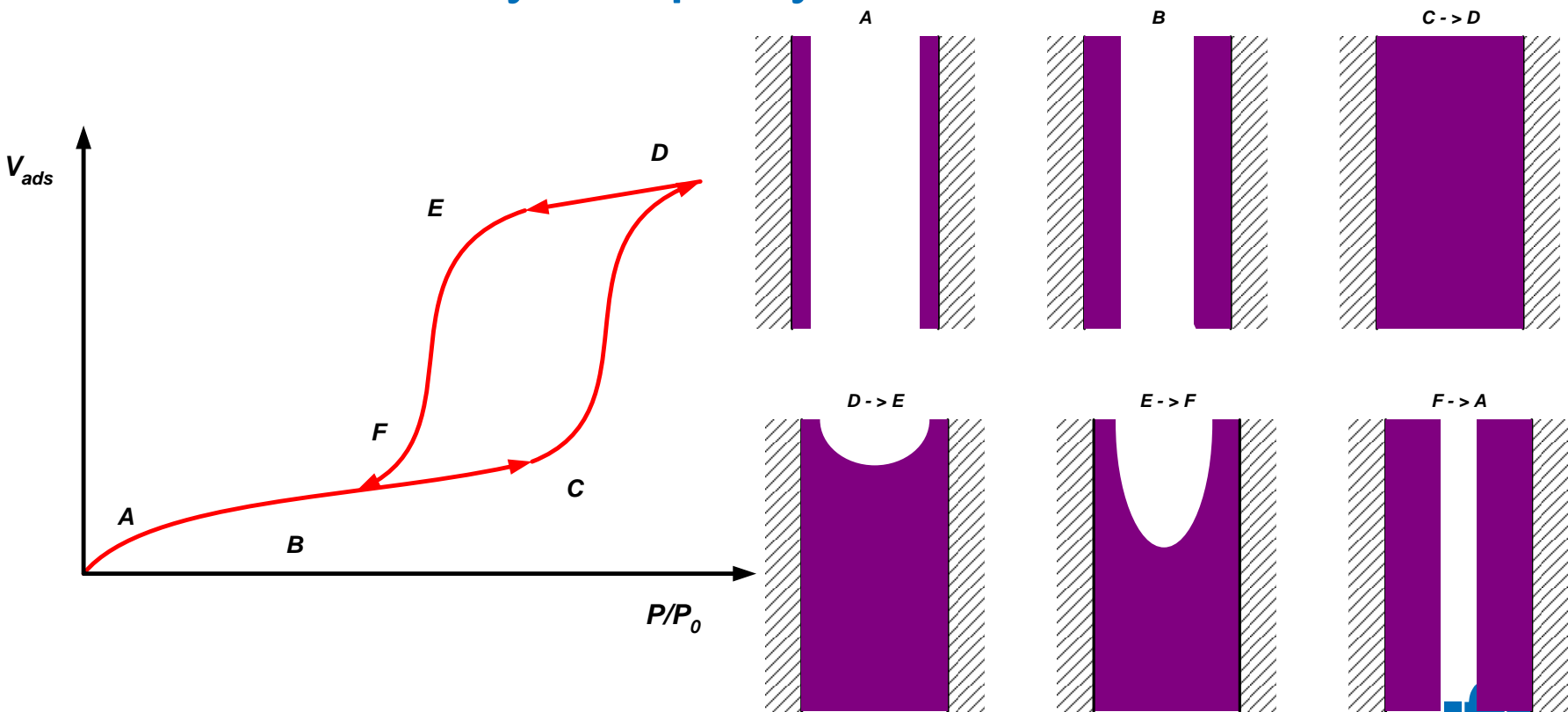


Micropore size distribution

- 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
 - Saito-Foley *Saito, Foley, AIChE Journal 1991, 37, 429.*
- Input parameters
 - pore geometry: slit-shaped, cylinder, sphere
 - parameters of the Lennard-Jones potential well: ϵ and σ_{ij}
 - not always well known for atypical solids
- Input data
 - high precision isotherm at very low pressure !

Mesopore size distribution

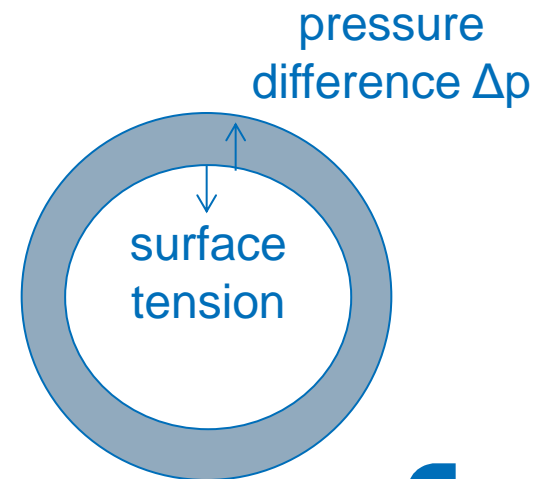
■ via the theory of capillary condensation



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

$$dA \cdot \gamma = dn_{capliq} \cdot \mu_{capliq} + dn_{liq} \cdot \mu_{liq}$$

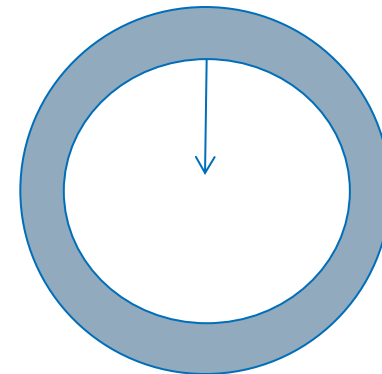
$$dn_{capliq} = -dn_{liq} = \frac{dV_{capliq}}{V_m}$$

$$dA \cdot \gamma = \frac{dV_{capliq}}{V_m} \cdot \mu_{capliq} - \frac{dV_{capliq}}{V_m} \cdot \mu_{liq}$$

$$dA \cdot V_m \cdot \gamma = dV_{capliq} (\mu_{capliq} - \mu_{liq})$$

$$(\mu_{capliq} - \mu_{liq}) = -\frac{dA}{dV_{cap,g}} \cdot V_m \cdot \gamma$$

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



$$\mu_{capliq} = \mu_0 + RT \ln \frac{p_{cap}}{p_0}$$

$$\mu_{liq} = \mu_0 + RT \ln \frac{p_{sat}}{p_0}$$

Generalized Kelvin equation

$$\ln \frac{p_{cap}}{p_{sat}} = -\frac{V_m \gamma}{RT} \cdot \frac{dA}{dV}$$

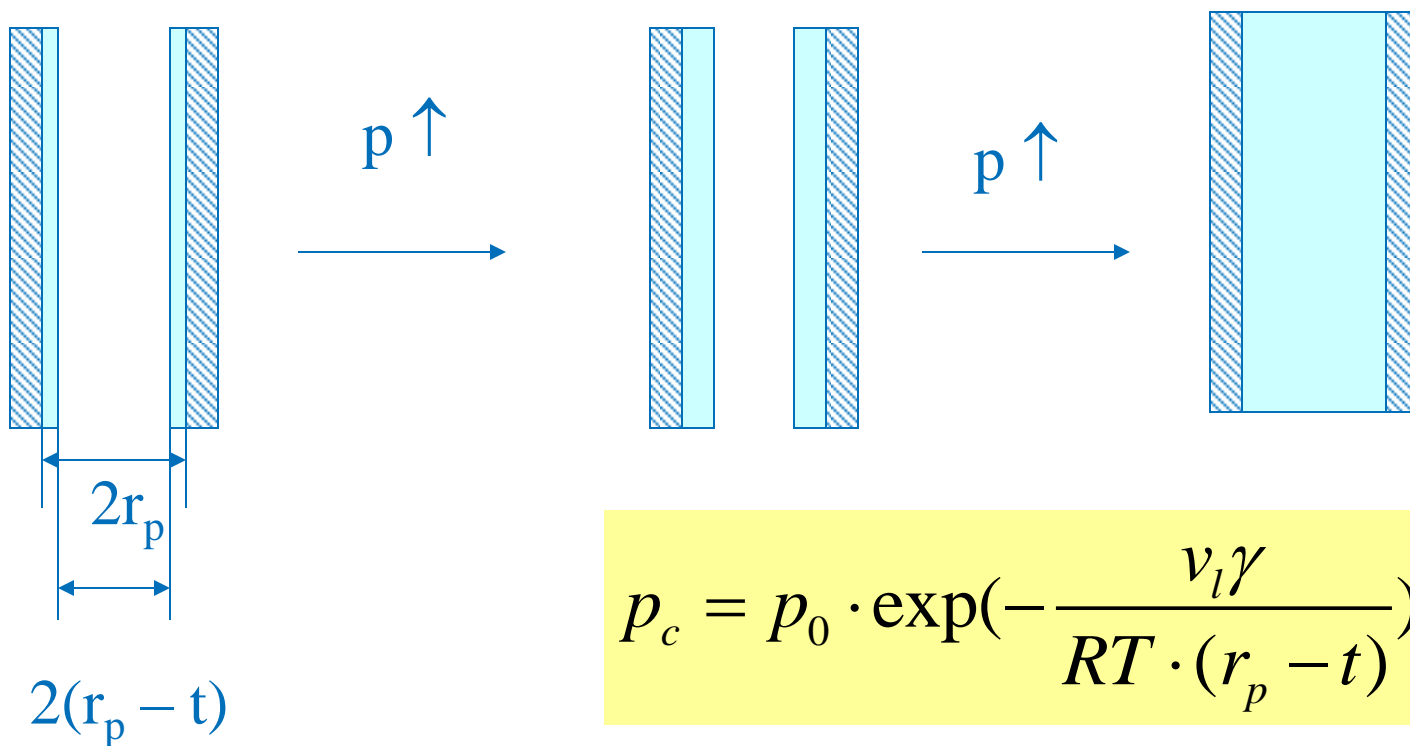
dV/dA = change in volume per change in interface area

V_m = molar volume

- 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

$$\ln \frac{p_{cap}}{p_{sat}} = -\frac{2}{r} \frac{V_m \gamma}{RT}$$

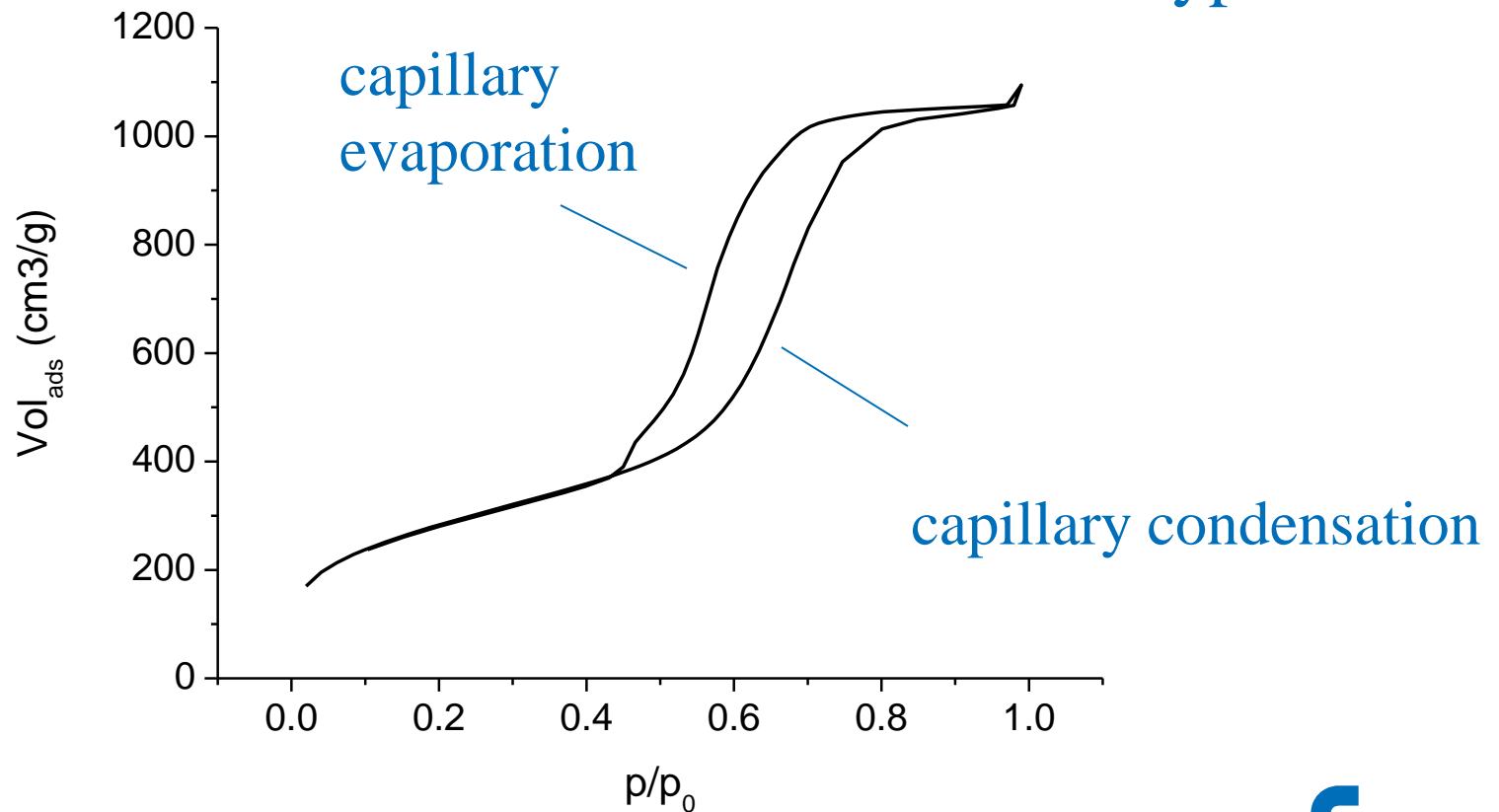
Capillary condensation



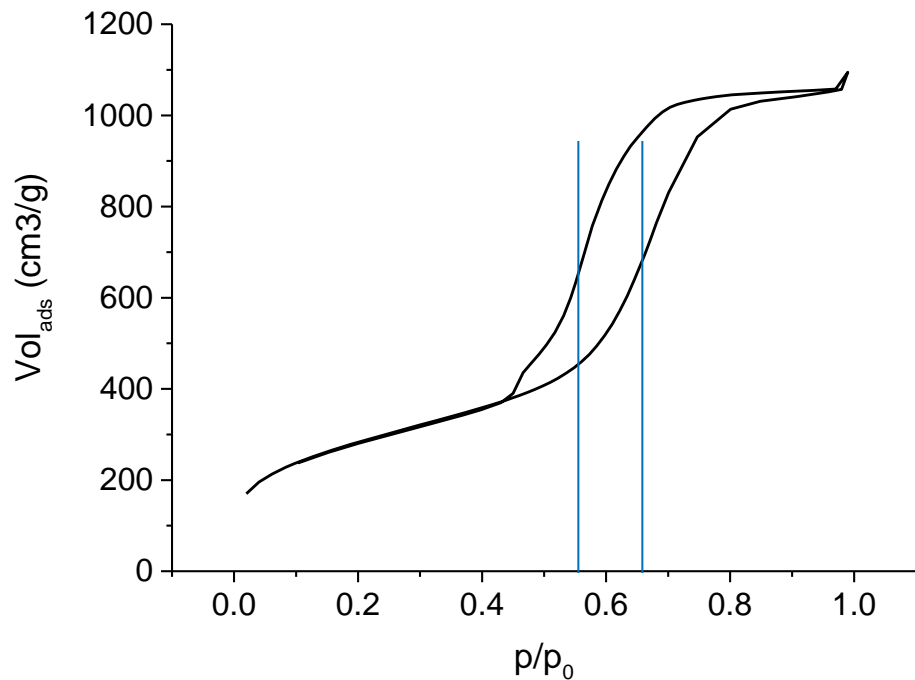
- Multilayer adsorption on the surface: layer thickness $t \uparrow$
- At a certain effective pore radius $r_p - t$, capillary condensation occurs
- Pore is filled. There is a step in the adsorption isotherm.

Example isotherm with hysteresis

Type H1



Application of the Kelvin equation



Harkins-Jura t-plot equation

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

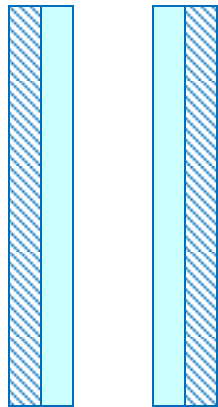
$$\log \frac{p}{p_0} = \frac{-4.14}{r_m}$$

Kelvin equation

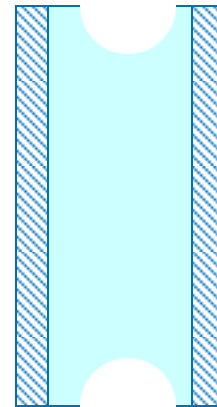
Cylinder !!

	p_c/p_0	$t(p_c)$	r_m	r_c	$r_p = r_c + t$
Ads	0.671	8.2	23.9	11.9	20.2
Des	0.565	7.0	16.7	16.7	23.7

Origin of the hysteresis



Adsorption:
cylindrical meniscus
 $r_m = 2r_{\text{eff}}$



Desorption:
hemispherical meniscus
 $r_m = r_{\text{eff}}$

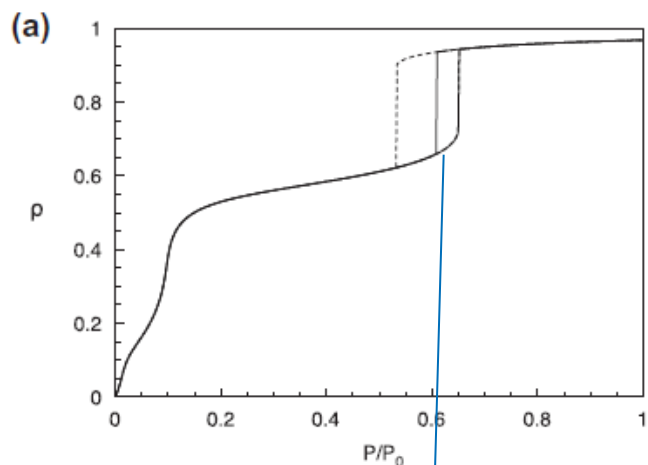
- The lower r_m , the lower is the pressure of capillary condensation/evaporation
 - $r_{m,\text{ads}} = 2 r_{m,\text{des}}$
 - Capillary evaporation at a lower pressure than capillary condensation
- Hysteresis loop in isotherm



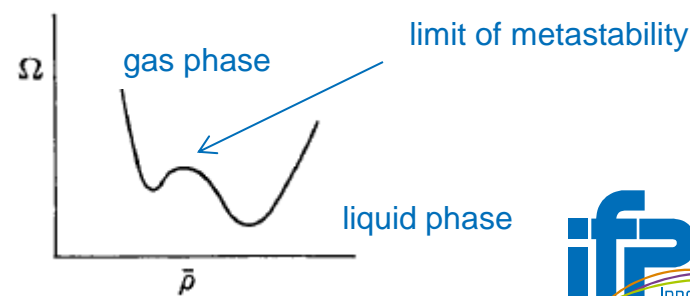
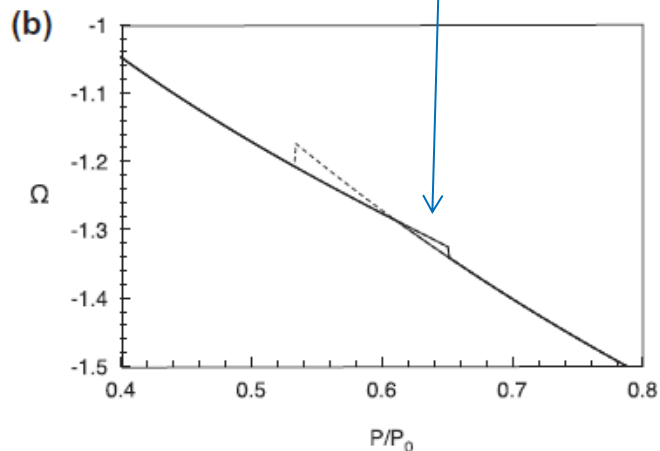
Origin of the hysteresis

- 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

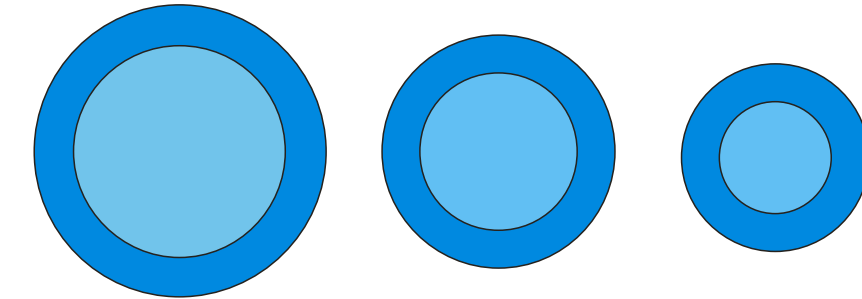


- Adsorption branch comprises metastable states.
 - grand free energy of filled pore is lower than that of the empty pore in the hysteresis
- Desorption branch is in thermodynamic equilibrium.
- Reason for metastability in adsorption branch
 - barrier of nucleation by formation of a liquid bridge across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

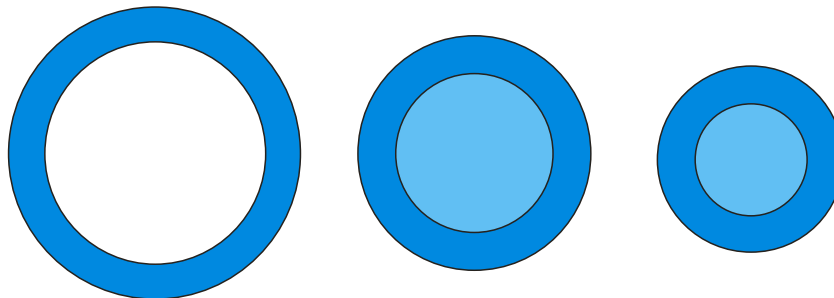


Monson, MMM, 2012.

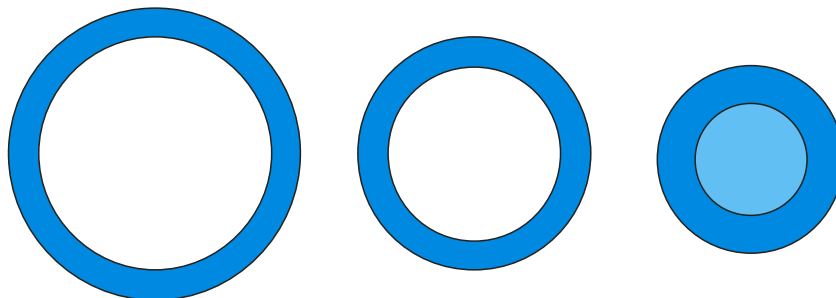
Pore size distribution – BJH model



p_0 – all pores filled

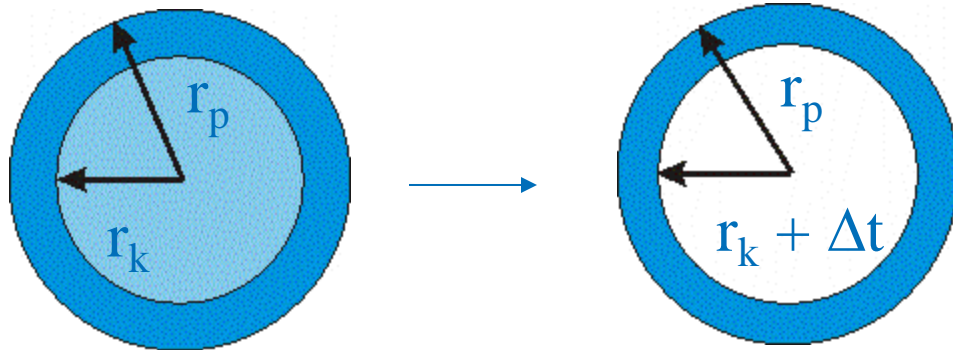


p_1 – capillary evaporation in largest pore
reduction of layer thickness



p_2 – capillary evaporation in 2nd largest pore
reduction of layer thickness in both pores

Mathematic description - BJH



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

- 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 (ΔV_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

ΔV_n

The BJH-equation

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

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

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: $r_p = r_k + t$

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

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

- Δt is the change in layer thickness in each desorption step
- ΔV_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

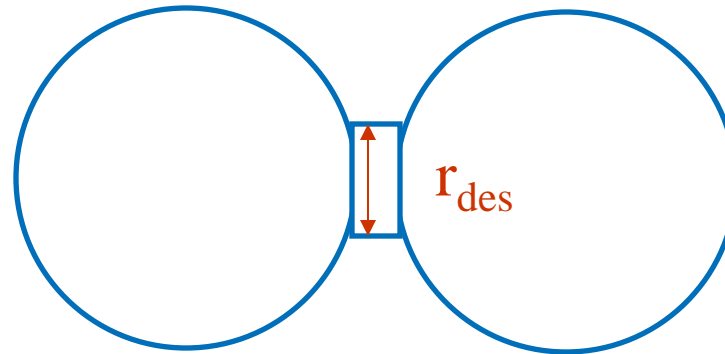
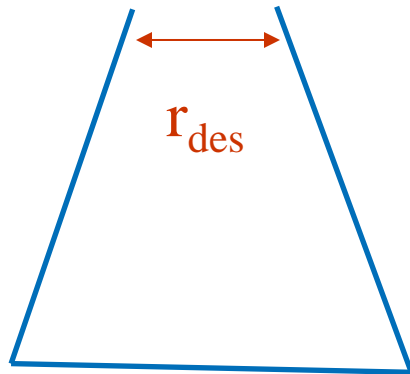
- Condensation can be delayed – not in thermodynamic equilibrium
- Cylindrical meniscus not stable – not advisable to use adsorption branch for cylindrical pores

■ 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

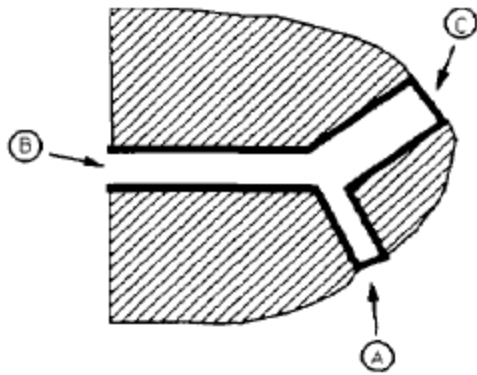
■ Conclusion: look at both and compare them

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

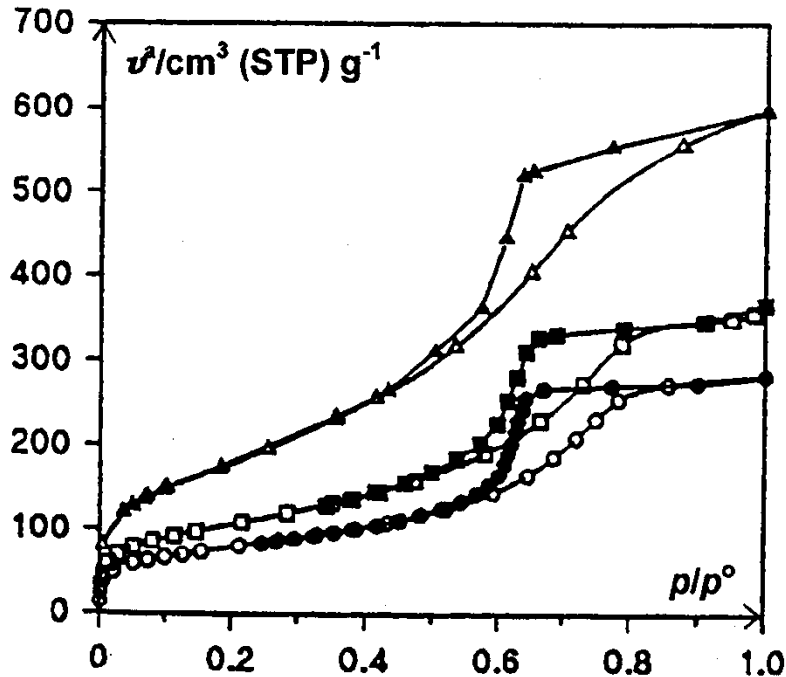


N_2 can only desorb from pore A and C if pore B has already been emptied.

Seaton, CES, 1991.

- 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 type hysteresis loop



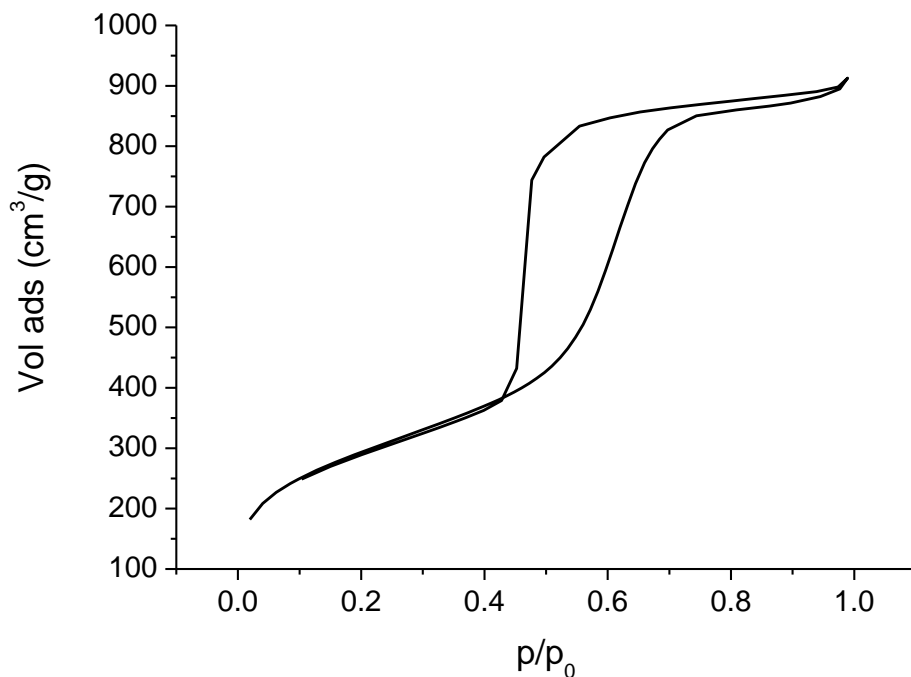
Type H2

Adsorbent:
xerogel and
alcogel

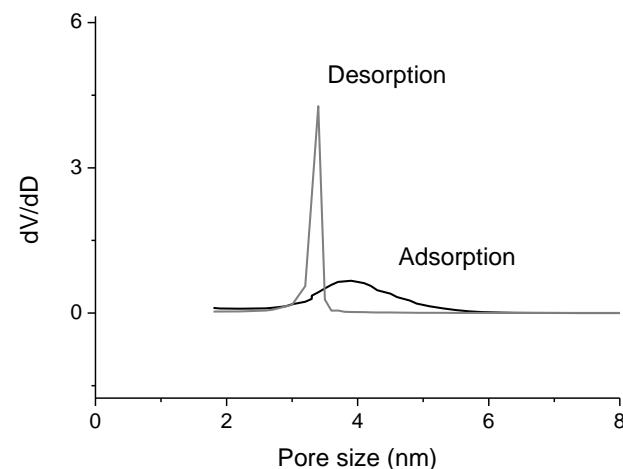
- If pore size distribution is calculated from desorption branch, an artificially narrow pore size distribution is obtained
- The adsorption branch has to be used to calculate the pore size distribution.

Ink-bottle type hysteresis loop

Isotherm

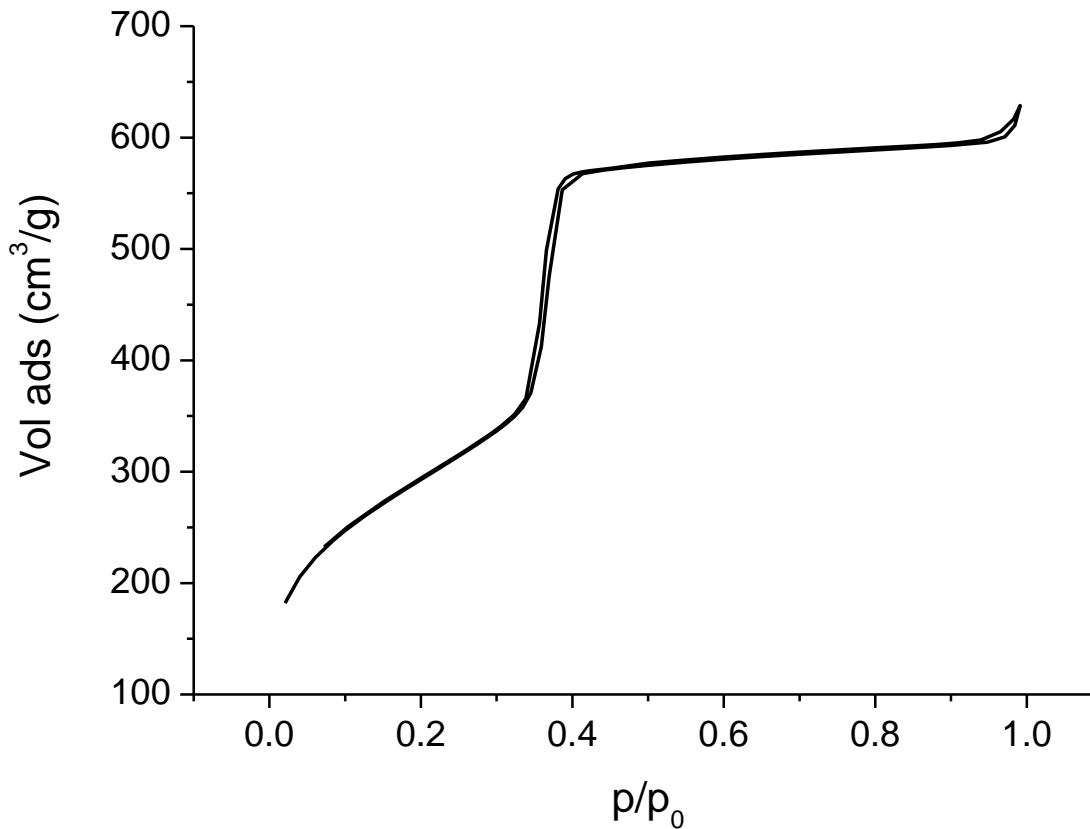


Pore size distribution



- 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:
 $T_{c,pore} < T_{c,bulk}$
- $T_{c,pore}$ decreases with decreasing pore diameter¹
- Above T_c no condensate-vapour meniscus
- For narrow pores $T_c < 77$ K
- No hysteresis for filling and emptying of these pores
- $T_{c,pore} < 77$ 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 N_2 isotherms don't²

[1] R. Evans, J. Phys. Condensed Matter 2 (1990) 8989.

[2] M. Thommes, R. Köhn, M. Fröba, J.Phys.Chem. B 104 (2000) 4982.



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

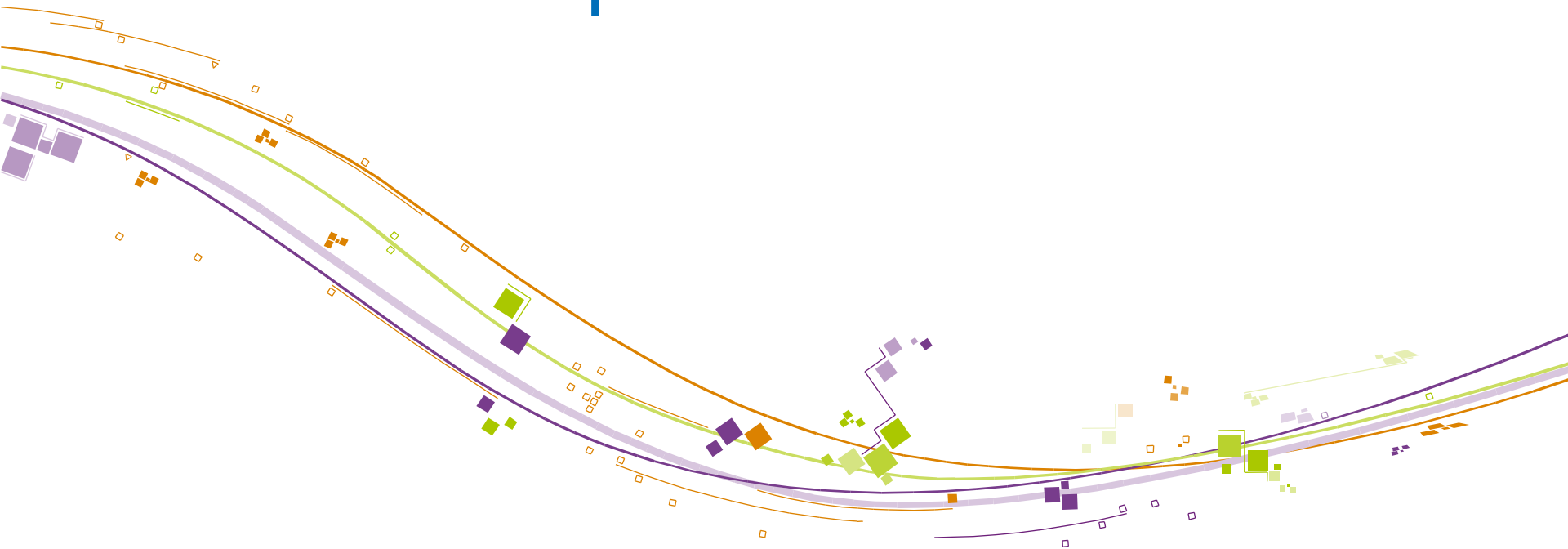
■ Textbooks on adsorption

- 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

- P.A. Monson, Understanding adsorption/desorption hysteresis for fluids in mesoporous materials using simple molecular models and classical density functional theory, Microporous Mesoporous Materials 160 (2012) 47.
- B. Coasne et al., Adsorption, intrusion and freezing in porous silica: the view from the nanoscale, Chem. Soc. Rev. 42 (2013) 4141.

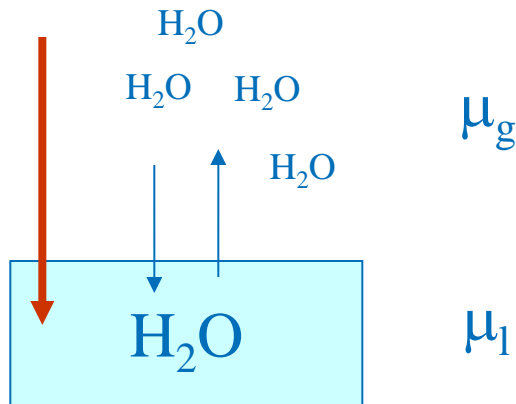
Alternative explanations of the Kelvin equation



Physical principles of capillary condensation

■ Vapour pressure of a liquid under external pressure

External pressure



p_g = new vapour pressure of H₂O
 $p_{g,0}$ = original vapour pressure of H₂O
 Δp_l = external pressure on liquid (H₂O),
which induces the change in vapour
pressure

v_l = molar volume of liquid (H₂O)

- Equilibrium gas-liquid $\mu_g = \mu_l$
vapour pressure $p_{g,0}$
- Equilibrium disturbed by external
pressure

$$d\mu_g = d\mu_l \rightarrow v_l dp_l = v_g dp_g$$

$$v_l dp_l = RT/p_g \cdot dp_g$$

$$v_l \Delta p_l = RT \ln (p_g/p_{g,0})$$

$$p_g = p_{g,0} \cdot \exp\left(\frac{v_l}{RT} \Delta p_l\right)$$

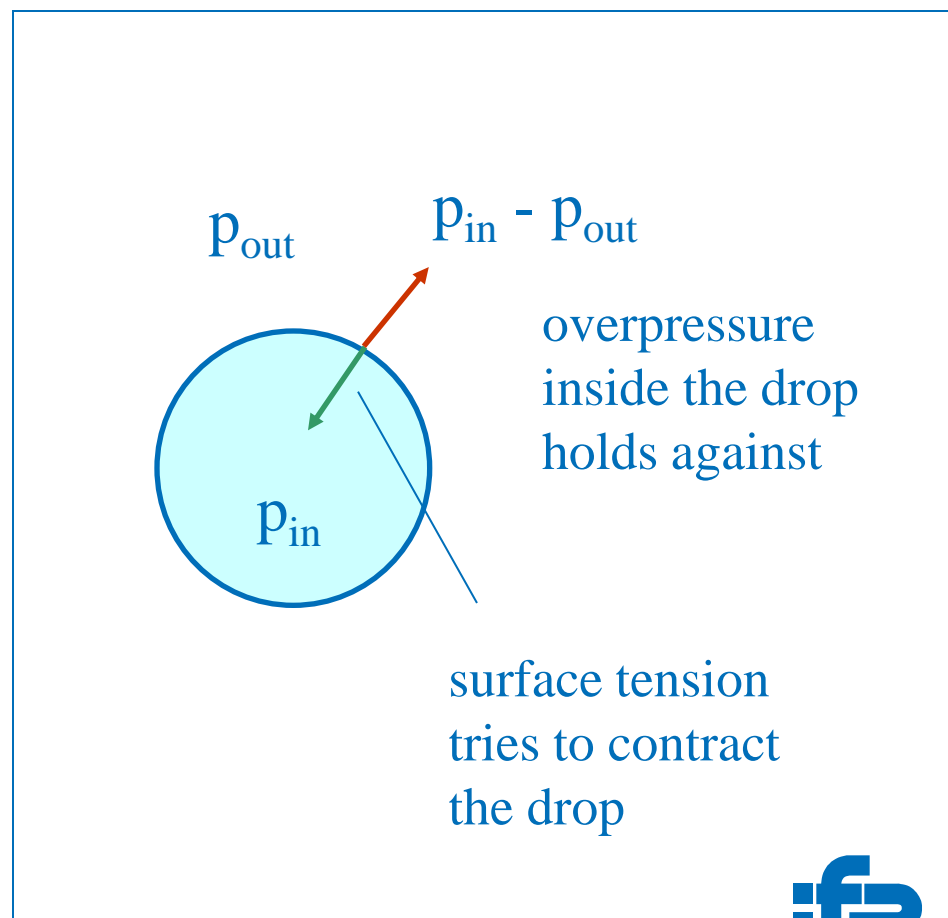
Vapour pressure of a drop of liquid

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

γ = surface tension
 r = radius of curvature

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

$$p_l = p + \frac{2\gamma}{r}$$

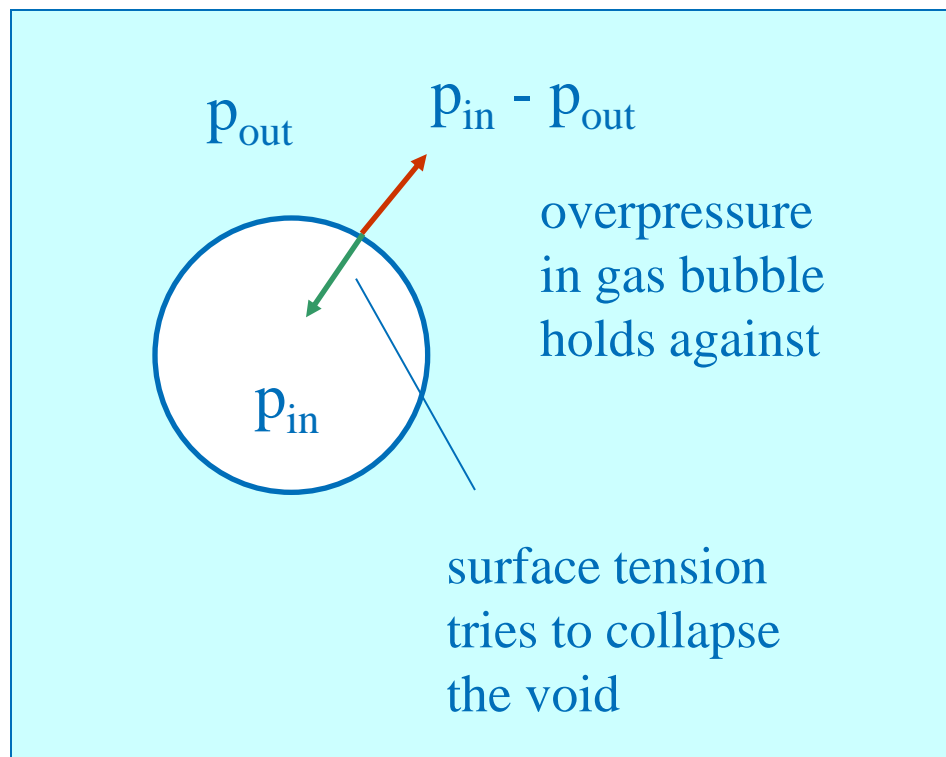


Vapour pressure of a liquid void

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

$$p_{in} - p_l = \frac{2\gamma}{r}$$

$$p_l = p - \frac{2\gamma}{r}$$



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

Kelvin equation: vapour pressure inside a void is lowered

Kelvin equation

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

$$\mu_{cap} = \mu_0 + RT \ln \frac{P_{cap}}{P_0} \quad \mu_{liq} = \mu_0 + RT \ln \frac{P_{sat}}{P_0}$$

Evaporate n moles from capillary and condense on a flat surface. You have to work against the surface tension γ .

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

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

$$n \cdot \Delta\mu = \frac{\Delta V}{V_m} RT \ln \frac{P_{sat}}{P_{cap}}$$

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

