CO_2 maîtrisé | Carburants diversifiés | Véhicules économes | Raffinage propre | Réserves prolongées

Physisorption and pore size analysis

Gerhard Pirngruber

Direction Catalyse et Séparation

gerhard.pirngruber@ifpen.fr

Innovation
Energie
Environnement

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 – 2018: hydrotreating and hydrocracking catalysts
    - 2018 – now: zeolites, oxide supports

Porous solids in catalysis

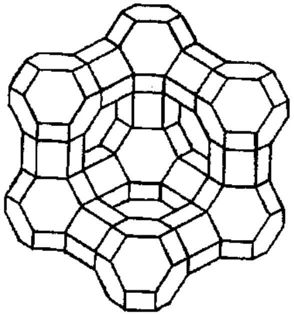
- Supported catalysts
  - e.g. noble metals, transition metal sulfides
  - Porous support
    - provides surface for dispersing the catalyst
    - provides mechanical stability
    - has an influence on diffusion of reactants and products
    - has an influence on adsorption of reactants and products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

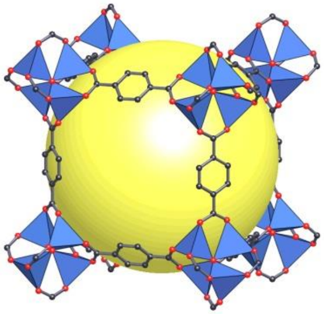
Optimising porosity is often the key to improving catalytic performance.

Innovation
Energie
Environnement

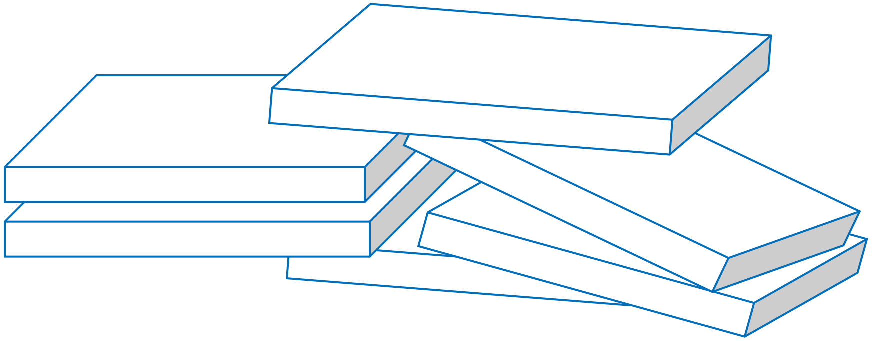
Types of porosity

- Porous cristalline 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.

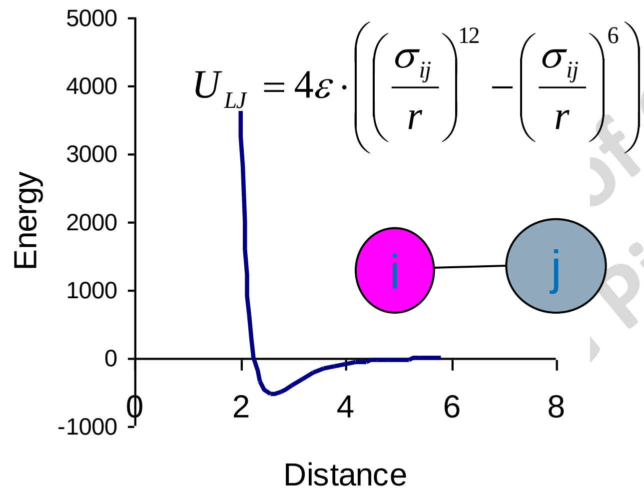
- Physisorption: no formation of chemical bonds, no transfer of electron density
- Chemisorption: formation of a chemical bond (exchange of electrons)

Innovation
Energie
Environnement

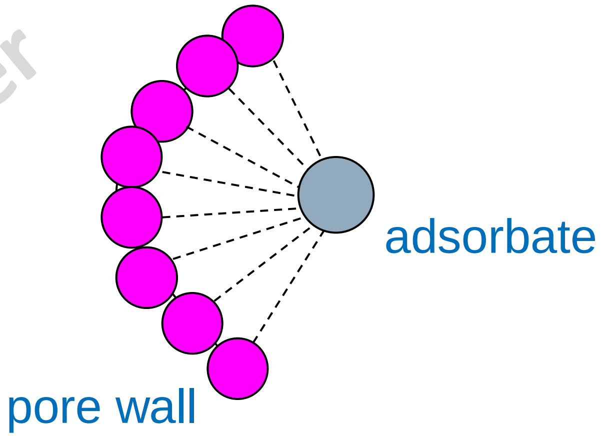
Forces involved in physisorption

van der Waals forces

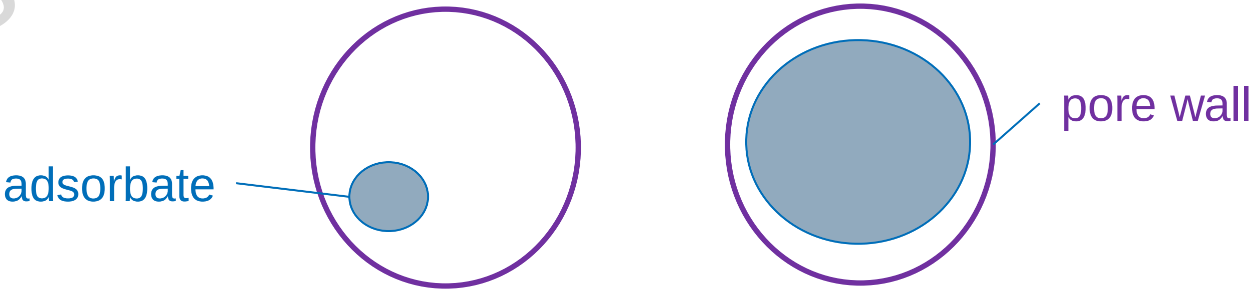
- amplified by multiple interactions with atoms or pore wall (i)



$$U_{LJ} = 4\varepsilon \cdot \left(\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^{6} \right)$$



- maximal when size of adsobate (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

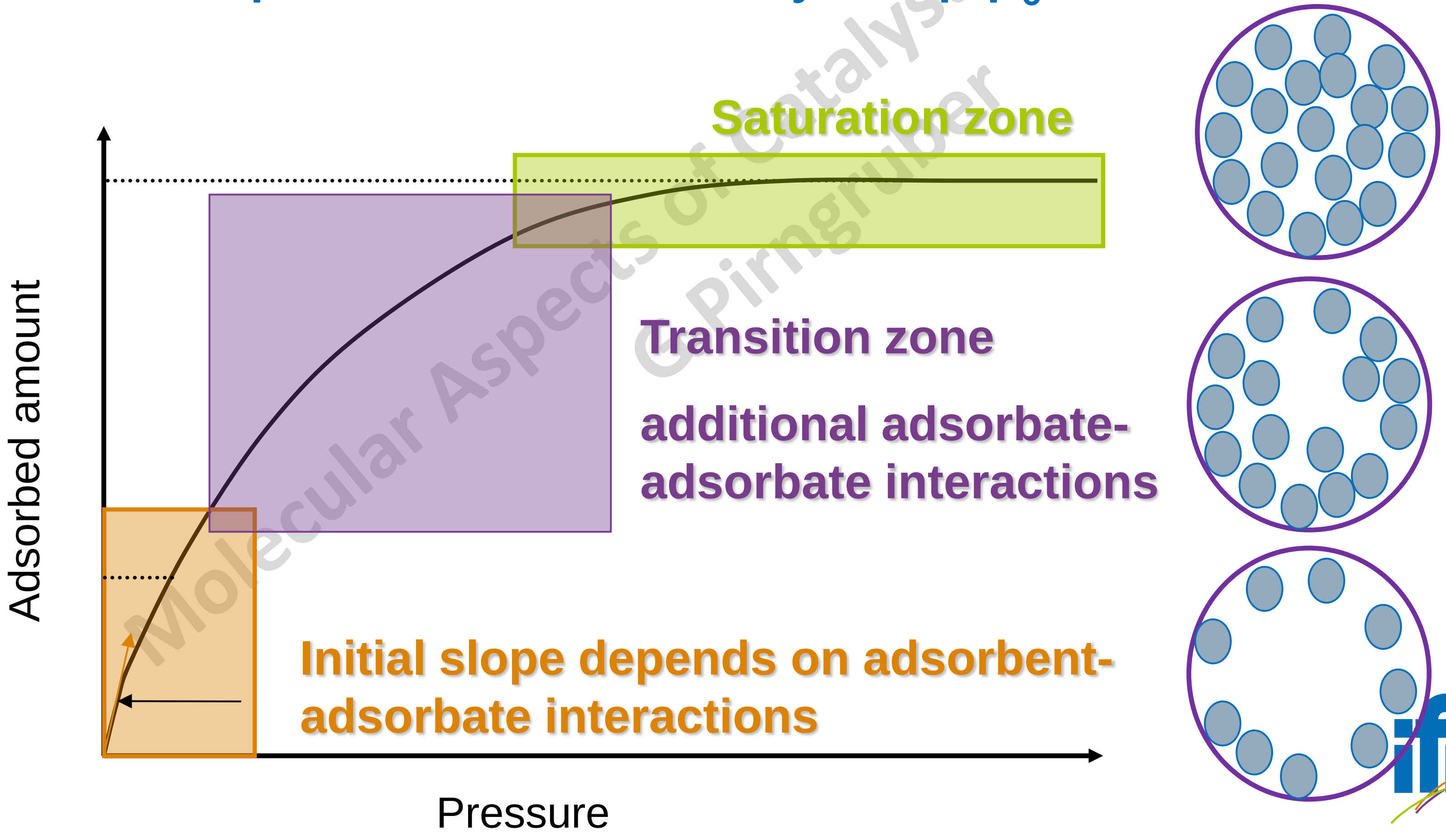
Innovation
Energie
Environnement

Terminology

- IUPAC distinguishes 3 catagories 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**



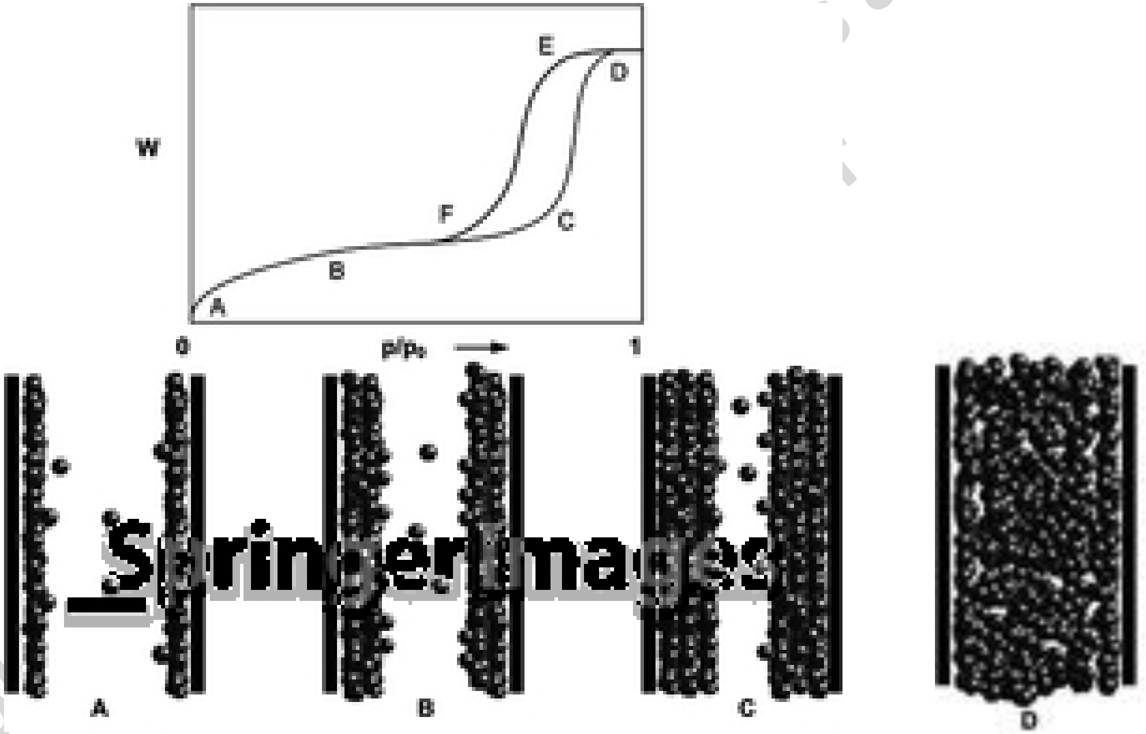
Saturation zone

Transition zone

additional adsorbate-adsorbate interactions

Initial slope depends on adsorbent-adsorbate interactions

Adsorption in mesopores



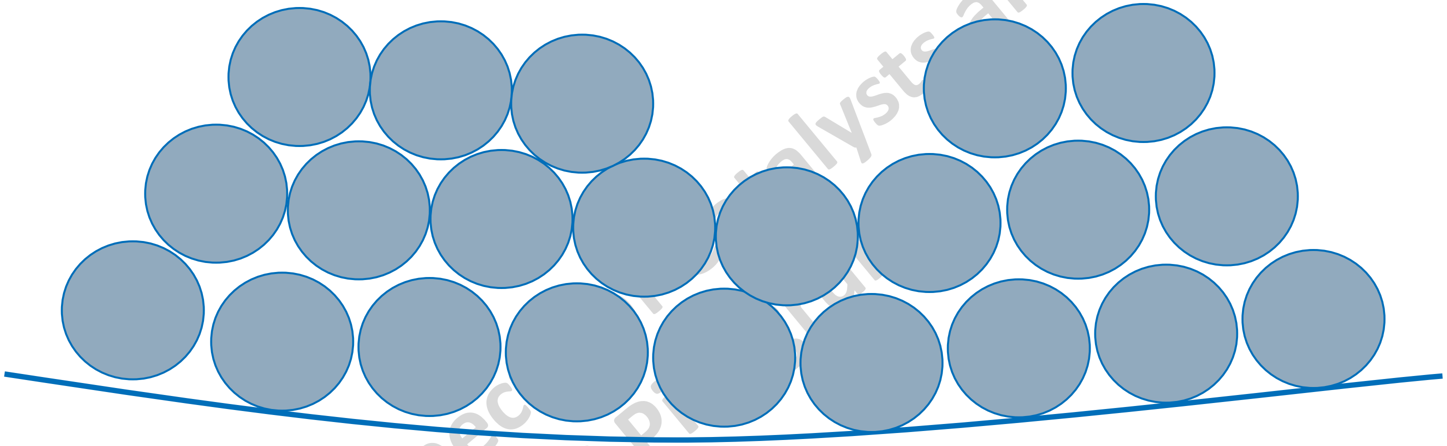
monolayer adsorption

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.

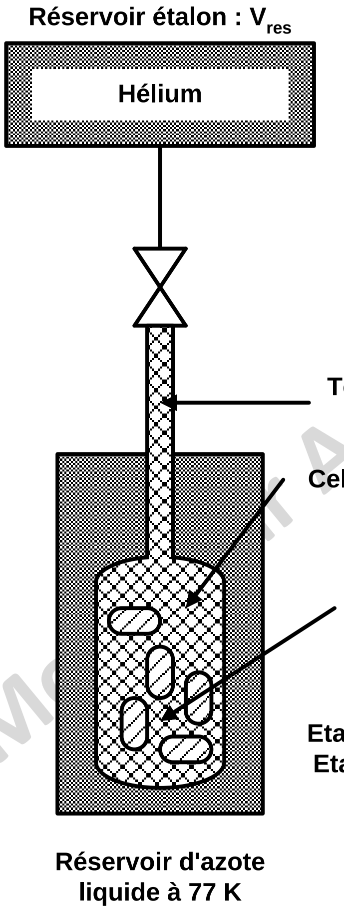
Innovation
Energie
Environnement

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



Etat initial : Pr_{iHe}, Tr_{iHe}
Etat final : Pr_{fHe}, Tr_{fHe}

Température ambiante

Cellule mesure : V_{cel}

Température N2 liquide 77 K

Etat initial : Pc_{iHe}, Tc_{iHe}
Etat final : Pc_{fHe}, Tc_{fHe}

Etat initial : Pr_{iN2}, Tr_{iN2}
Etat final : Pr_{fN2}, Tr_{fN2}

Bilans Matières : He et N_2

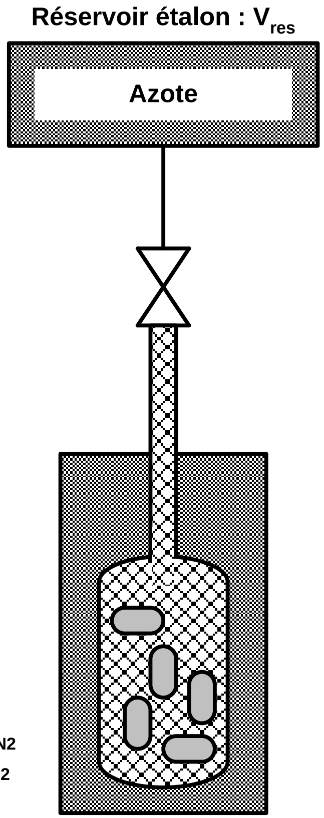
$$\Delta n_{He} = \left(\frac{P^i_{rHe}}{T^i_{rHe}} - \frac{P^f_{rHe}}{T^f_{rHe}}\right)\frac{V_{res}}{R}$$

$$\Delta n_{He} = \left(P_c^f - P_c^i\right)\frac{V_{cel}}{RT_m}$$

$$\Delta n_{N2} = \left(\frac{P^i_{rN2}}{T^i_{rN2}} - \frac{P^f_{rN2}}{T^f_{rN2}}\right)\frac{V_{res}}{R}$$

$$\Delta n_{N2} = \left(P_c^f - P_c^i\right)\frac{V_{cel}}{RT_m} + n^{ads}_{N2}$$

Etat initial : Pc_{iN2}, Tc_{iN2}
Etat final : Pc_{fN2}, Tc_{fN2}



Masse d'adsorbant : M_{sol}

Quantité adsorbée : Qads=n_{N2}^{ads}/M_{sol}

Material balance

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

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

- with adsorption (N_2)

determined with He

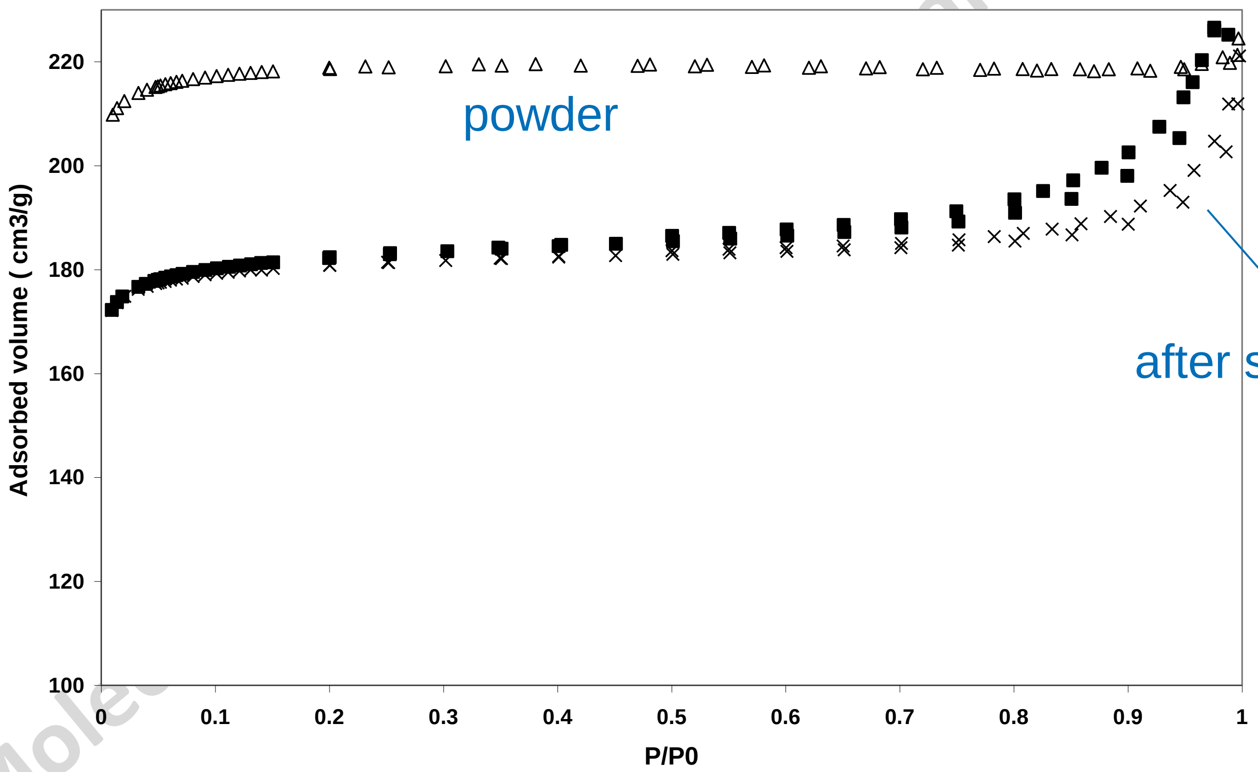
quantity initially present in the reservoir

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

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

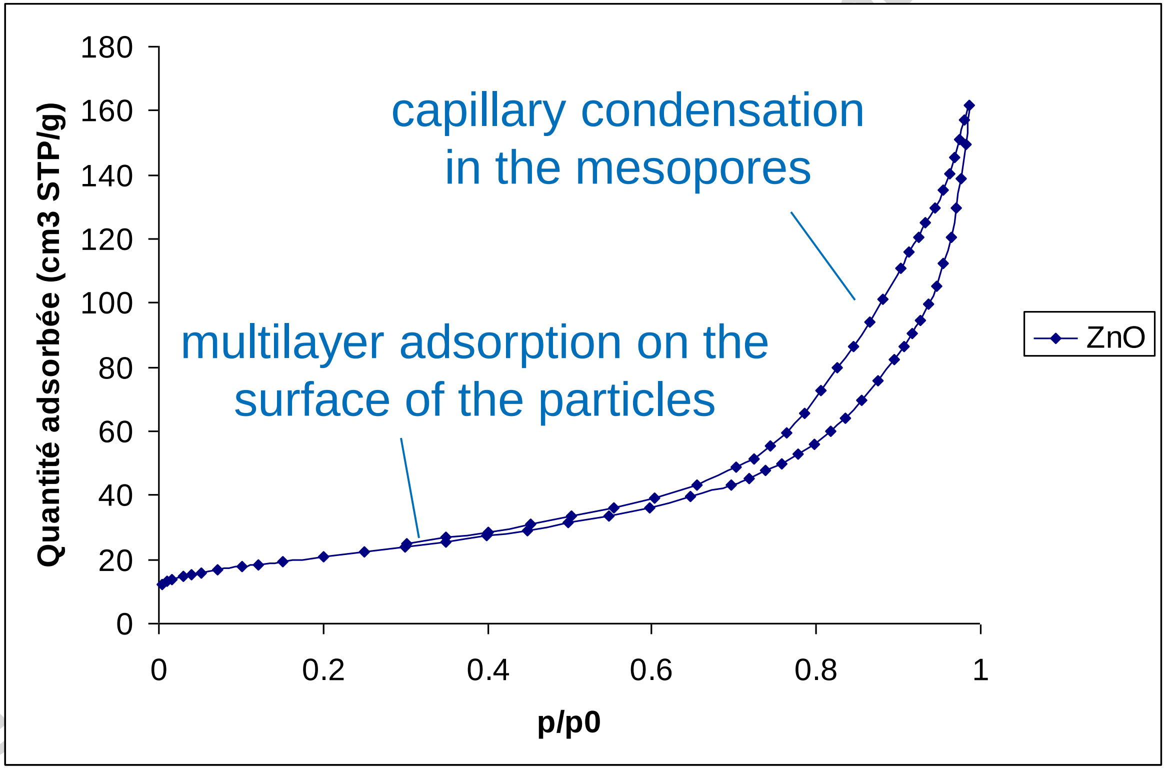


powder

after shaping with a binder

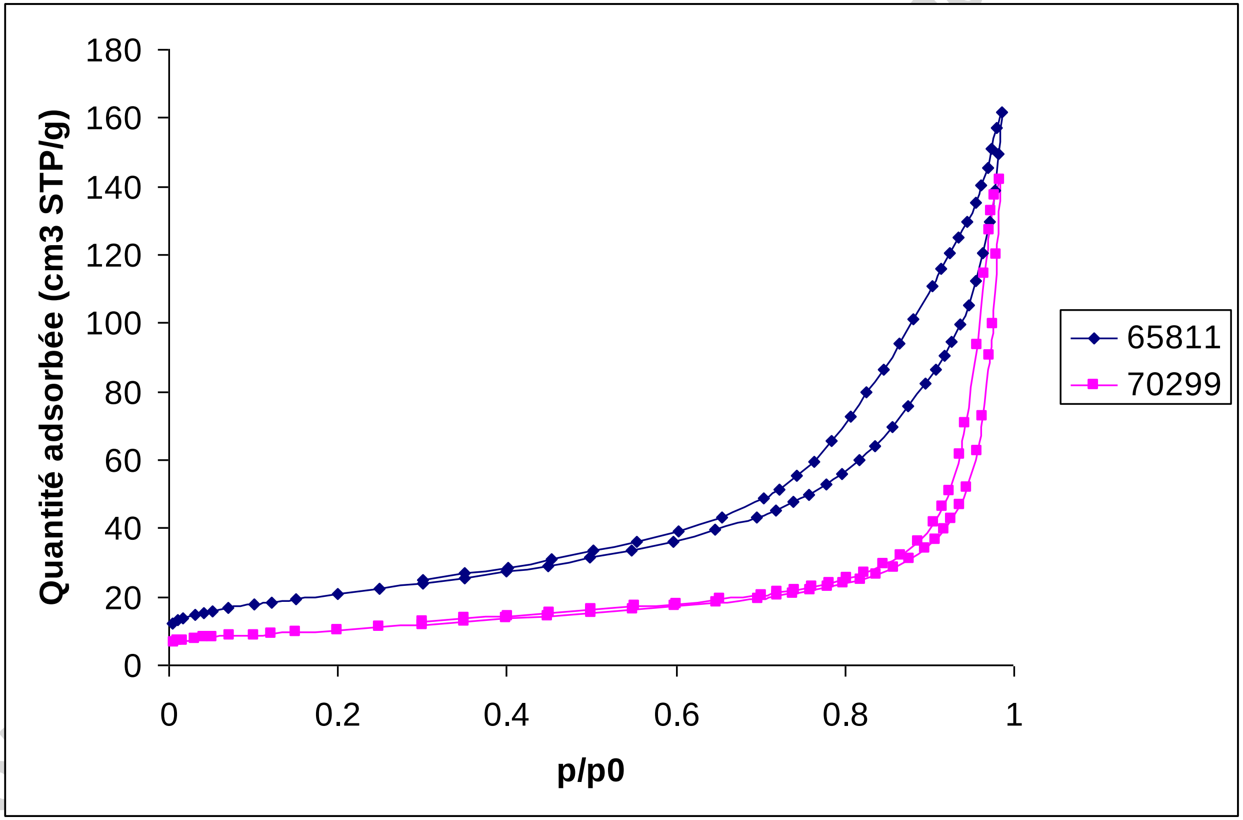
- Micropores are entirely filled at very low pressure.
- Isotherm is totally flat once micropores are filled.
  - saturation zone

Examples - ZnO



- no micropores
- mesopores generated by stacking of inidividual particles

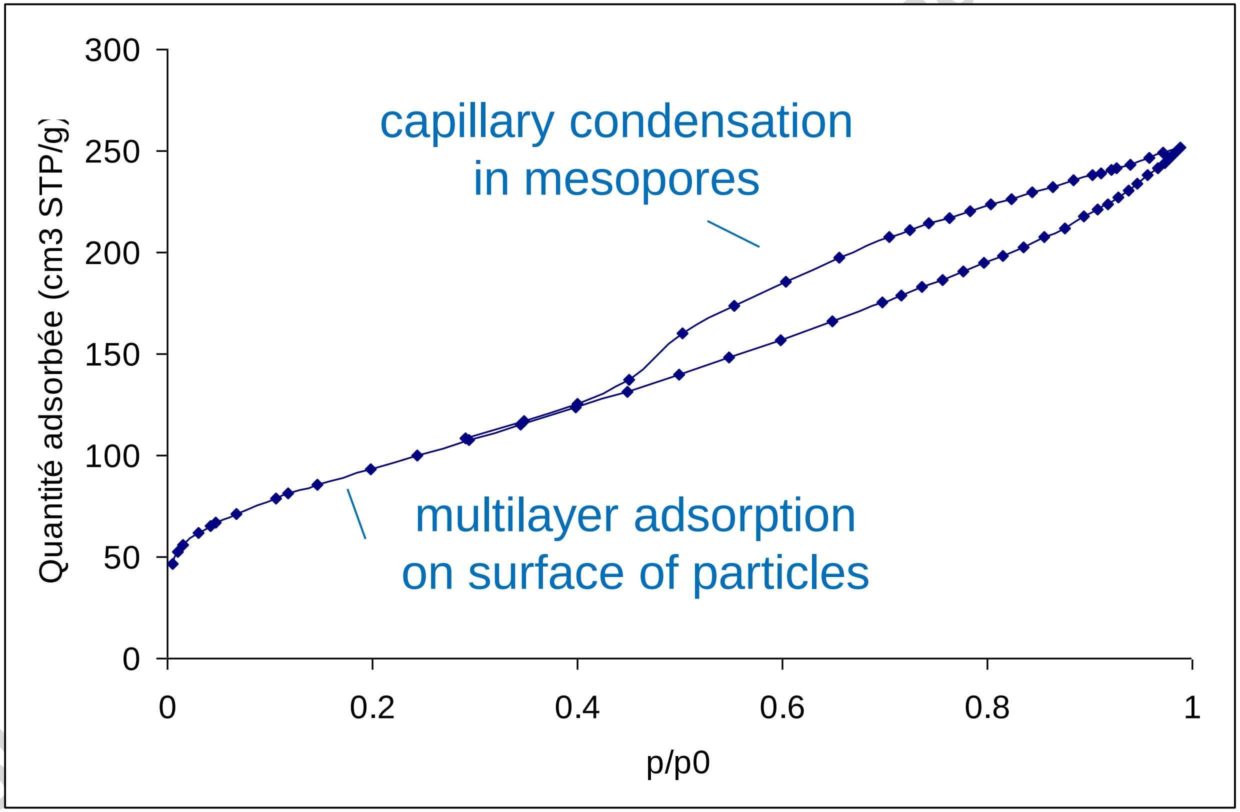
Comparison of two ZnO samples



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

Innovation
Energie
Environnement

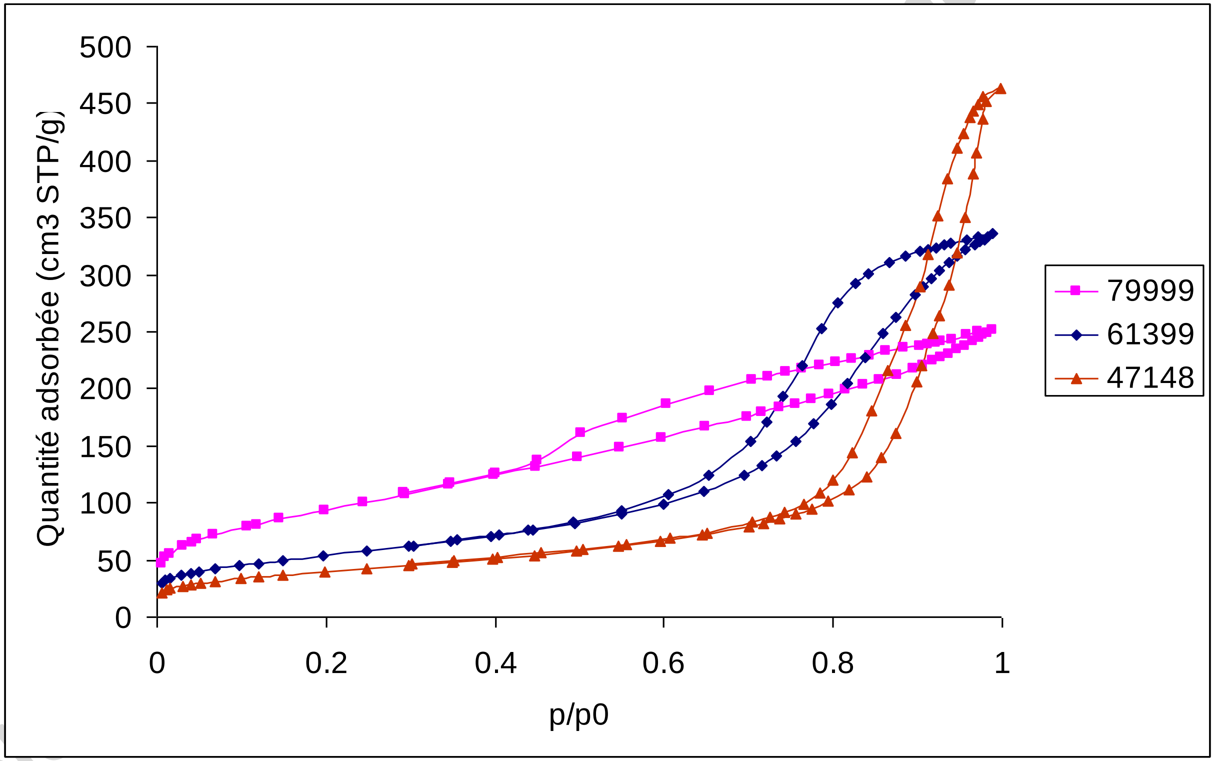
Example – Al_2O_3



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

Innovation
Energie
Environnement

Comparison Al_2O_3



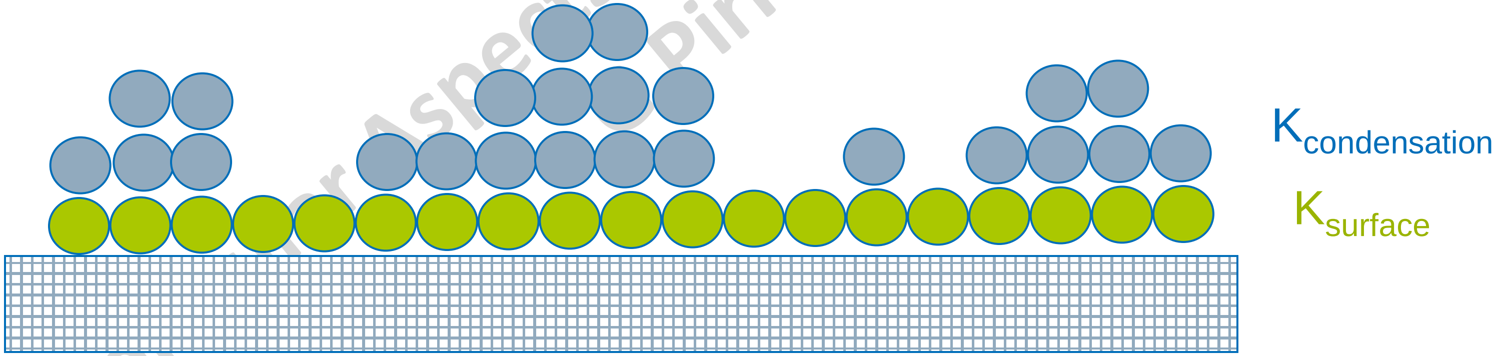
- **Surface : 79999 > 61399 > 47148**
- **Pore size : 47148 > 61399 > 79999**

Quantitative treatment of N_2 isotherms

- Pore volume: V_{micro}, V_{meso}, V_{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 = number of surface adsorption sites (monolayer)
n_{ads} = total number of adsorbed molecules

BET equation

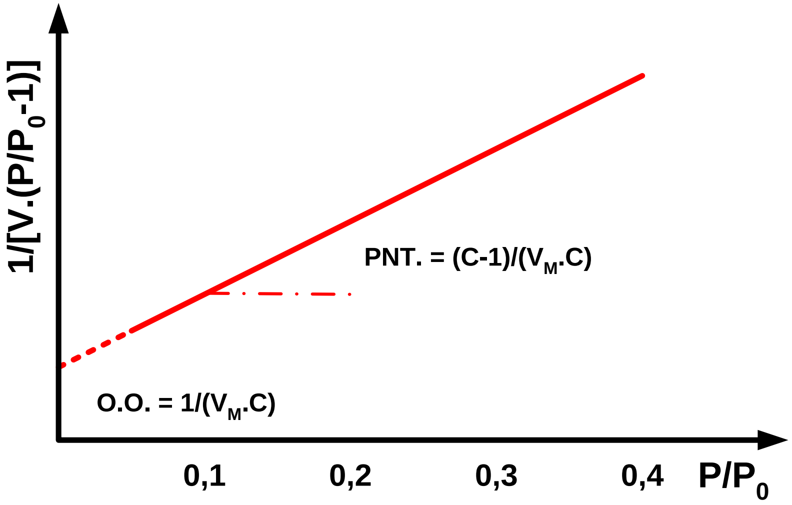
- **BET equation**

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

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

  - 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 Å^2)

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

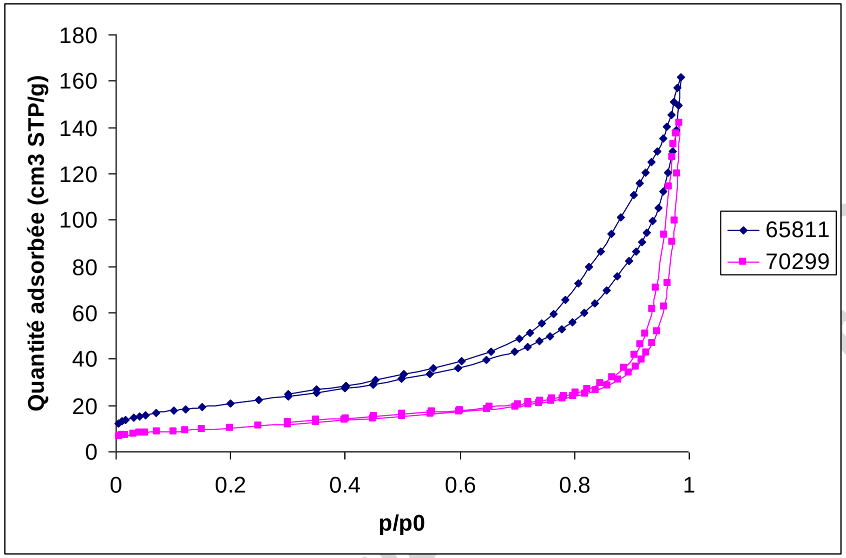


$$S_{BET} = a.\frac{p_0 V_M}{R \cdot 273K}.N_A$$

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

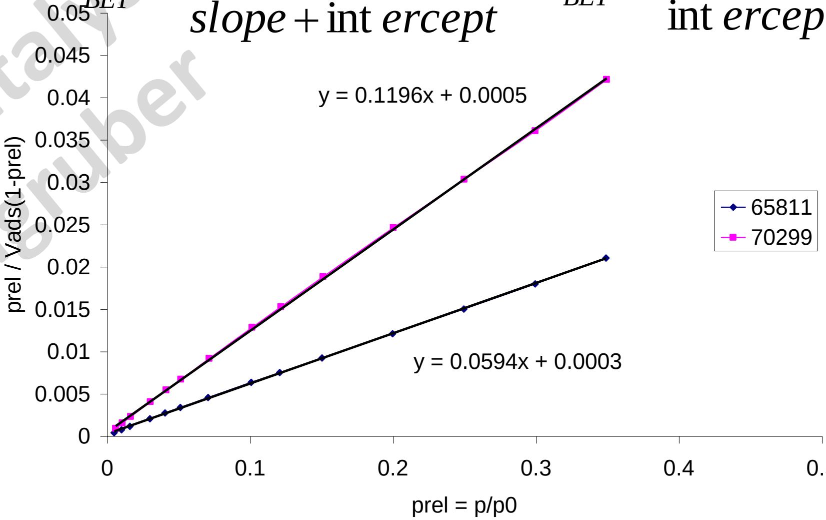
Exemple ZnO

Isothermes



BET plot

$$S_{BET} = \frac{4.355}{slope + \text{int}\,ercept} \qquad C_{BET} = \frac{slope}{\text{int}\,ercept} + 1$$

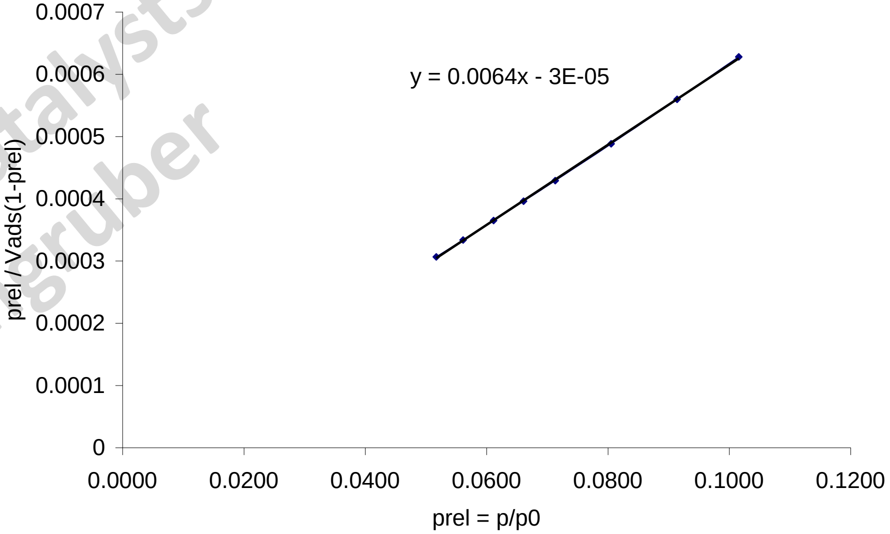


	S_{BET} (m^2/g)	C_{BET}
65811	**74**	**136**
70299	**36**	**237**

Innovation
Energie
Environnement

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



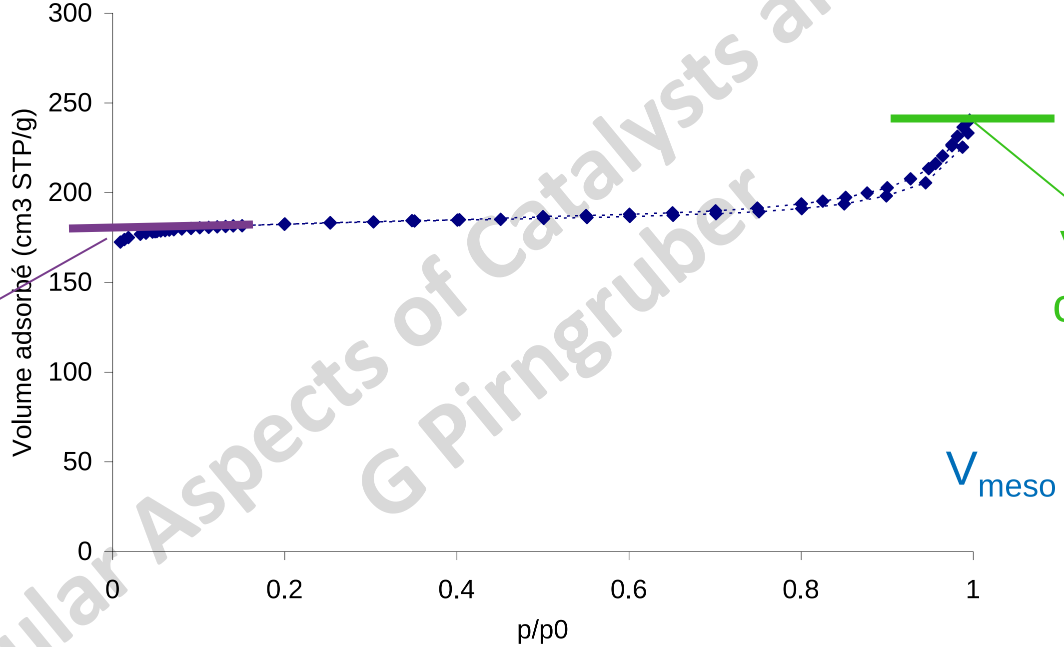
$$S_{BET} = \frac{4.355}{0.0064 - 0.00003} = 685 m^2/g$$

Langmuir Surface Area

- Langmuir theory
  - is a model of monolayer adsorption
  - this hypothesis is never fulfilled
- Do not use Langmuir surface areas !!
- $S_{Langmuir}$ is always > S_{BET} because multilayer adsorption is treated like monolayer adsorption.

Innovation
Energie
Environnement

Determination of the pore volume



V_{ads} = 178 cm^3 STP/g
→ V_{micro}

V_{ads} = 240 cm^3 STP/g
→ V_{total}

$V_{meso} = V_{total} - V_{micro}$

- **In some cases possible without using any model.**

Conversion gas volume – pore volume

- Volume of adsorbed gas correponds 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 N_2 at 77 K : 0.807 g/ml

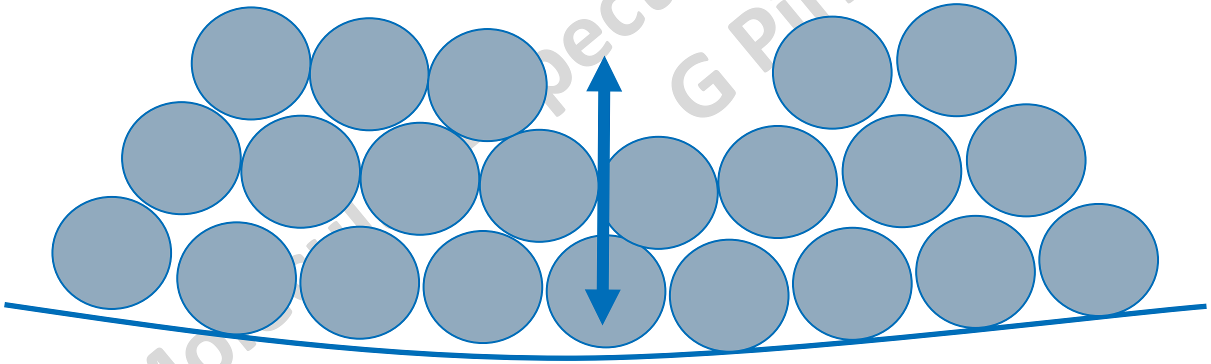
$$V_p = \frac{m_{N2}}{\rho_{N2,liq}} = \frac{n_{ads} \cdot M_{N2}}{\rho_{N2,liq}}$$

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

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 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

$$t = 3,54\left[\frac{5}{\ln\left(\frac{P_0}{P}\right)}\right]^{1/3}$$

$$t = \frac{V_{ads}}{S_{BET}}$$

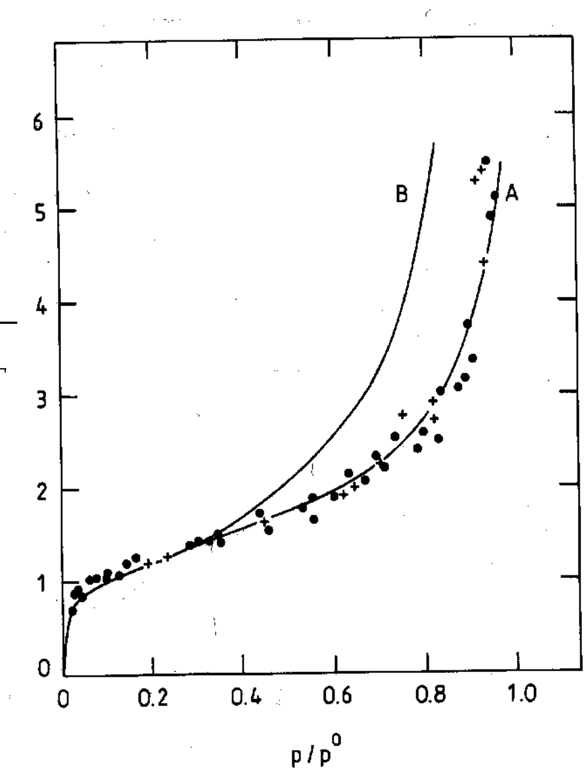
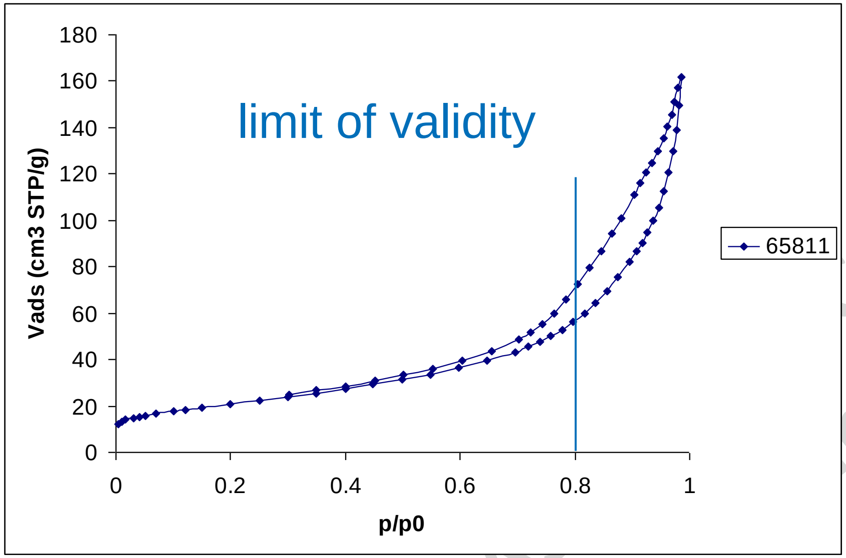
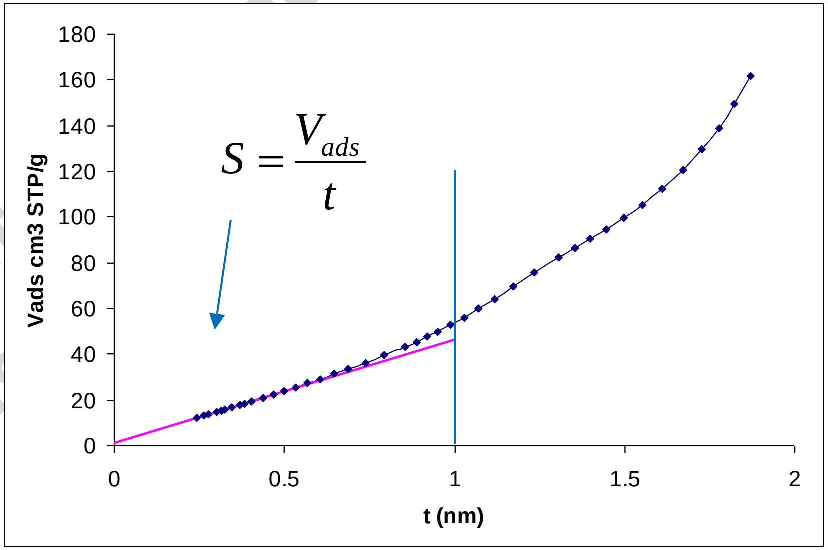


Fig. 12.3. The adsorption of nitrogen on nonporous samples of silica and alumina, the surface areas ranging from 2.6–11.5 $m^2\,g^{-1}$ for silica and from 58–153 $m^2\,g^{-1}$ for alumina. n/n_m is plotted against $p/p°$. n is the number of moles adsorbed per gram of adsorbent and n_m is the monolayer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



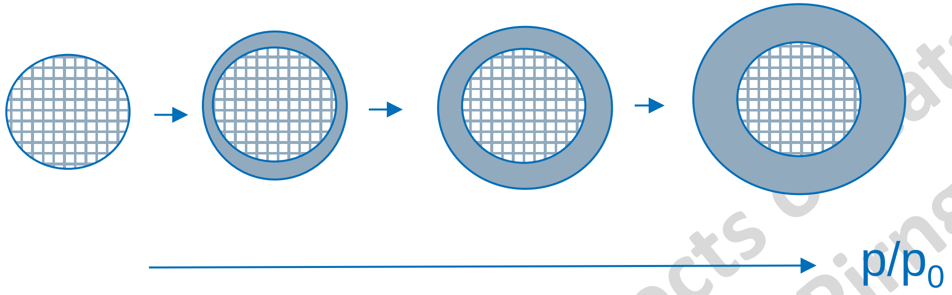


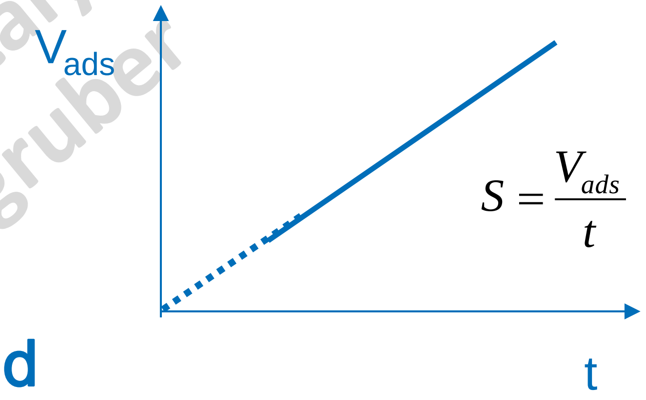
$$t = \left(\frac{13.99}{-\log \frac{p}{p_0} + 0.034}\right)^{1/2}$$

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

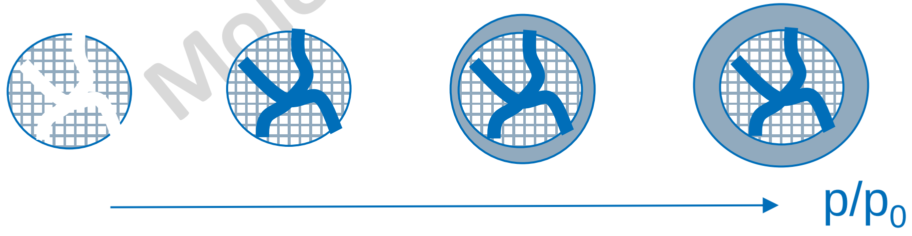
Interpretation of t-plots

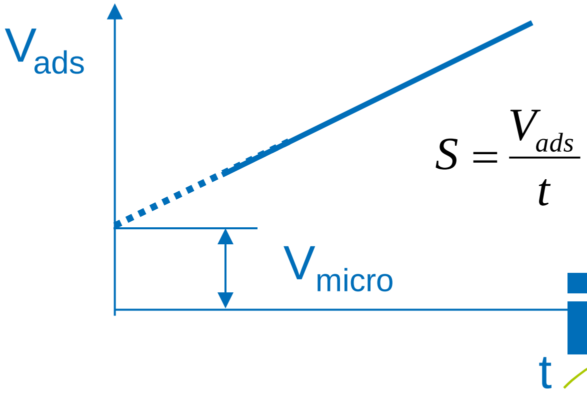
- Adsorption on a non-porous solid





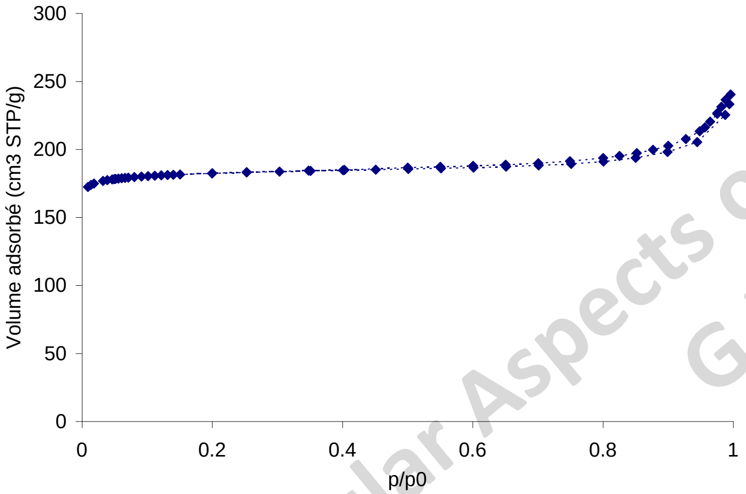
- Adsorption on a microporous solid
  - micropores rapidly filled
  - then adsorption on external surface



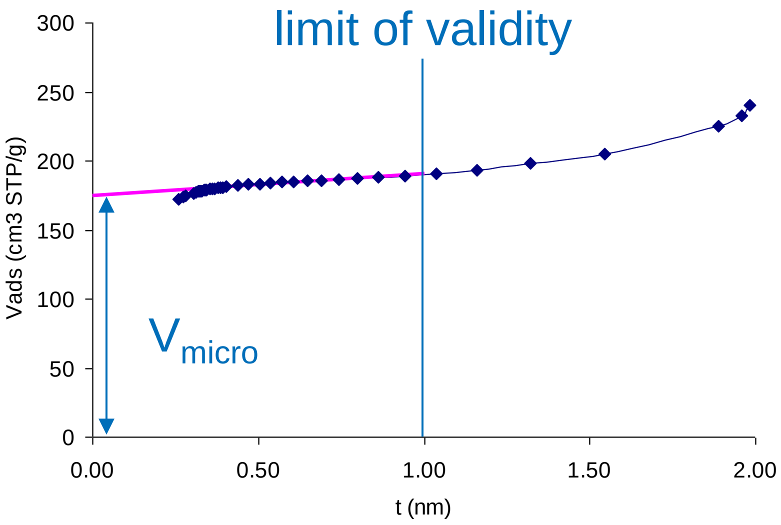


Example zeolite NaX

Isotherm



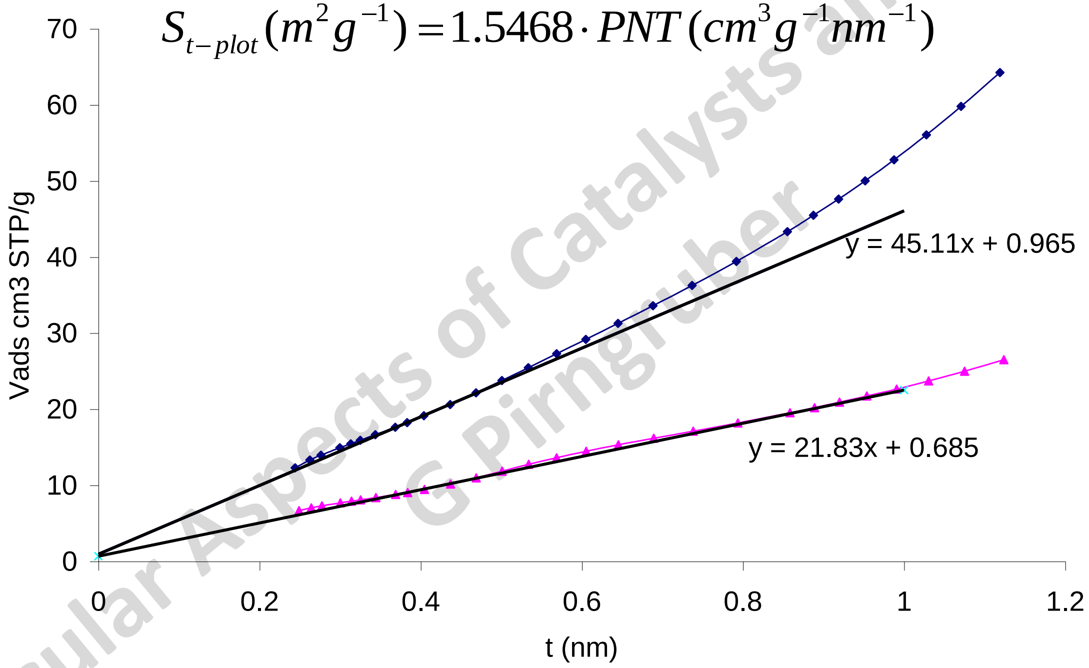
t-plot



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

Innovation
Energie
Environnement

Surface BET vs. Surface t-plot

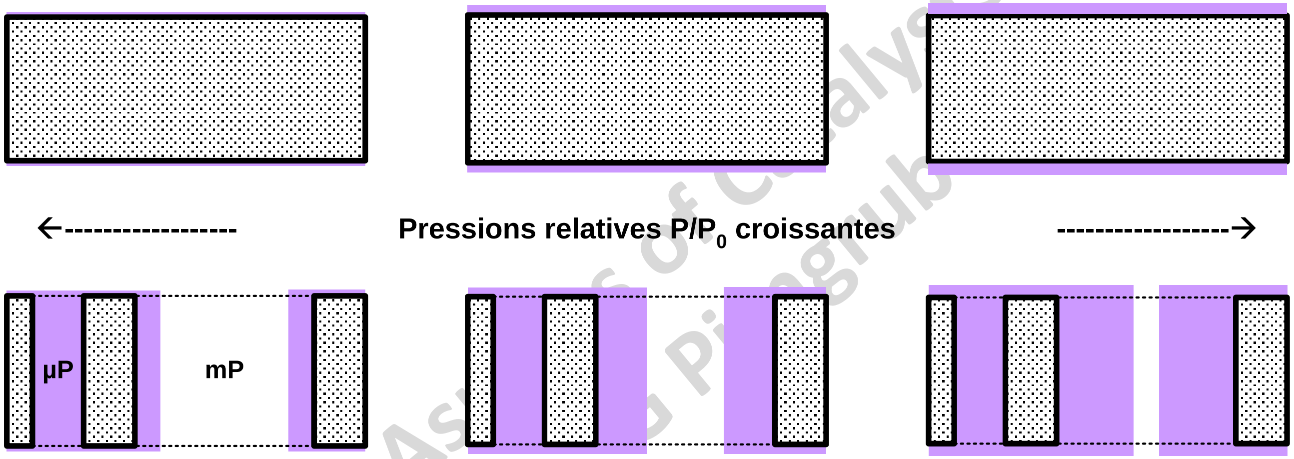


$$S_{t-plot}\,(m^2 g^{-1}) = 1.5468 \cdot PNT\,(cm^3 g^{-1} nm^{-1})$$

	S_{BET} (m²/g)	$S_{t\text{-}plot}$
65811	74	70
70299	36	34

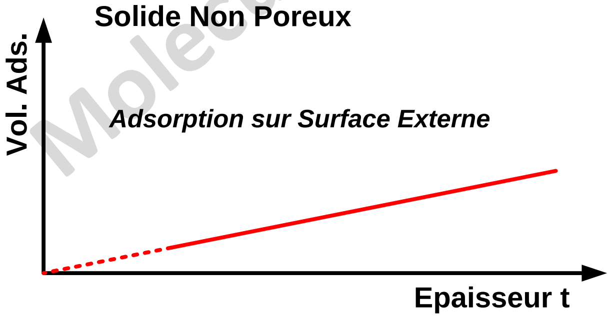
Micro- and mesoporous solids

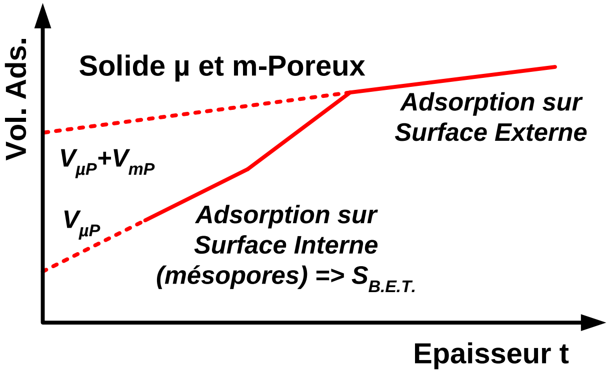
Solide non poreux : Adsorption sur Surface Externe - Courbe t = t(P/P_0)



←------------------ Pressions relatives P/P_0 croissantes ------------------→

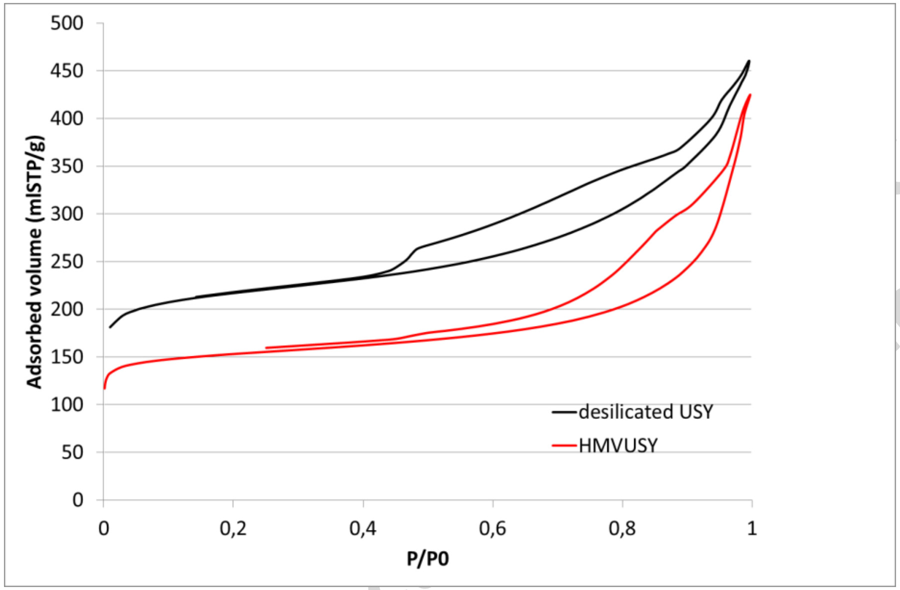
Solide poreux : Adsorption sur Surfaces Interne & Externe

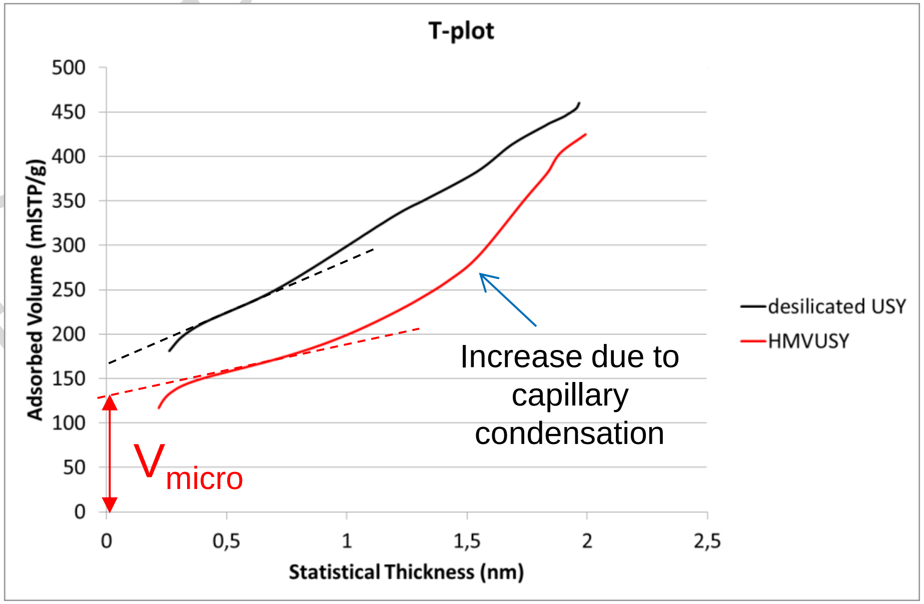




t-plot of micro/mesoporous zeolites

Dealuminated USY zeolites





Increase due to capillary condensation

V_{micro}

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

Average pore size

- From geometrical rules
  - Cylindrical Pore:
    - V = pore volume
    - S = surface

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

  - Spherical pore :

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

  - Slit pore :

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

Micropore size distribution

- Based on the relation between adsorption strength and the ratio between adsorbate size and pore size
  - condition: adsorption controled by van der Waals interactions only
- Mathematical models
  - Horvath-Kawazoe: slit-shaped pores
  - Saito-Foley: cylinder pores *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 !

Example of micropore size distribution

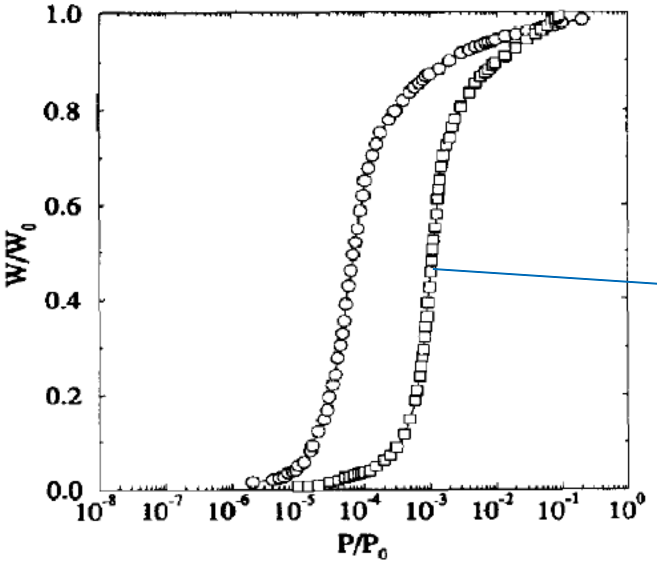
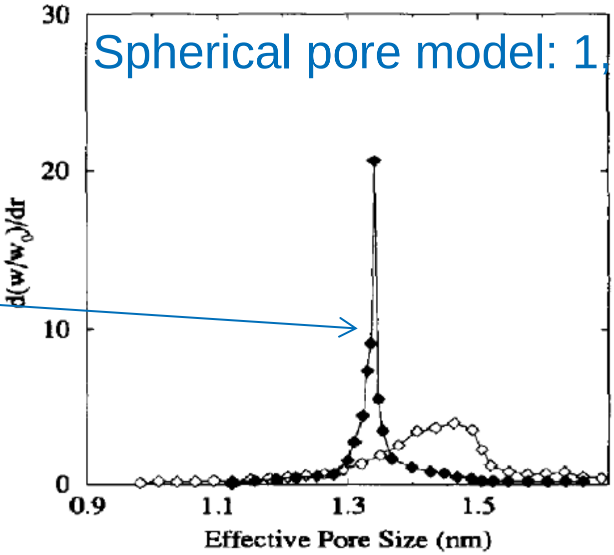


Fig. 4. Adsorption isotherms of argon on 5A (Venero and Chiou, 1988) and faujasite zeolites (Borghard *et al.*, 1991) at 87 K: (○) 5A zeolite; (□) faujasite.



Spherical pore model: 1,3 nm

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

Slit pore model: 0,8 nm

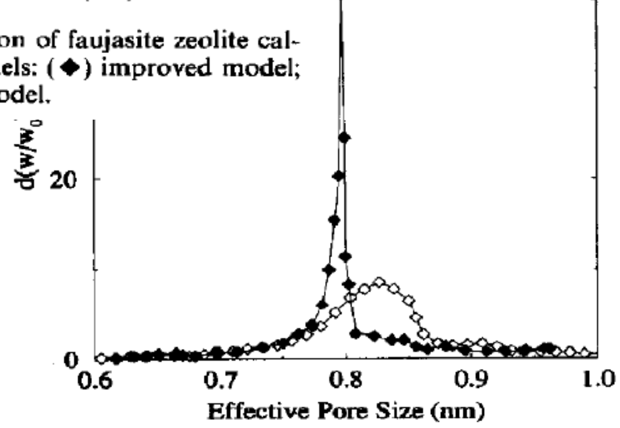


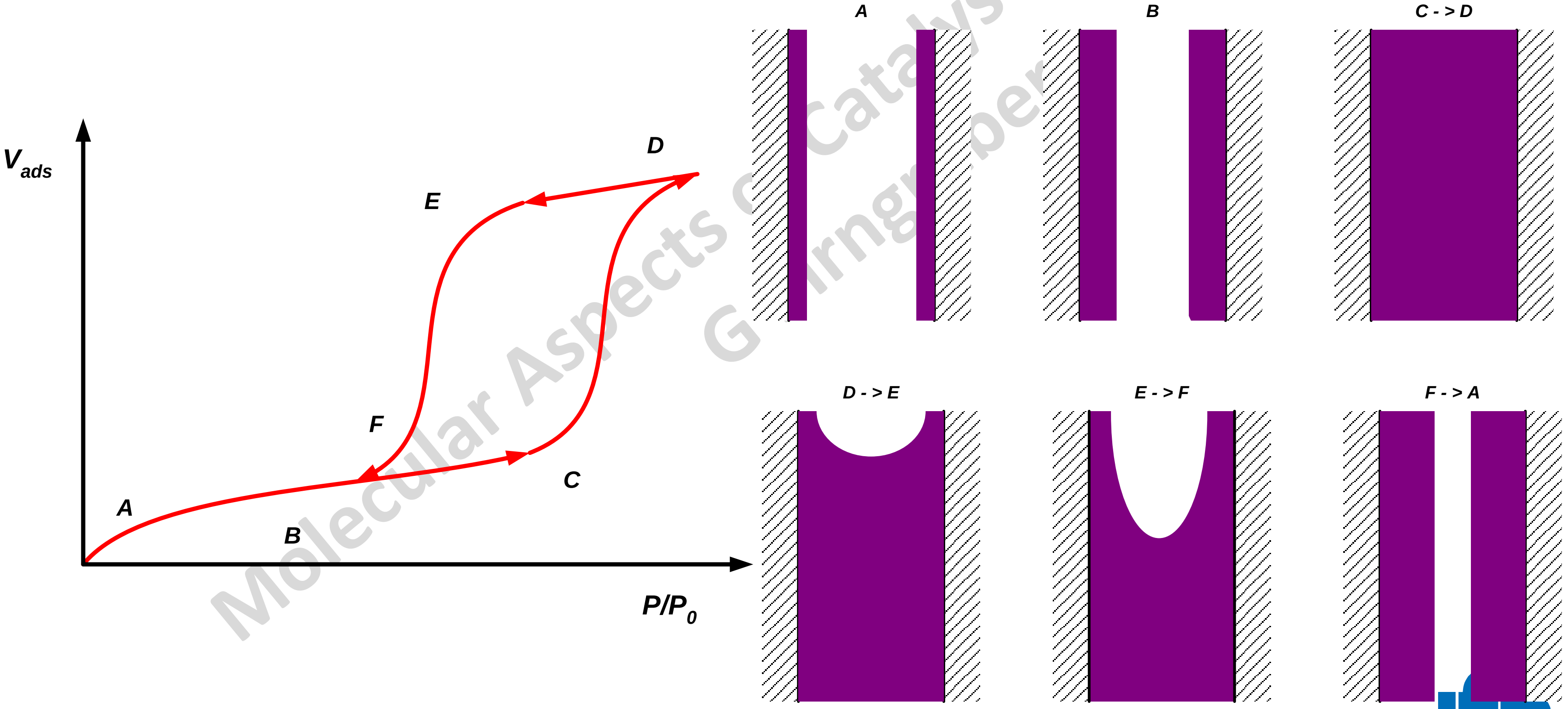
Fig. 6. Micropore size distributions of faujasite zeolite calculated from slit pore models: (◆) improved model; (◇) H–K model.

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

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

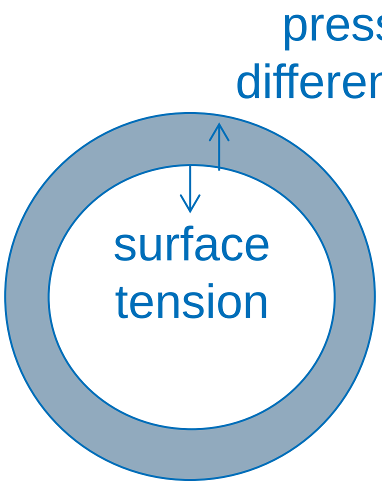
Mesopore size distribution

- 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

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

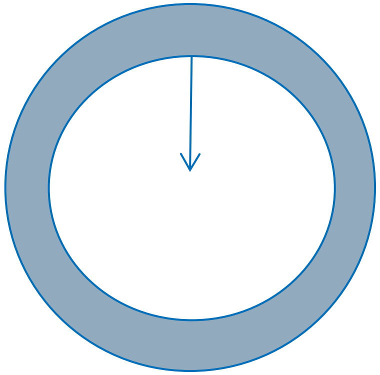
$$dn_{capliq} = -dn_{liq} = \frac{dV_{capliq}}{V_m}$$

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

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

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

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



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

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

Generalized Kelvin equation

Relation to curvature of the pore

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

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

Vm = molar volume

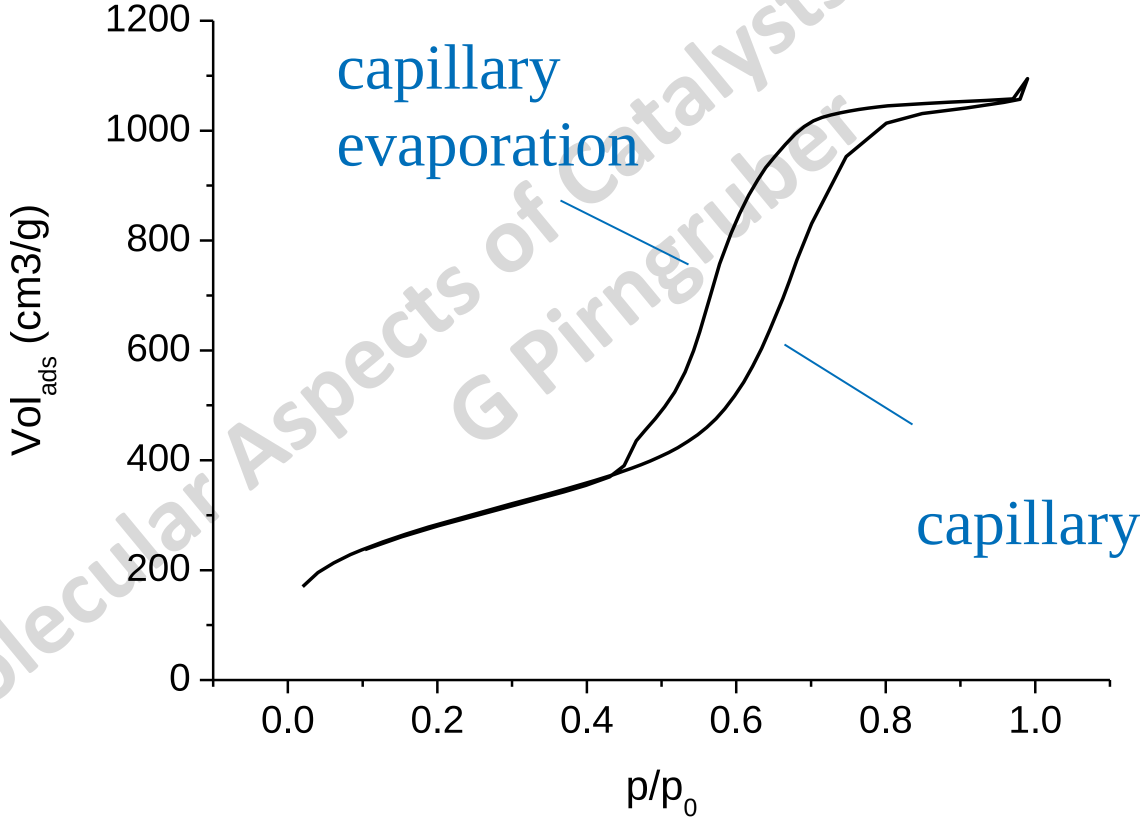
$$\frac{dV}{dA} = r_{curvature}$$

Inverse relationship with curvature radius.

- Curvature depends on the pore geometry
  - Sphere: dV/dA = r/2
  - Cylinder dV/dA = r
  - Slit dV/dA = d distance between slits

Capillary condensation associated with hysteresis

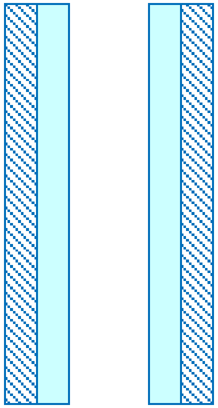
Type H1



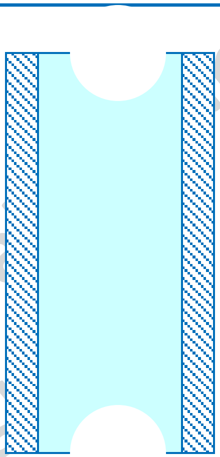
capillary evaporation

capillary condensation

Origin of the hysteresis – Cohan's theory



Adsorption:
cylindrical meniscus
$r_{curv} = r_{eff}$



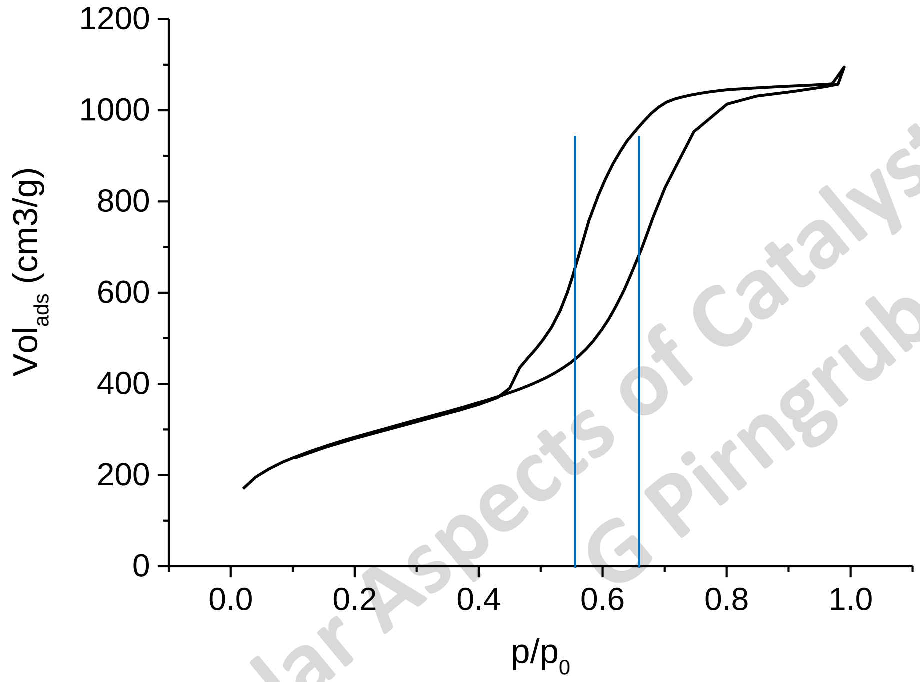
Desorption:
hemisperical meniscus
$r_{curv} = r_{eff} / 2$

- The lower r_m, the lower is the pressure of capillary condensation/evaporation
- $r_{curv,ads} = 2\ r_{curv,des}$
- 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

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

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

Kelvin equation

Cylinder !!

	p_c/p_0	$t(p_c)$	$r_{curvature}$	R_c	$r_p = r_c + t$
Ads	0.671	8.2	11.9	= 11.9	20.2
Des	0.565	7.0	8.35 x 2	= 16.7	23.7

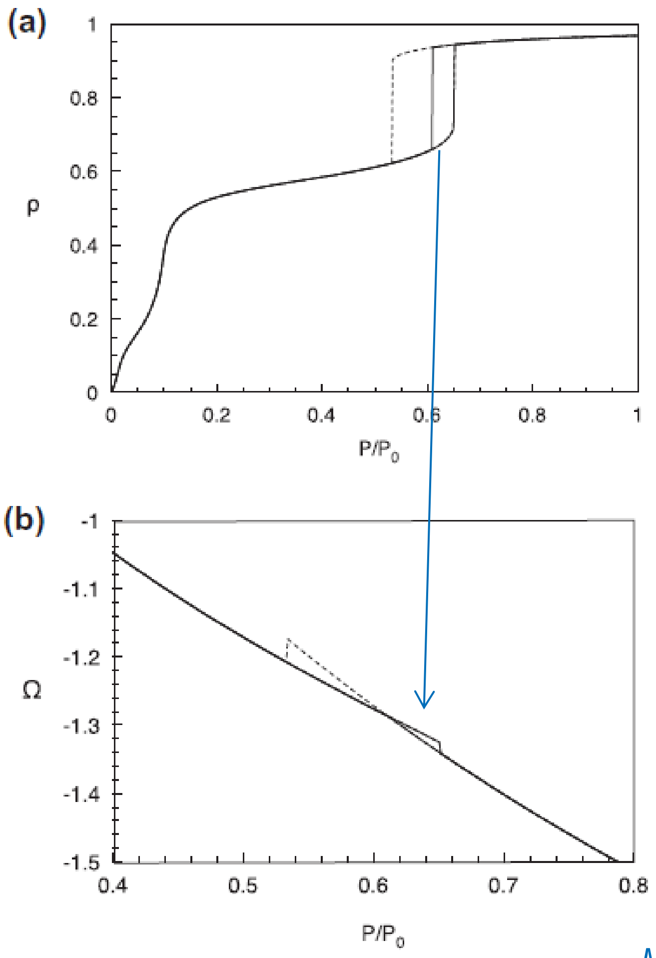
Sphere !!

Origin of the hysteresis

- Truth seems to be complicated than in Cohan's theory.
- Cohan's theory, based on the shape of mensiscus, 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.

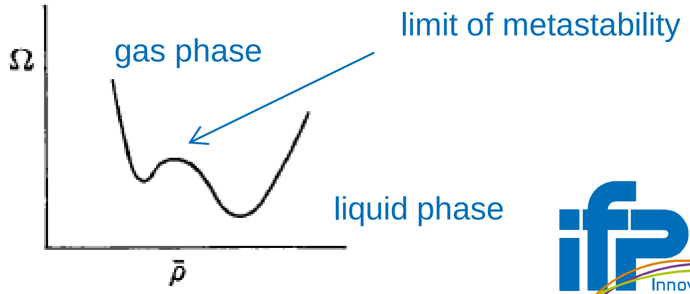
Innovation
Energie
Environnement

Hysteresis and metastability



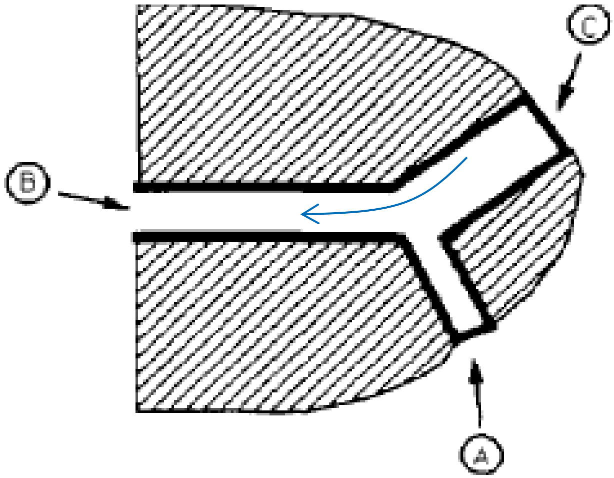
- Adsorption branch comprises metastable states.
  - grand free energy of filled pore is lower than that of the empty pore in the hysteresis
- Desorption branch is in thermodynamic equilibrium.
- Reason for metastability in adsorption branch
  - barrier of nucleation by formation of a liquid bridge across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

Monson, MMM, 2012.



Peterson, JCS Farad 2, 1986.

Pore network effects

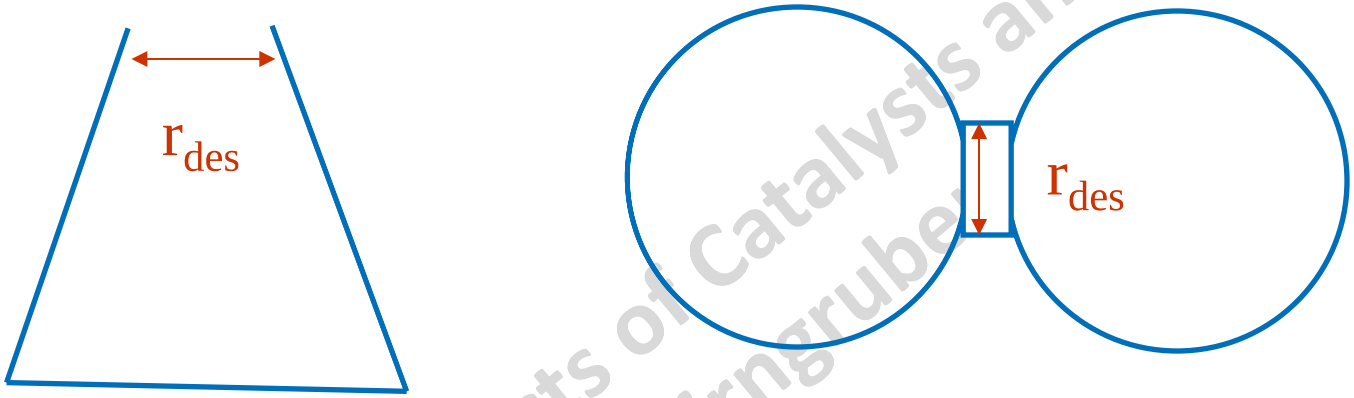


Order of capillary evaporation:
C before B and A, but
N_2 can only desorb from pore C if pore B has already been emptied.

Seaton, CES, 1991.

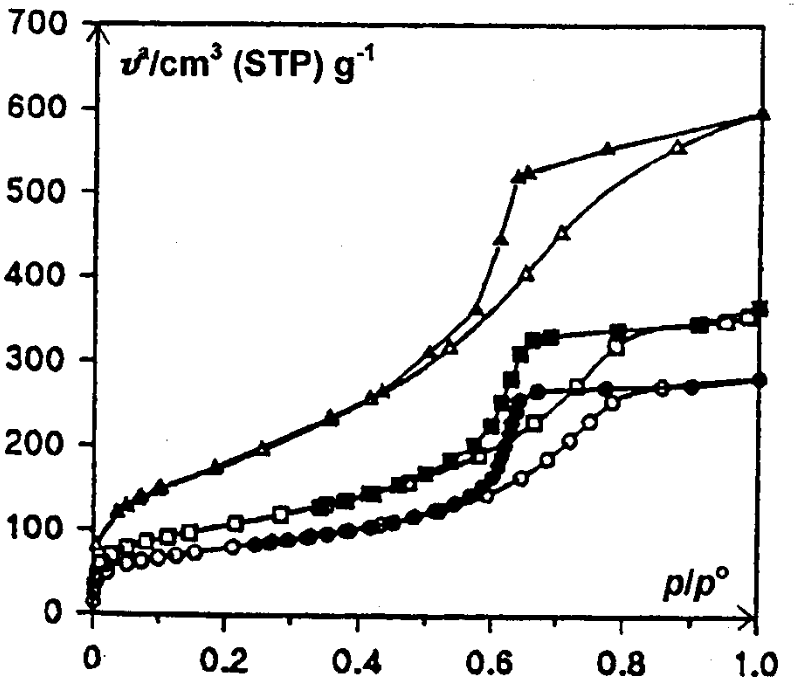
- **Desorption branch of isotherm not in thermodynamic equilibrium any more, due to pore blocking.**
- **Desorption is controlled by a percolation process.**
    - probability that the pore is connected to the outer surface.

Ink-bottle 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



Type H2

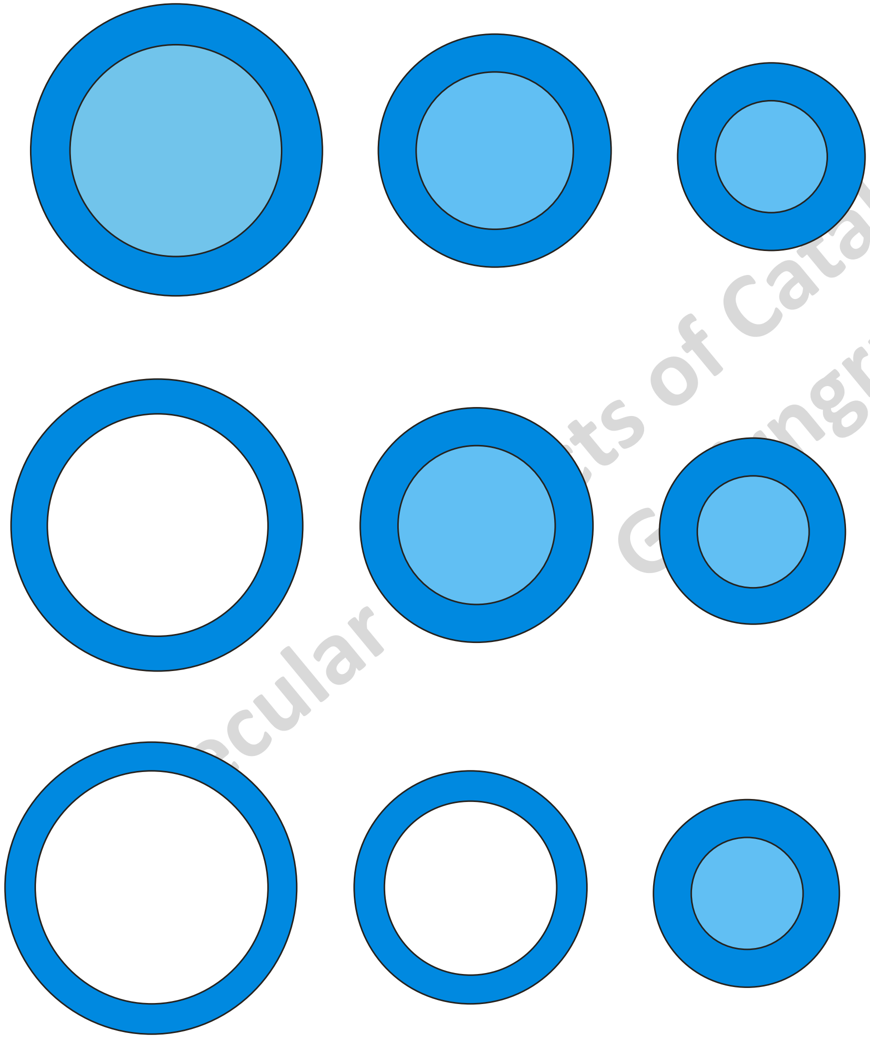
Adsorbent: xerogel and alcogel

- 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.

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 openening 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

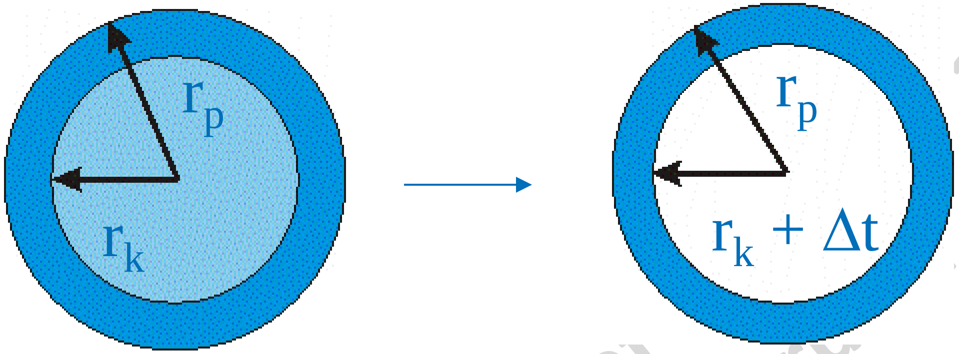


p_0 – all pores filled

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

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 to ΔV_n.

The BJH-equation

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

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

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

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: $r_p = r_k + t$

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

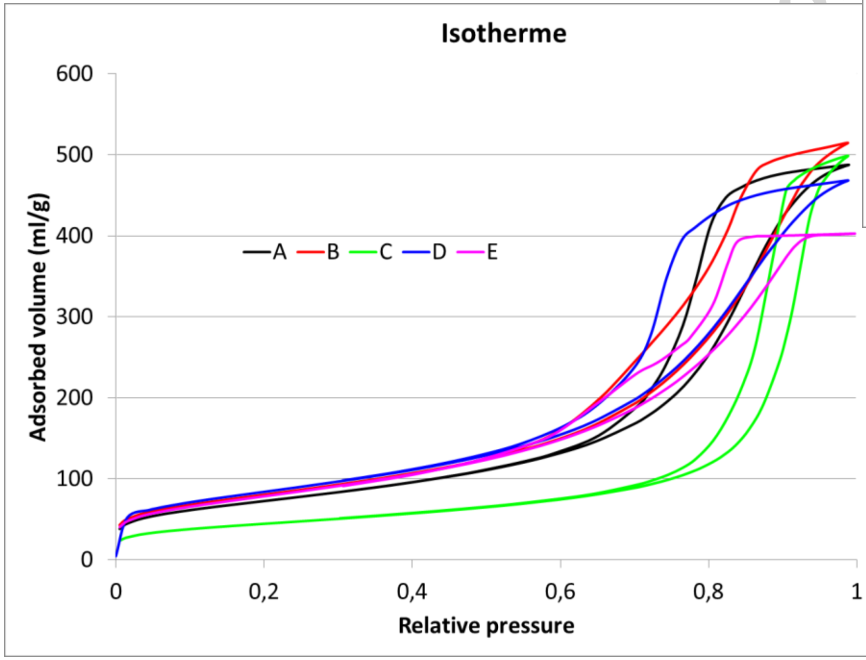
$$\log \frac{p}{p_0} = \frac{-4.14}{r_k}$$

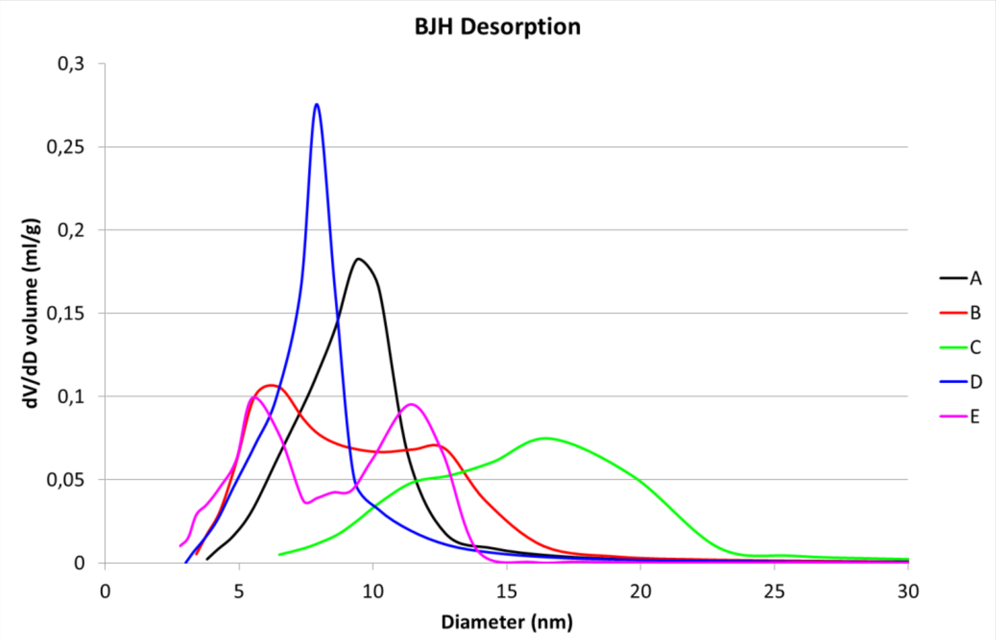
  - Δt is the change in layer thickness in each desorption step
  - ΔV_n is the volume desorbed in each step

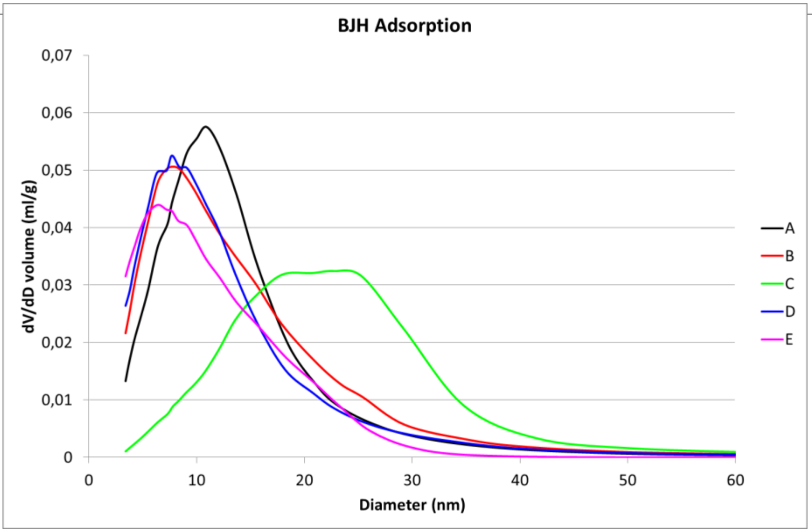
→ A plot of pore volume vs. pore radius is obtained.

Example of pore size distribution

- Alumina supports
  - Significant differences between PSD from adsorption and desorption







Limits of the BJH-model

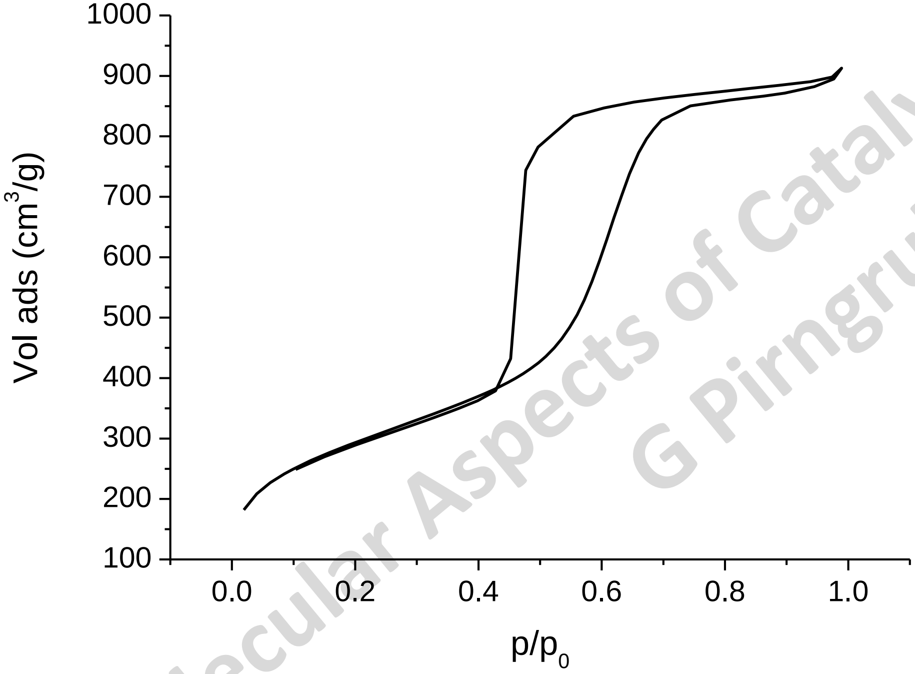
- BJH underestimates the pore size below 7.5 nm – WHY?
  - Model separates the adsorbed film and the capillary condensate – not a realistic picture
  - Fluid-wall interactions are neglected
  - Kelvin equation may not be valid in very narrow pores
    - Surface tension might increase with curvature

- One should speak about a BJH-value rather than pore diameter.

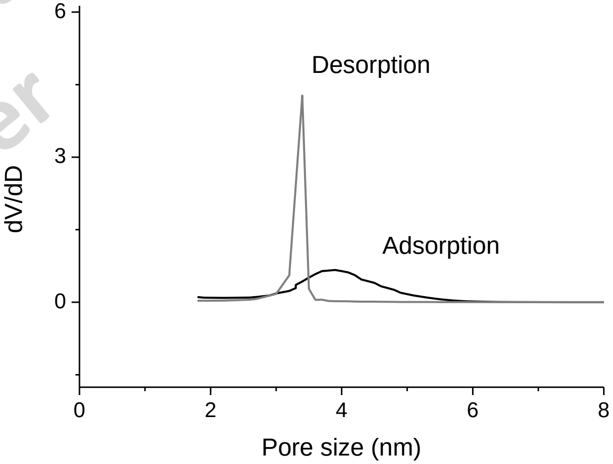
Innovation
Energie
Environnement

Ink-bottle type hysteresis loop

Isotherm



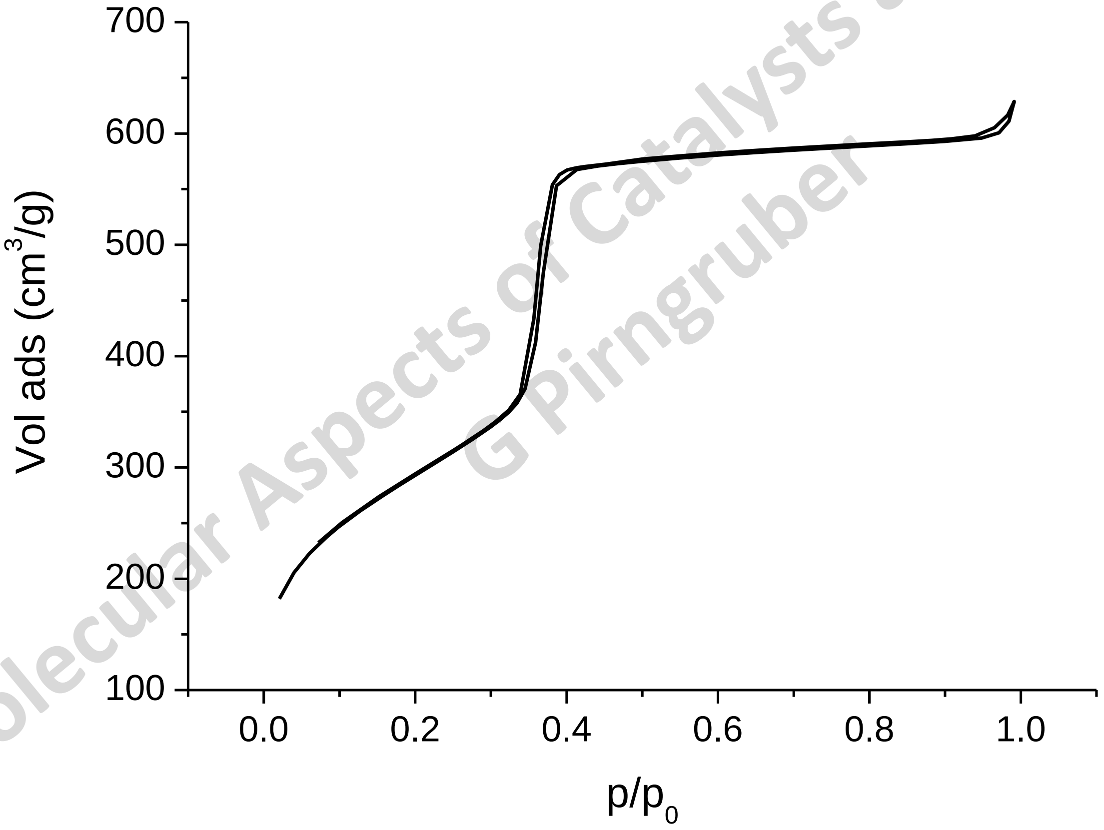
Pore size distribution



- Narrow peak in the pore size distribution of the adsorption branch is an artefact caused by the forced closure of the isotherm at $p/p_0 = 0.43$

Innovation
Energie
Environnement

Isotherm without hysteresis loop



Innovation
Energie
Environnement

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 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
- $T_{c,pore} < 77$ K for pores, which show capillary condensation at $p/p_0 = 0.4$ → closure point of isotherm
- $T_c(Ar) > T_c(N_2)$ → Ar isotherms show hysteresis when N_2 isotherms don't[2]

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

[2] M. Thommes, R. Köhn, M. Fröba, J.Phys.Chem. B 104 (2000) 7932.

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.

Innovation
Energie
Environnement

DFT is becoming state of the art

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

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

  - ρ(**r**) = fluid density at position **r**
  - F(ρ) = Helmholtz energy of the system due to fluid-fluid interactions, in the absence of an external field
  - V(r) = external potential at position **r**
  - μ = chemical potential

Expression for the grand potential

$$\Omega[\rho(\mathbf{r})] = \overbrace{k_B T \int \rho(\mathbf{r})\left[ln\left(\Lambda^3(\mathbf{r})\right) - 1\right] d\mathbf{r}}^{\text{Ideal gas}} + \overbrace{k_B T \int d\mathbf{r}\, \Phi\left(\{\bar{n}_\alpha\}(\mathbf{r})\right)}^{\text{Excess energy (non-ideality)}}$$

$$\underbrace{+\frac{1}{2}\int d\mathbf{r} \int \rho(\mathbf{r})\rho(\mathbf{r}')\phi_{att}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'}_{\text{Fluid-fluid interaction}} \underbrace{- \int \rho(\mathbf{r})[\mu - \phi_{ext}(\mathbf{r})]\, d\mathbf{r}}_{\text{External potential}}$$

- Everything is in the experssion of Φ_{ext}
  - Solid-fluid interaction
  - Effet of pore size and pore geometry (confinement)
    - Similar to the HK, SF models of micropore size analysis

ifp Innovation Energie Environnement

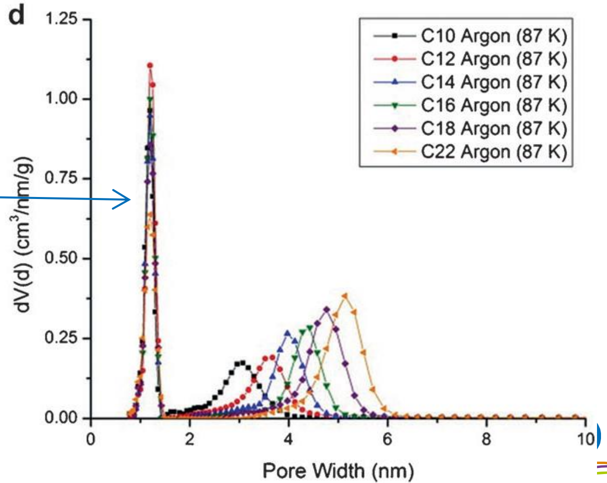
Pore size analysis with DFT

- 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 intergrated 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

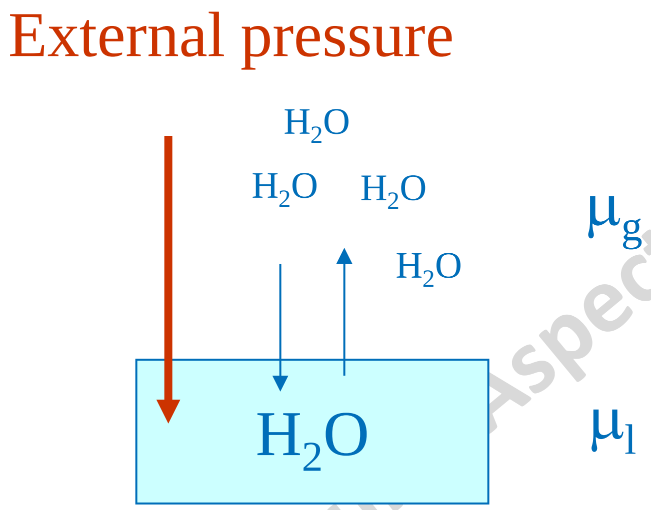
- Textbooks on adsorption
  - D.A. Ruthven, Principles of Adsorption and Adsorption Processes, Wiley
  - D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press
- Review articles discussing a more moderne view of hysteresis effects and pore size analysis
  - P.A. Monson, Understanding 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.

Innovation
Energie
Environnement

Alternative explanations of the Kelvin equation

Physical principles of capillary condensation

- Vapour pressure of a liquid under external pressure



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

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

$$v_l\, dp_l = RT/p_g * dp_g$$

$$v_l \Delta p_l = RT \ln (p_g/p_{g0})$$

p_g = new vapour pressure of H_2O
p_{g0} = orignial vapour pressure of H_2O
Δp_l = external pressure on liquid (H_2O), which induces the change in vapour pressure
v_l = molar volume of liquid (H_2O)

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

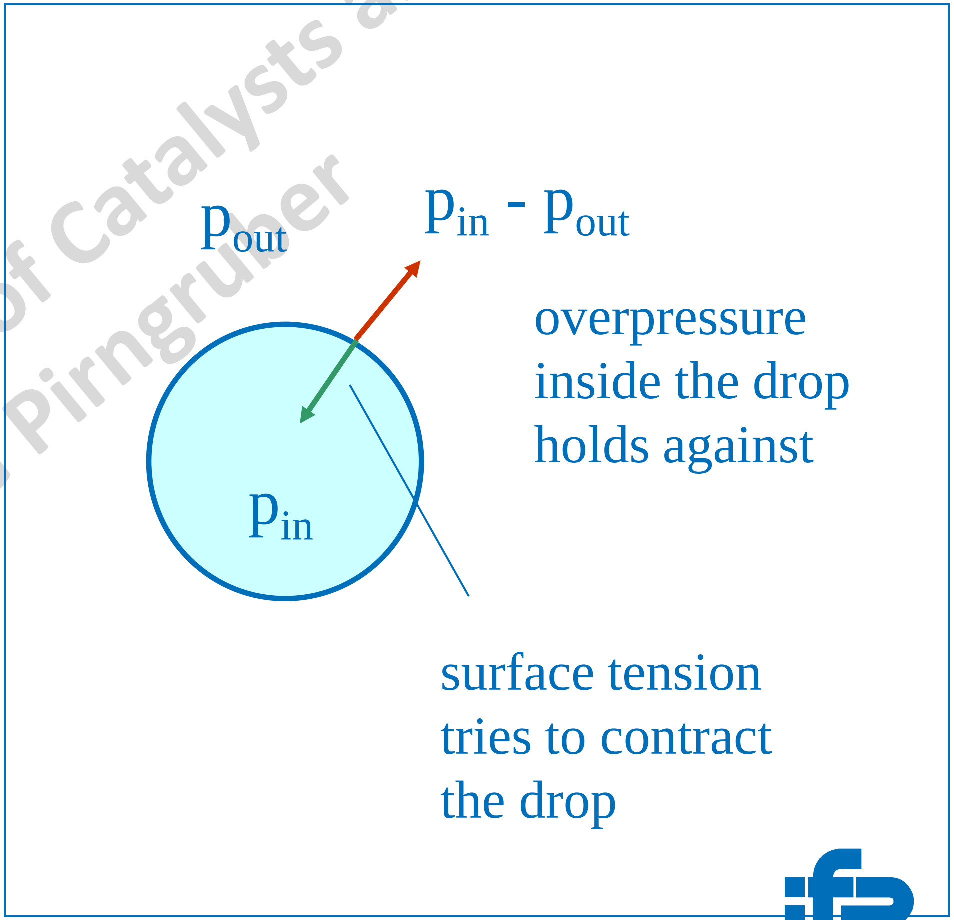
Vapour pressure of a drop of liquid

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

γ = surface tension
r = radius of curvature

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

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



p_{out}

p_{in} - p_{out}

overpressure
inside the drop
holds against

p_{in}

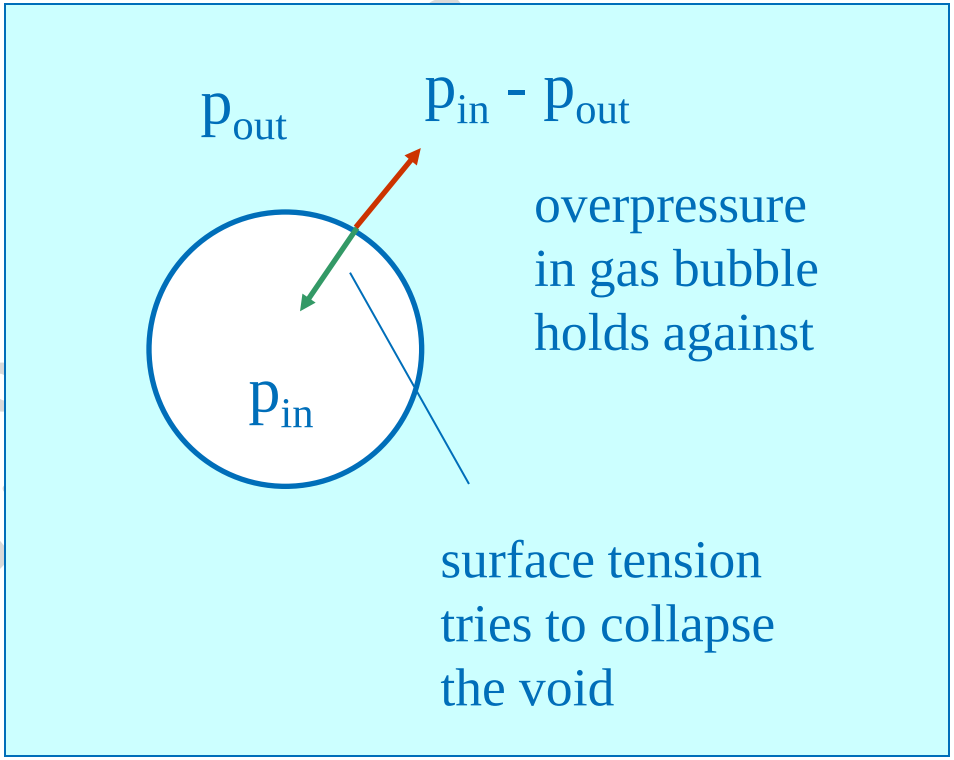
surface tension
tries to contract
the drop

Vapour pressure of a liquid void

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

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

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



overpressure in gas bubble holds against

surface tension tries to collapse the void

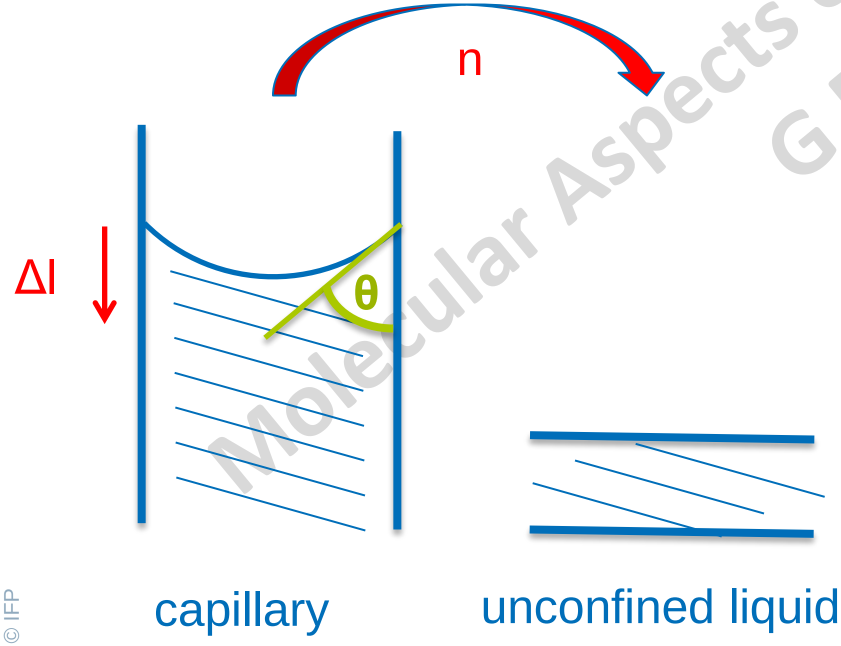
$$p_g = p_{g,0} \cdot \exp(-\frac{2v_l\gamma}{RT \cdot r})$$

Kelvin equation: vapour pressure inside a void is lowered

Kelvin equation

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

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



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.