TEXTURAL ANALYSIS OF CATALYSTS
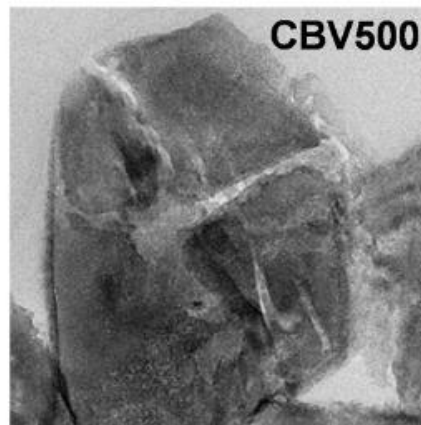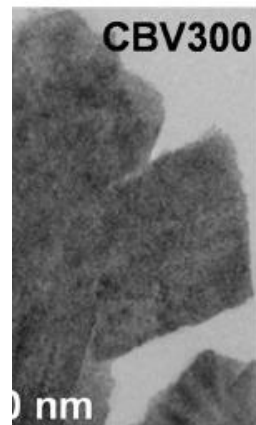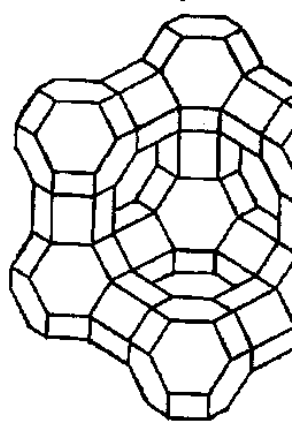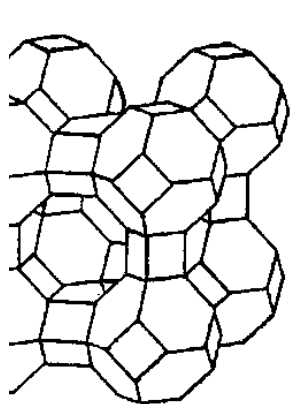## SOUS-TITRE / SUB-TITLE
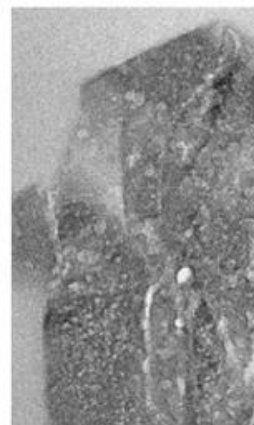
POROUS SOLIDS IN CATALYSIS

- 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.

- Porous cristalline structures
  - Zeolites,
  - Metal Organic Frameworks

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

20 nm
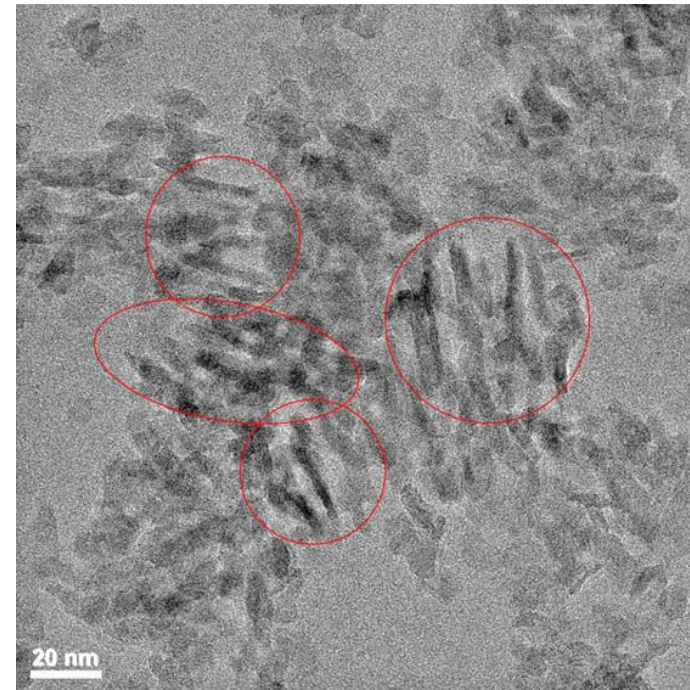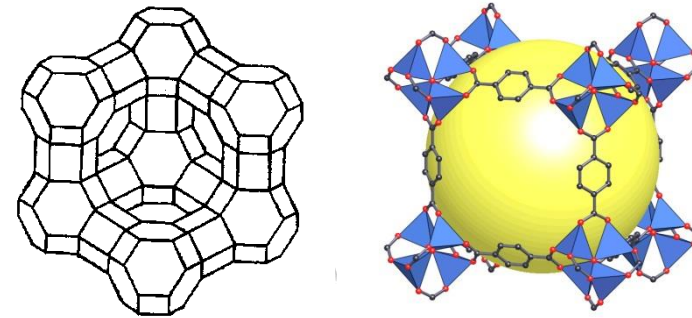
WHAT DO WE WANT TO CHARACTERIZE?

- Surface area: area available for adsorption of reactants
- Pore volume
  - Influence on transport properties
  - Catalyst density => mass of catalyst loaded in the reactor
  - For cristalline solids, comparison with theoretical pore volume gives indication on crystallinity, pore blockage
- Pore size (distribution)
  - Confinement effects
  - Accessibility (with respect to the size of the molecules)
- Connectivity of the pore network
  - Transport properties
  - Accessibility (detect occluded pore volumes)

WHICH METHODS CAN BE USED?

- 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
- NMR methods
  - Cryoporometry: freezing point of H_2O depends on pore size, liquid water measured by NMR
  - Relaxometry: NMR relaxation time depends on pore size, can be measured by specific pulse sequences
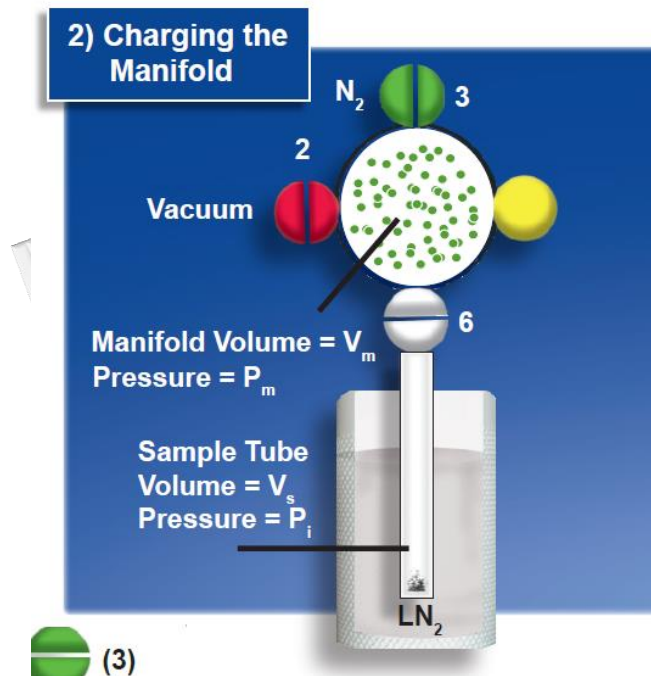
PHYSISORPTION

SOME BASICS

● For the textural characterization of solids, we use the physisorption of inert molecules like N_2 or Ar

● Why use inert molecules instead of CO_2, H_2O, etc?

➤ We want to avoid any specific interactions with the surface, which would depend on its chemical nature.

➤ Only van de Waals interactions between the surface and the adsorbate molecule should be operating.

• Ar is ideal because it is perfectly spherical and non-polar.

• N_2 is not spherical and has an electric quadrupole moment => may have some specific interactions with the surface.

  • Still the most common physisorption probe because of the availability of liquid N_2.
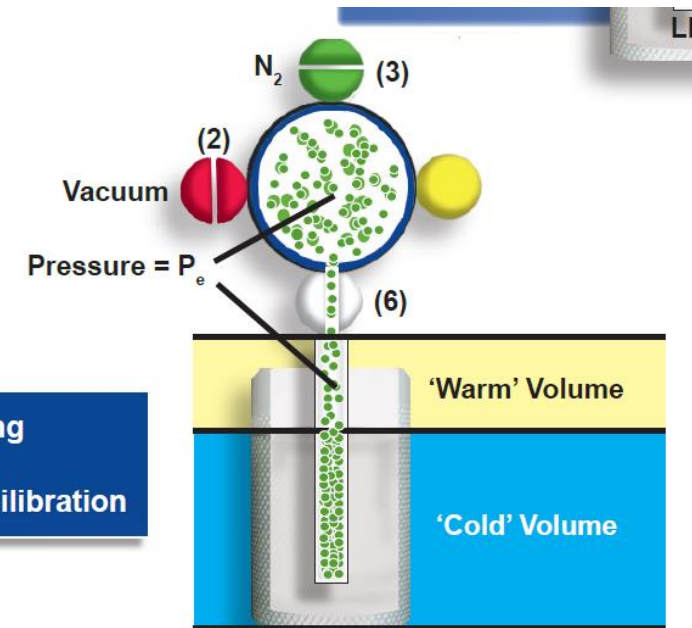
HOW TO MEASURE A PHYSISORPTION ISOTHERM?

- Volumetric method:
  - manifold of known volume is filled with the adsorbate
  - Pressure and temperature is recorded
  - Calculate initial number of gas molecules in manifold by an equation of state

- Expand manifold content into sample tube, allow for equilibration.

- Pressure drops due to expansion and due to adsorption.

- Calibrate expansion effect with a non-adsorbing gas (Helium).

2) Charging the Manifold

N_2 3

2

Vacuum

Manifold Volume = V_m
Pressure = P_m

6

Sample Tube
Volume = V_s
Pressure = P_i

LN_2

(3)

N_2 (3)

(2)

Vacuum

Pressure = P_e

(6)

'Warm' Volume

3) Sample Dosing and Pressure Equilibration

'Cold' Volume

LN_2

Images from www.micromeretics.com

SOME PRACTICAL CONSIDERATIONS

- The sample tube is plunged in liquid N_2. Why?

- At the temperature of liquid nitrogen (77 K), the equilibrium vapor pressure of N_2 is 1 bar.

    - $P_{vap} = P_0 = 1$ bar

- Hence the whole range of thermodynamic potentials can be explored between vacuum and atmospheric pressure.
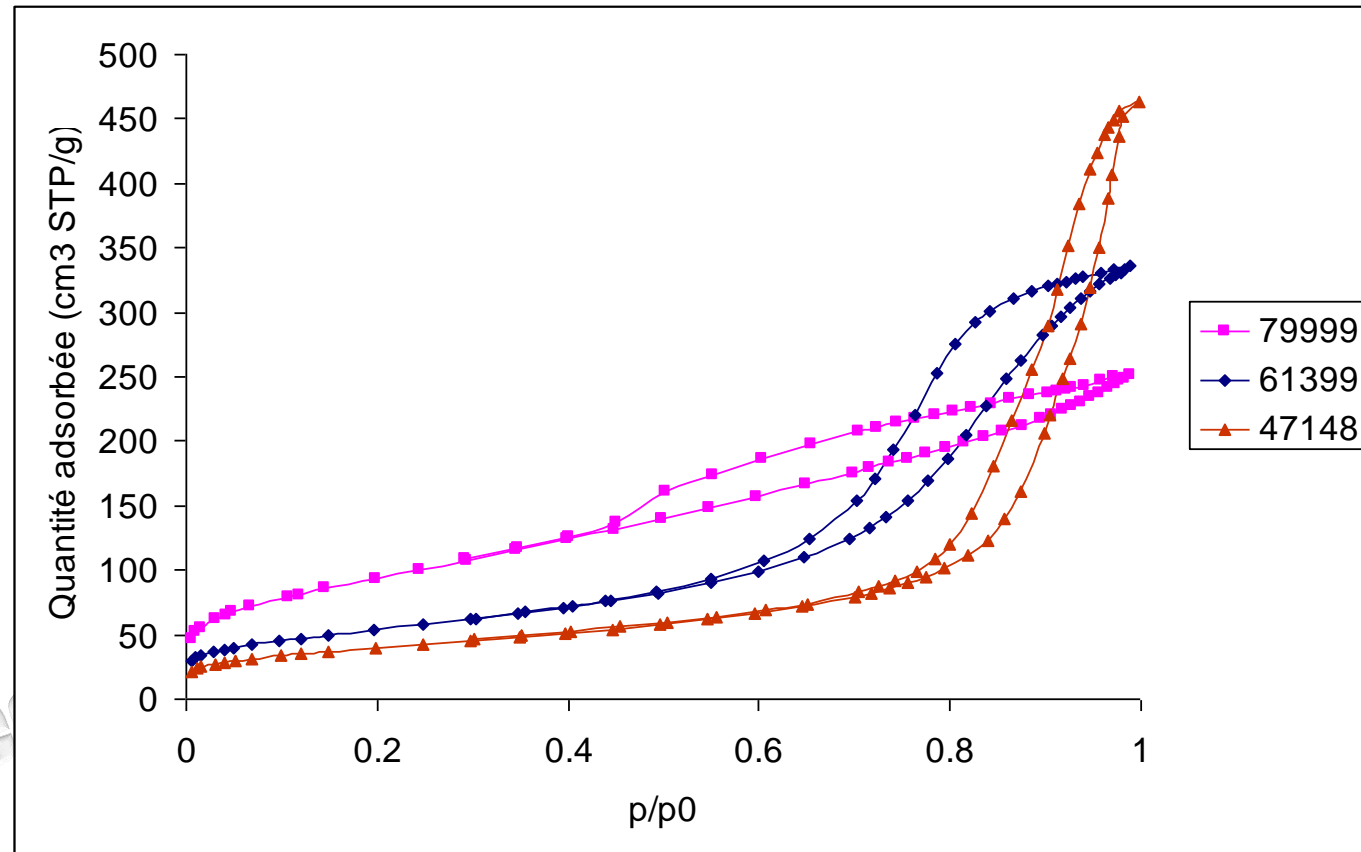
$$\mu = \mu_0 + RT \ln \frac{P}{p_{vap}}$$

- The boiling point of Ar is 87 K. Since liquid Ar is not available, a thermostat is required for measuring the Ar isotherm at 87 K.

HOW TO READ A N2 ADSORPTION ISOTHERM?
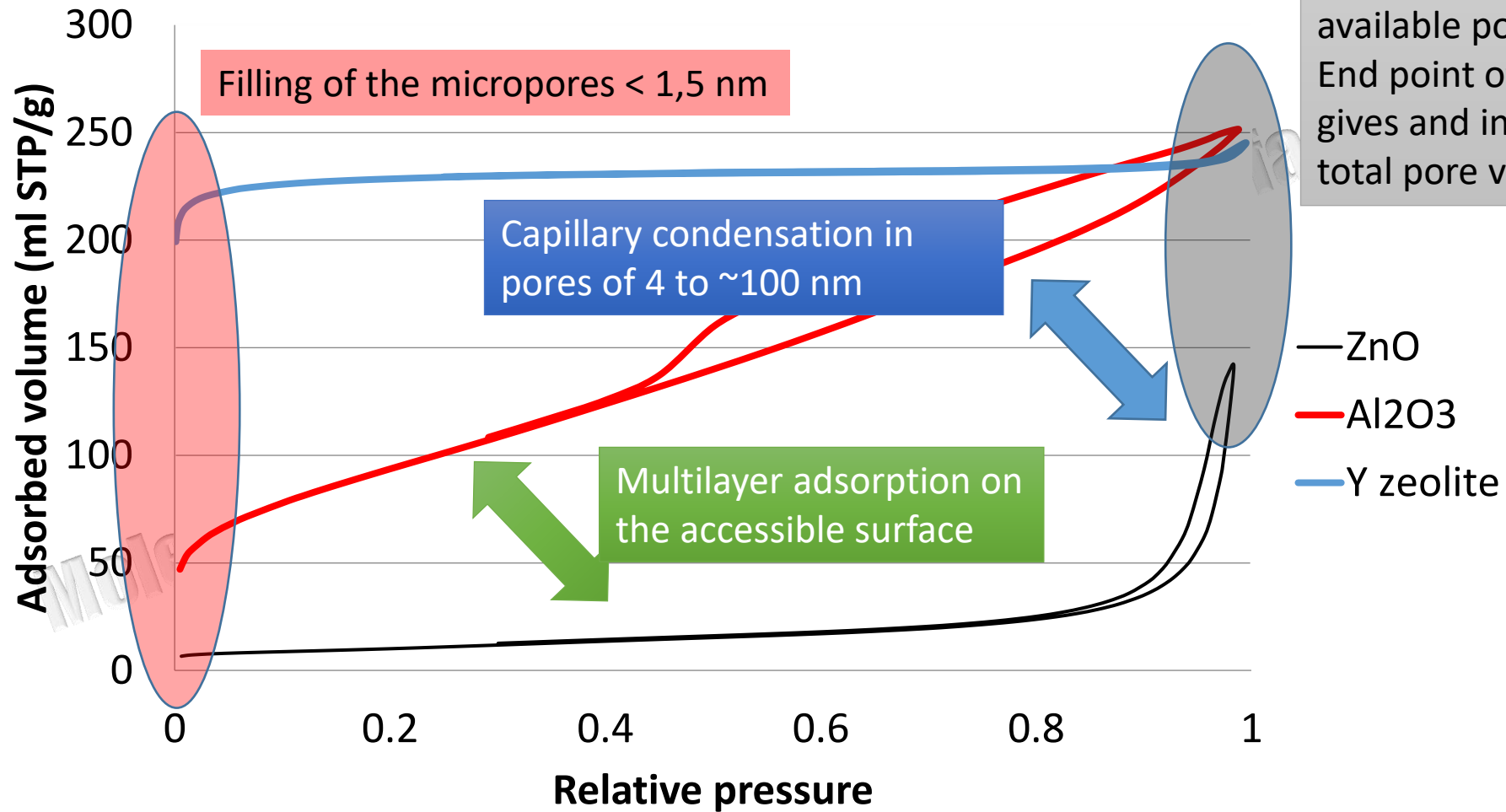
Close to $P/P_0 = 1$, N_2 condenses in the entire available pore volume.
End point of the isotherm gives and indication of the total pore volume.

Filling of the micropores < 1,5 nm

Capillary condensation in pores of 4 to ~100 nm

Multilayer adsorption on the accessible surface

Adsorbed volume (ml STP/g)

300
250
200
150
100
50
0

0   0.2   0.4   0.6   0.8   1

Relative pressure

—ZnO
—Al2O3
—Y zeolite

# QUALITATIVE COMPARISON OF ISOTHERMS

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

QUANTITATIVE TREATMENT OF N_2 ISOTHERMS

- Surface area
  - BET (Brunauer-Emerett-Teller)
  - Langmuir
- Pore volume: V_{micro}, V_{meso}, V_{total}
  - t-plot
- 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

$K_{condensation}$
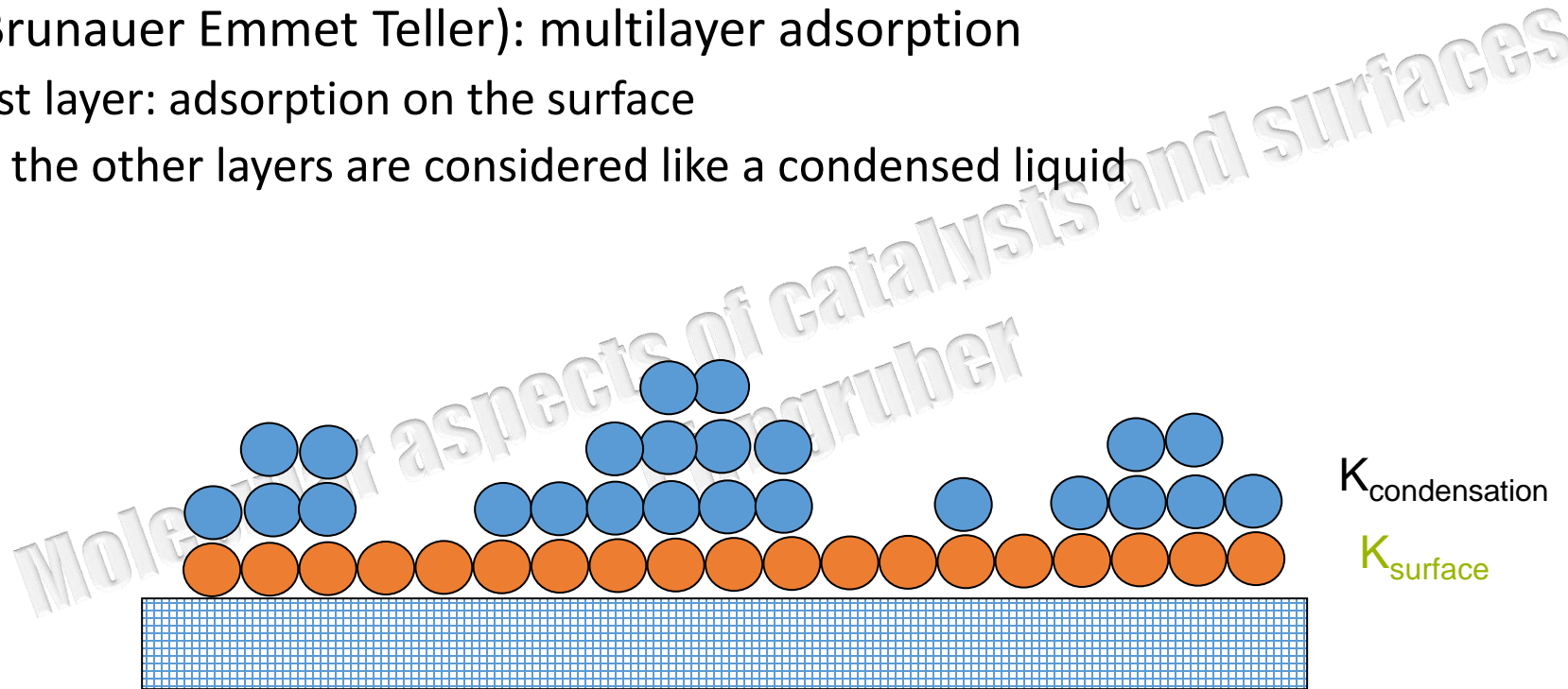
$K_{surface}$

n_m = number of surface adsorption sites (monolayer)
n_{ads} = total number of adsorbed molecules

- BET equation

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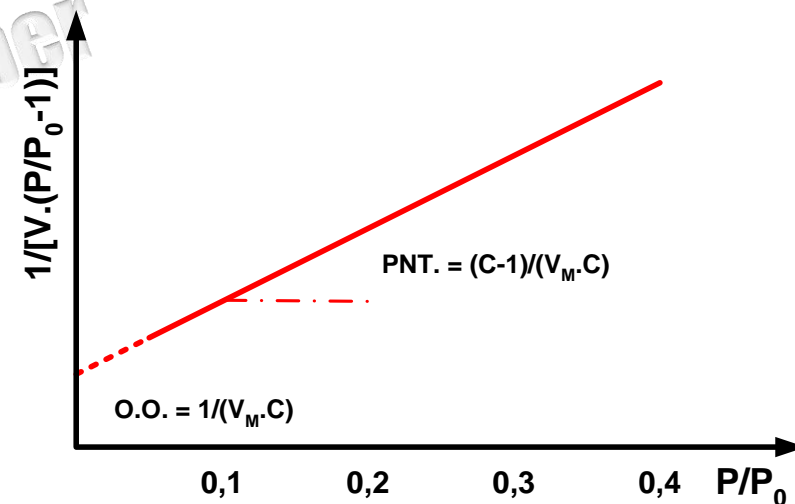
$$C = \frac{K_{surface}}{K_{condensation}}$$

  - 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)
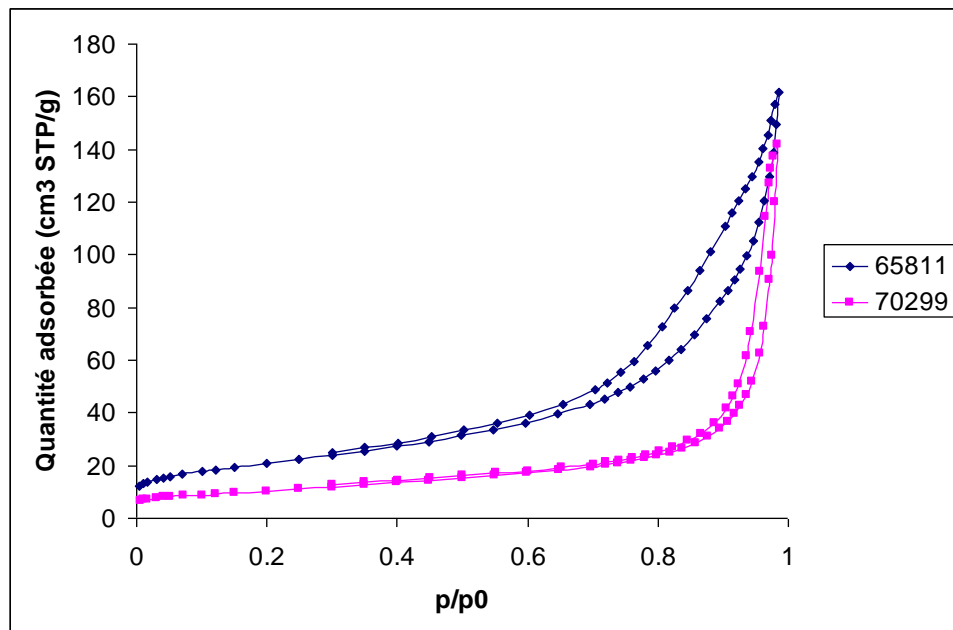
Recommended range of p/p$_0$: 0,05 - 0,35 max.
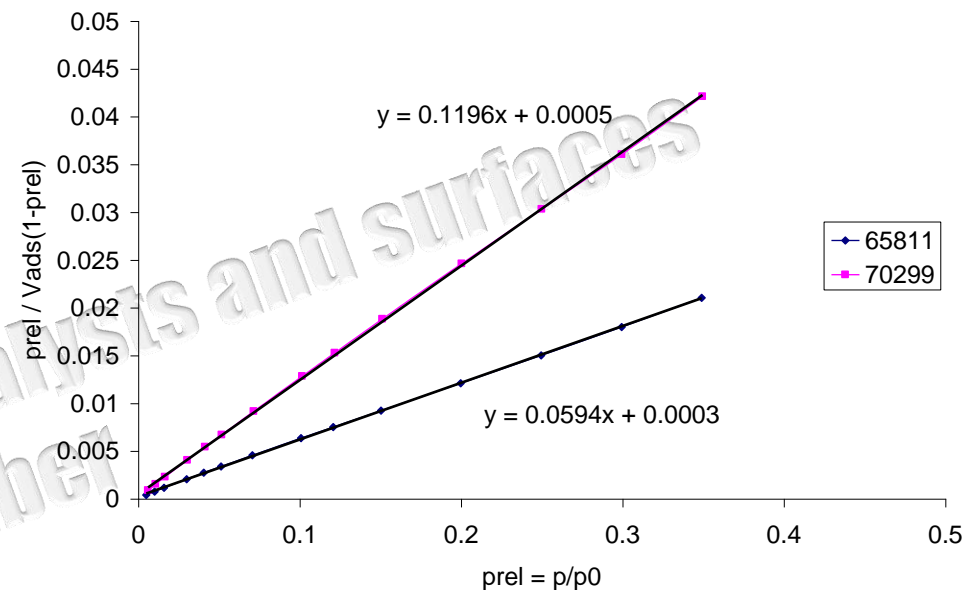

$$S_{BET} = a.\frac{p_0 V_M}{R \cdot 273K}.N_A$$

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

EXAMPLE

Isothermes

BET plot



y = 0.1196x + 0.0005

y = 0.0594x + 0.0003

	S_{BET} (m²/g)	C_{BET}
65811	74	136
70299	36	237

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

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

EXAMPLE ZEOLITE X

- The multilayer adsorption model does not apply well to microporous solids when the pores are filled.
  - To be rigorous avoid using the term surface area, rather speak of BET value.
- 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

NaX

y = 0.0064x - 3E-05
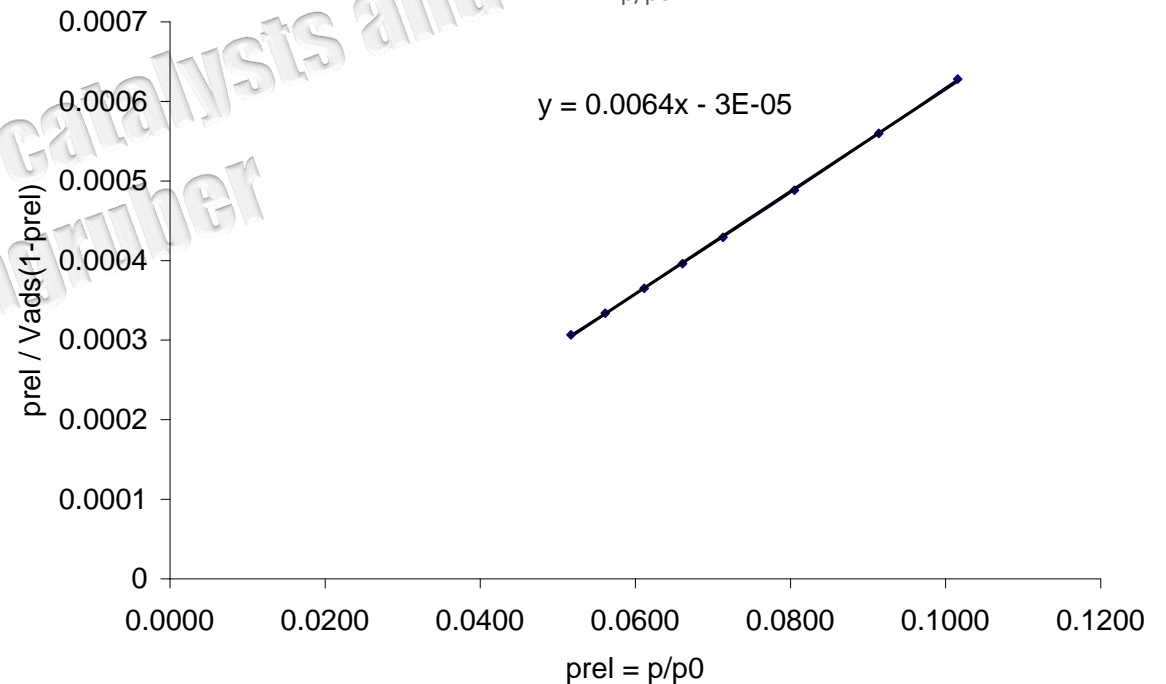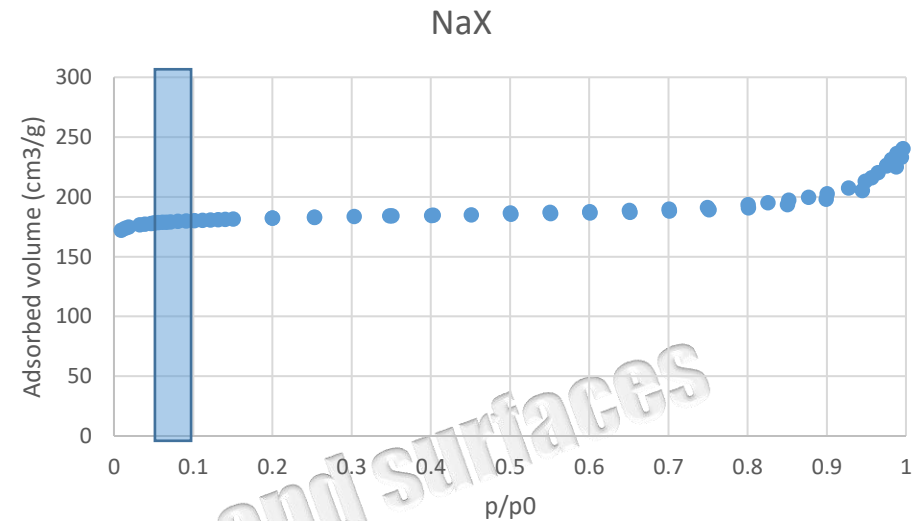
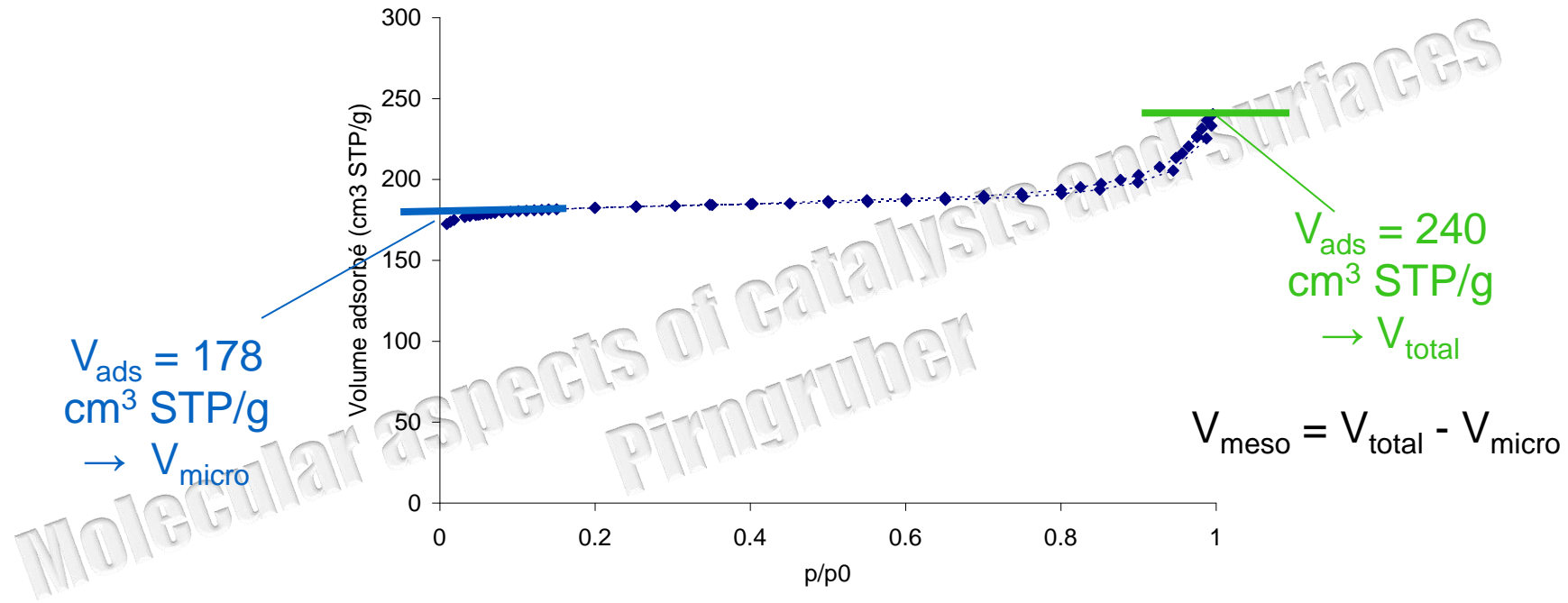$$S_{BET} = \frac{4.355}{0.0064 - 0.00003} = 685 m^2 / g$$

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.

DETERMINATION OF THE PORE VOLUME

● In some cases possible without using any model.

$V_{ads} = 178$ cm^3 STP/g
$\rightarrow V_{micro}$

$V_{ads} = 240$ cm^3 STP/g
$\rightarrow V_{total}$

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

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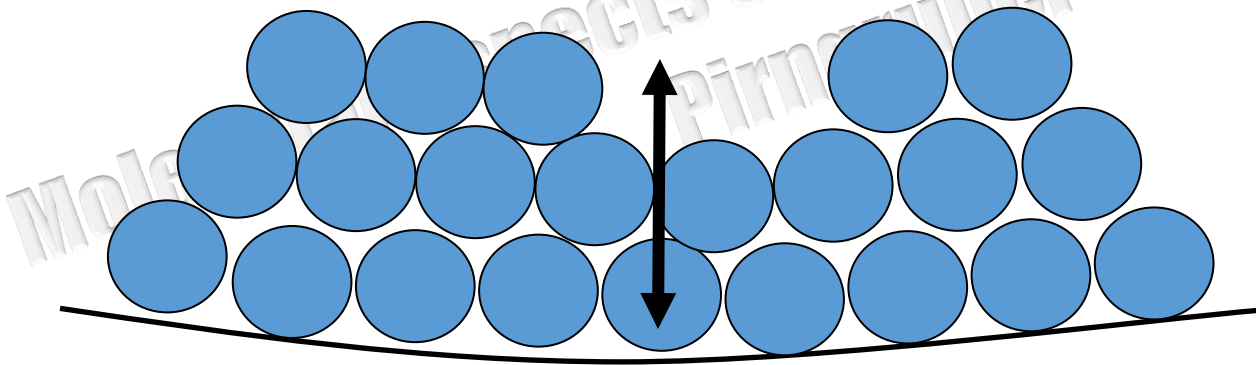
$$n_{ads} = \frac{V_{ads} p}{RT}$$

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

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

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 $p/p_0 = 0.1 - 0.8$

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

Harkins
Jura

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

Halsey

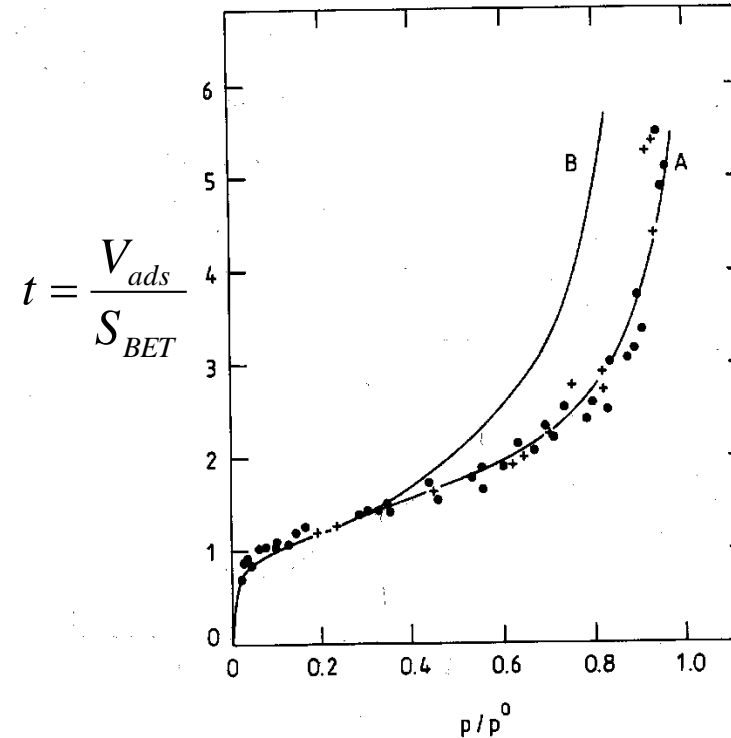$$t = 3{,}54 \left[\frac{5}{\ln\left(\dfrac{P_0}{P}\right)}\right]^{1/3}$$

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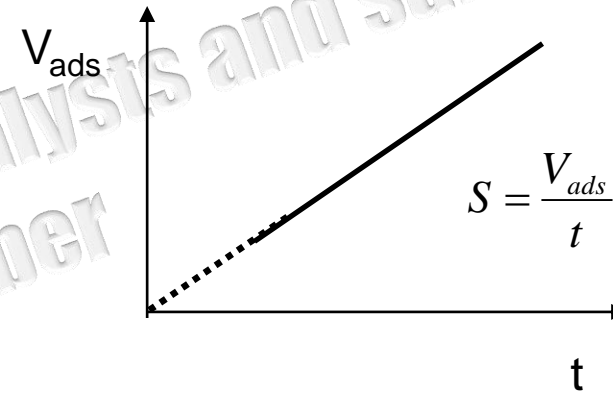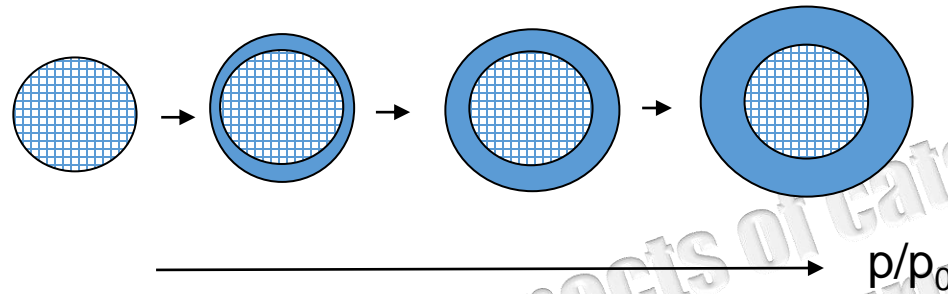
$$t = \left(\frac{13.99}{-\log \dfrac{p}{p_0} + 0.034} \right)^{1/2}$$

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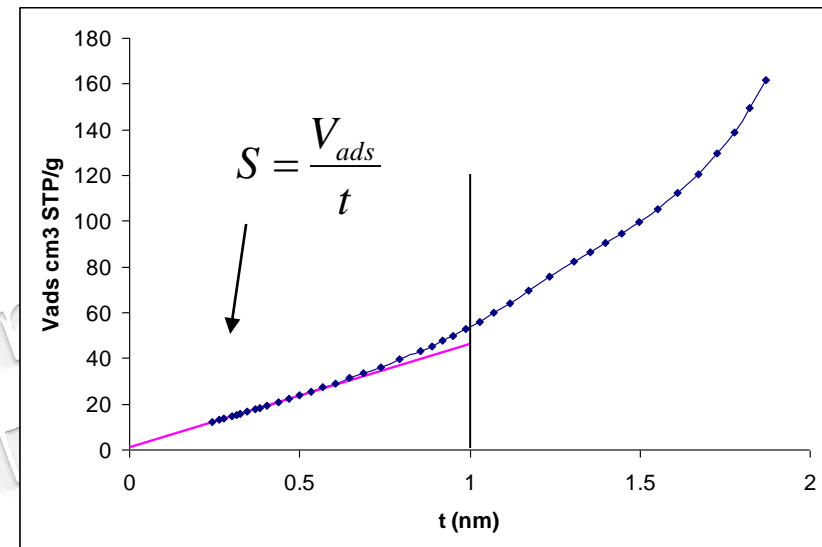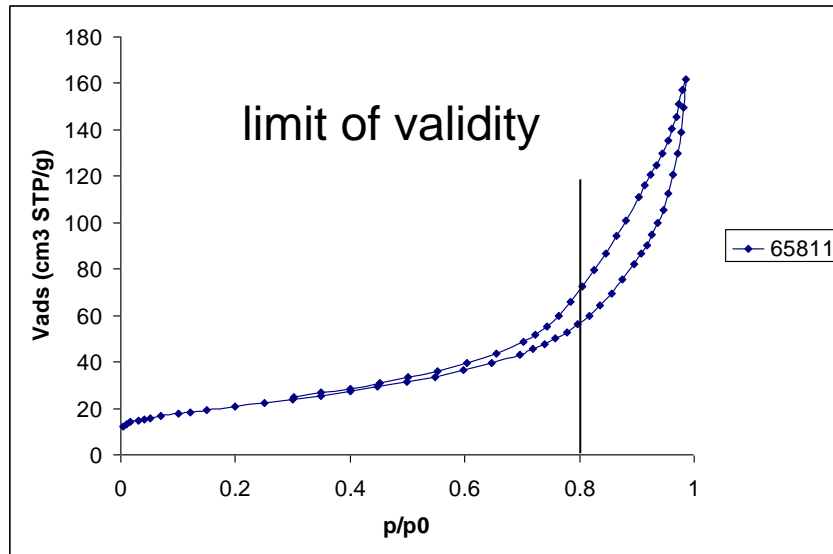
t = thickness that the adsorbed phase would have on a non-porous material

- Adsorption on a non-porous solid

$$S = \frac{V_{ads}}{t}$$

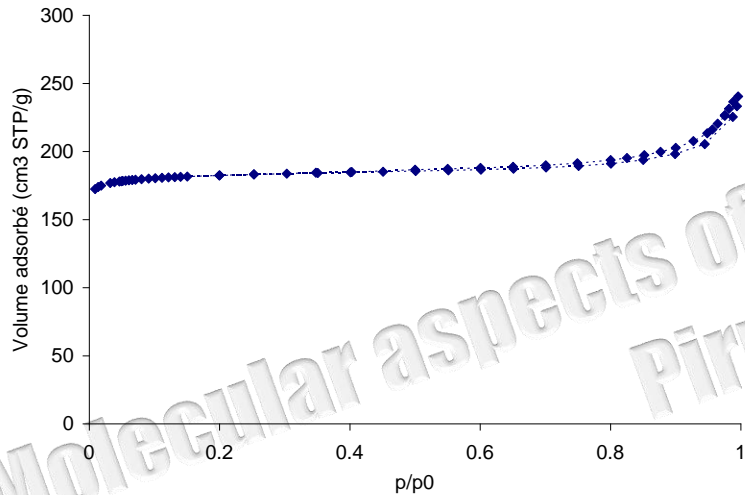- Adsorption on a microporous solid
  - micropores rapidly filled
  - then adsorption on external surface

$$S = \frac{V_{ads}}{t}$$

Isotherm

t-plot

limit of validity
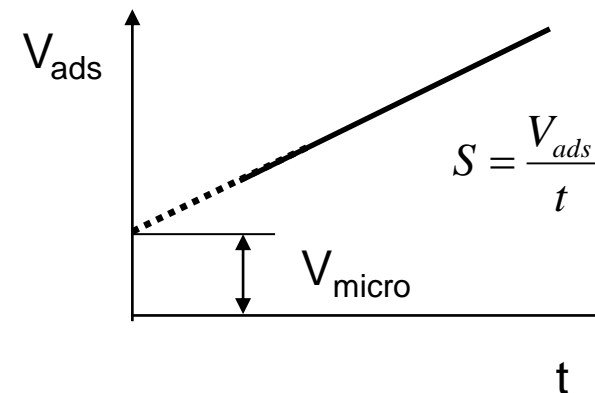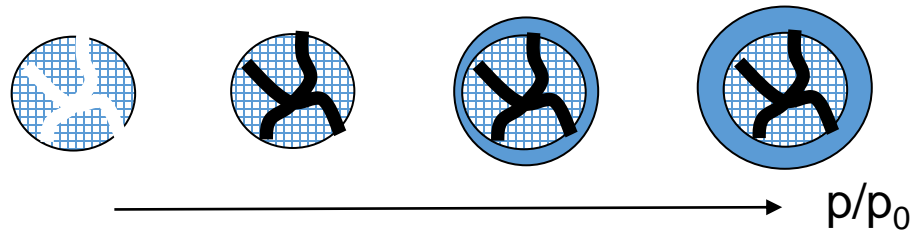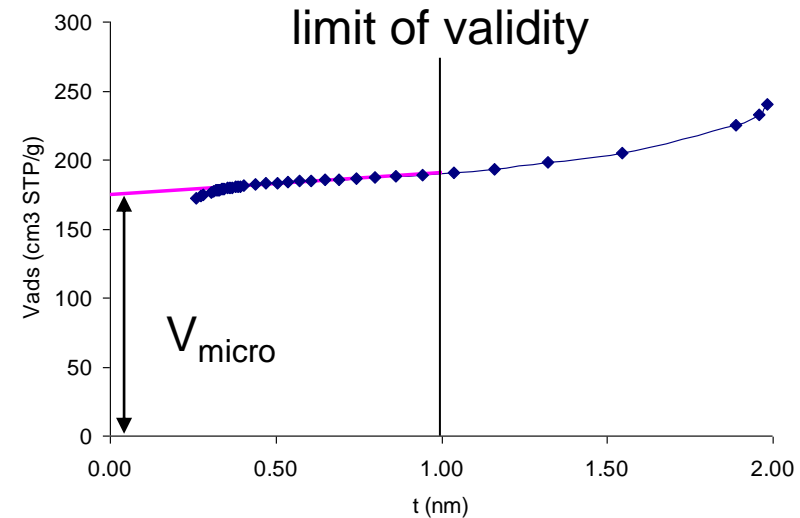
V_{micro}

- V_{micro} = 175 cm³ STP/g = 0.271 ml/g
- Slope of the t-plot can be used to calculate the external surface area of the crystals.

$$S_{t-plot}(m^2 g^{-1}) = 1.5468 \cdot Slope(cm^3 g^{-1} nm^{-1})$$
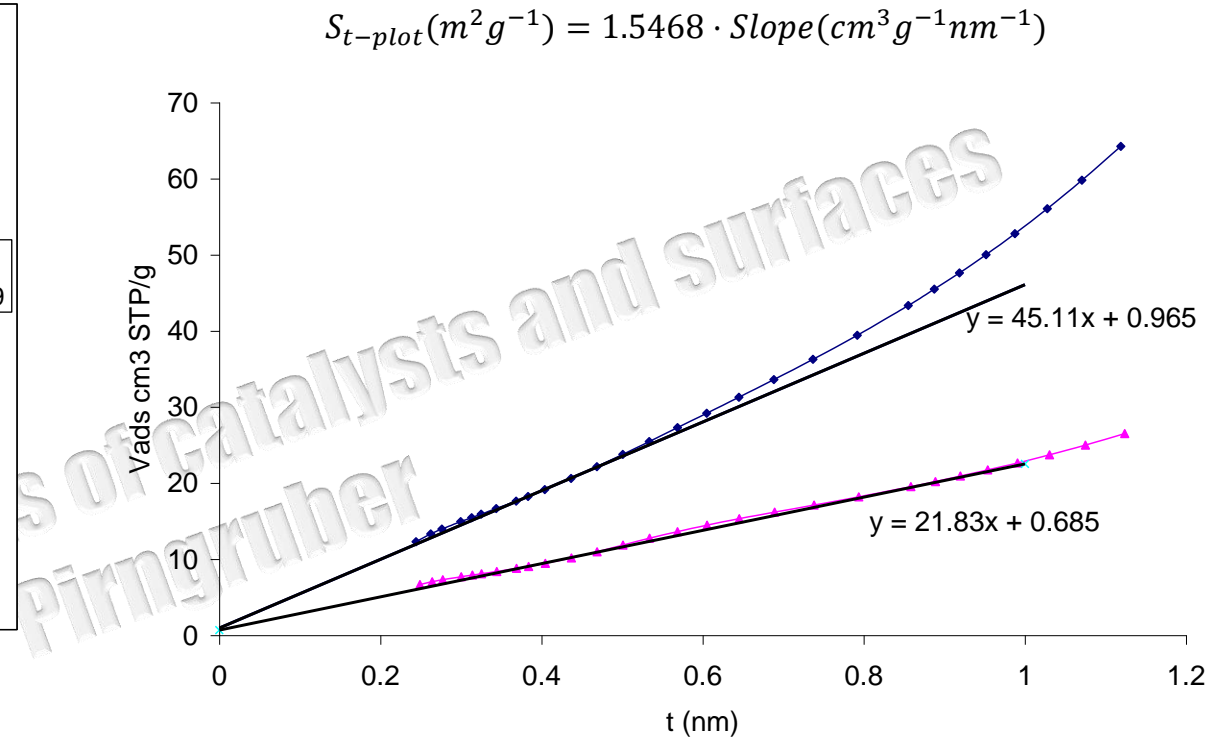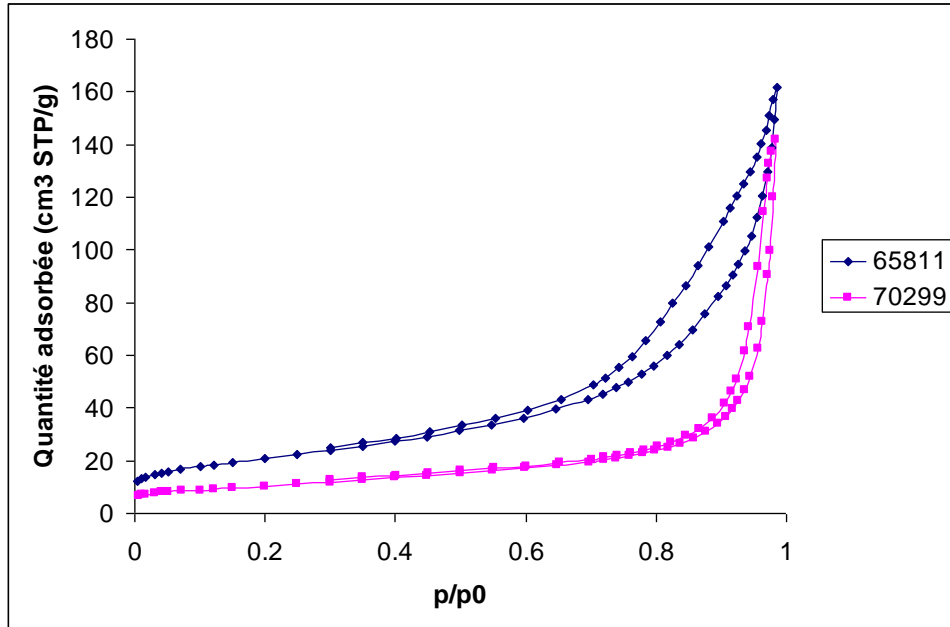
- Values in good agreement with BET method.
- Validates the t-plot approach.

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

Solide non poreux : Adsorption sur Surface Externe   -   Courbe t = t(P/P$_0$)

← - - - - - - - - - - - - - - - -   Pressions relatives P/P$_0$ croissantes   - - - - - - - - - - - - →

µP   mP
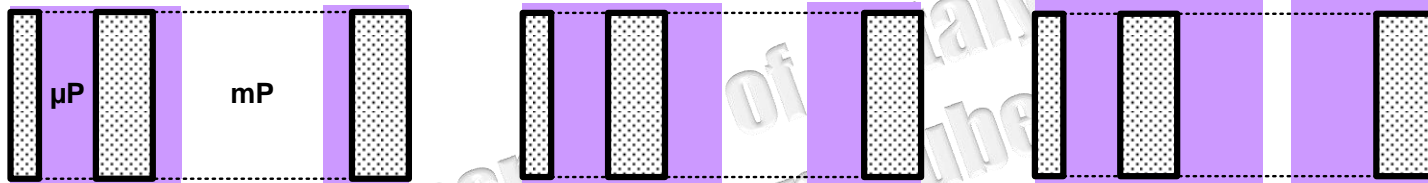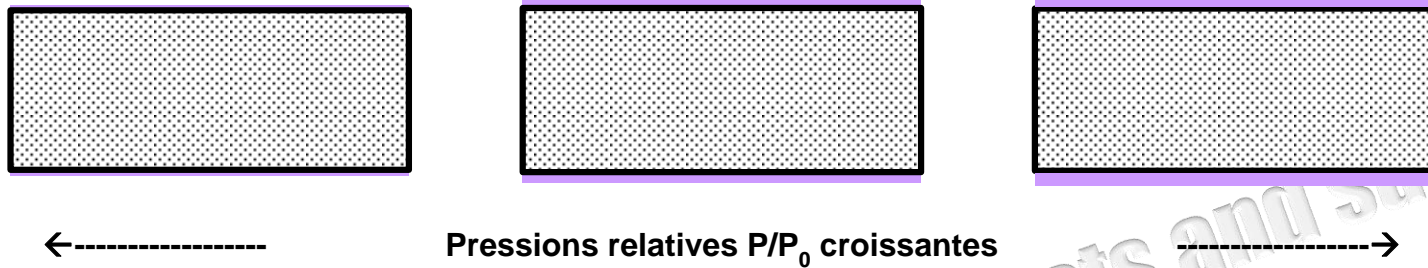
Solide poreux : Adsorption sur Surfaces Interne & Externe

Solide Non Poreux

Vol. Ads.

Adsorption sur Surface Externe

Epaisseur t

Solide µ et m-Poreux

Vol. Ads.

Adsorption sur Surface Externe

$V_{µP}+V_{mP}$

$V_{µP}$

Adsorption sur Surface Interne (mésopores) => S$_{B.E.T.}$

Epaisseur t
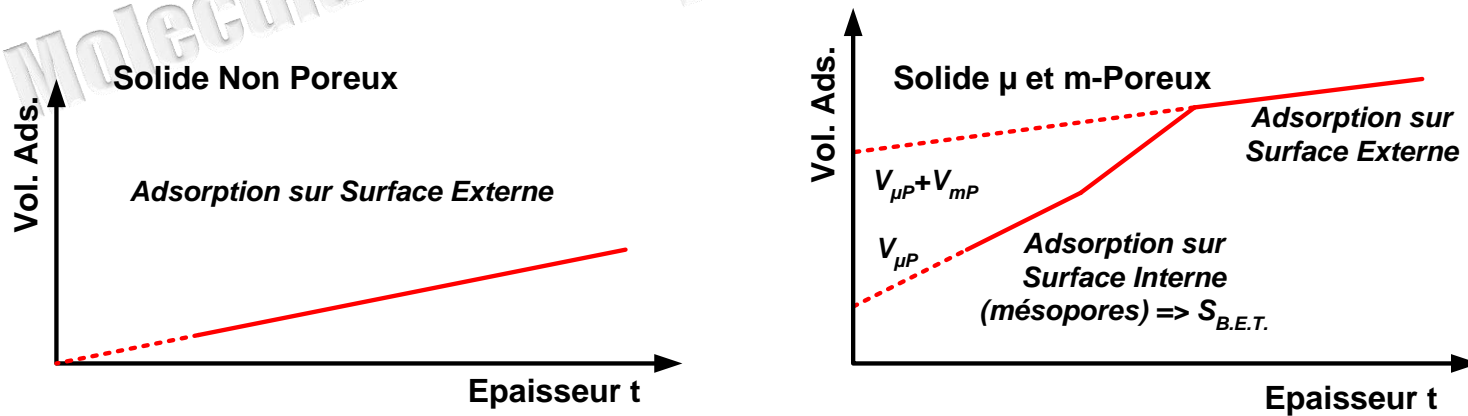
T-PLOT OF MICRO/MESOPOROUS ZEOLITES

- Dealuminated USY zeolites

  - Intercept gives micropore volume
  - Slope gives surface area of mesopores
  - Results may be ambiguous and depend on the pressure range chosen for linearisation
  - Fundamental problem is that micropore filling and multilayer adsorption cannot be strictly separated.
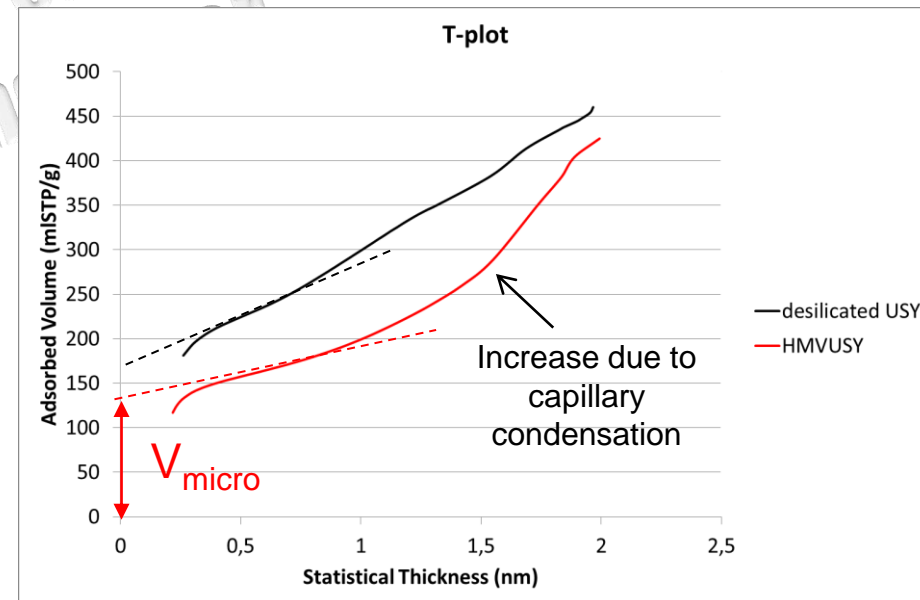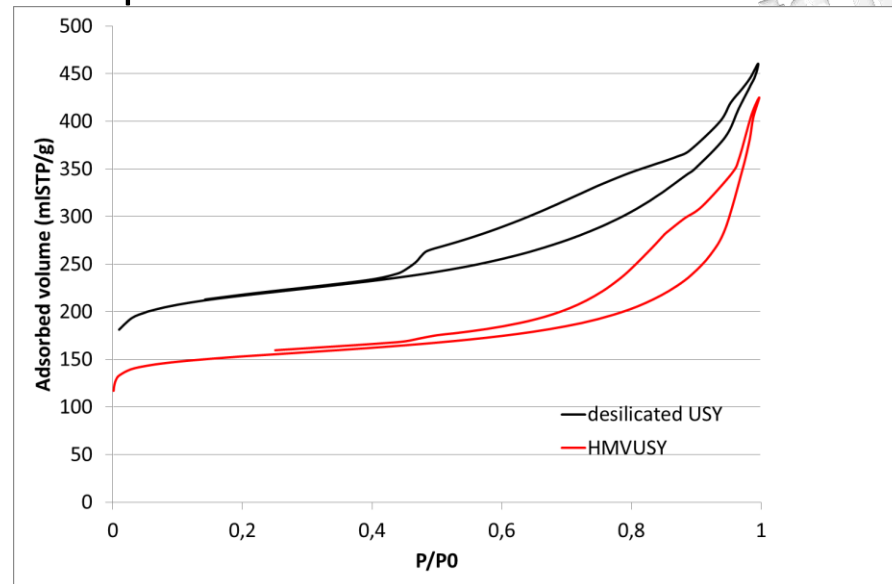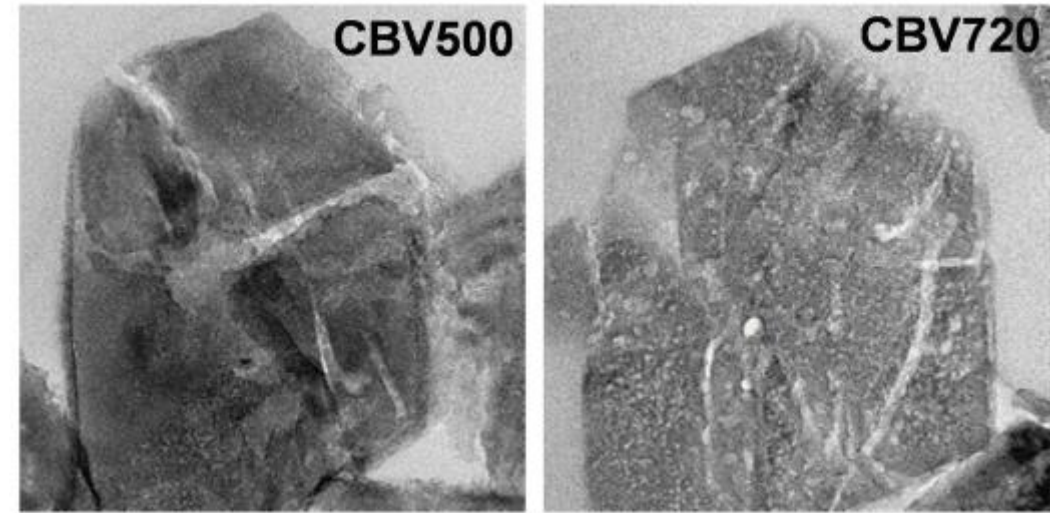
AVERAGE PORE SIZE

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

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

  - Spherical pore :

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

  - Slit pore :

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

MICROPORE SIZE DISTRIBUTION

- Based on the relation between adsorption strength and the ratio between adsorbate size and pore size
  - condition: adsorption 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 !

- van der Waals forces
    - amplified by multiple interactions with atoms or pore wall (i)

$$U_{LJ} = 4\varepsilon \cdot \left(\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^{6} \right)$$
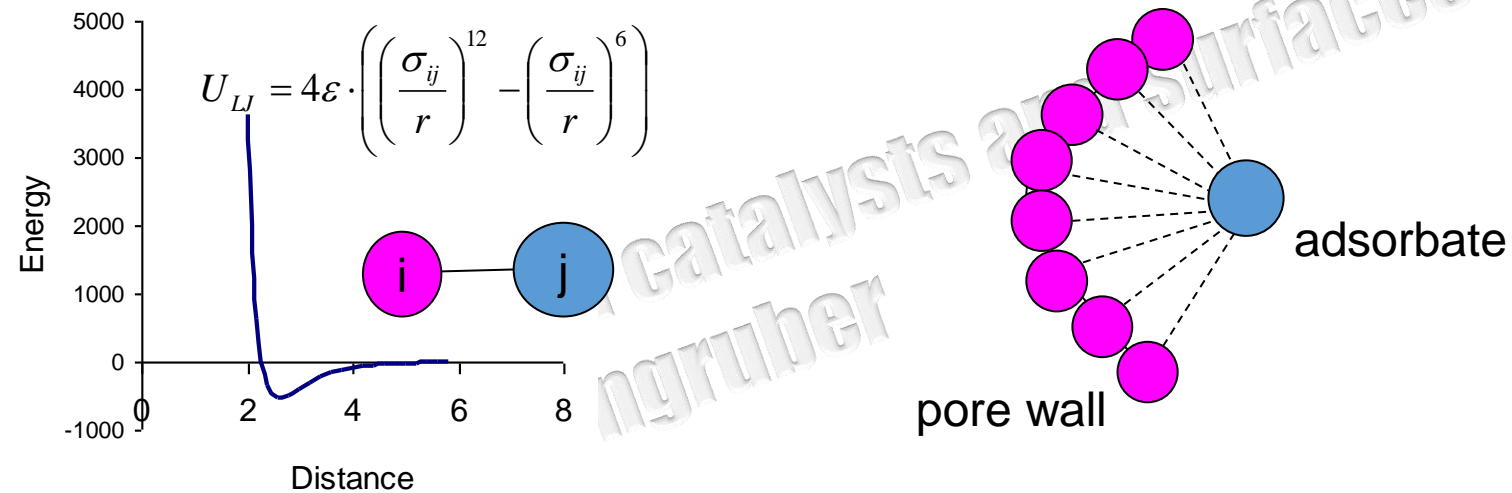
    - maximal when size of adsobate (j) close to pore size
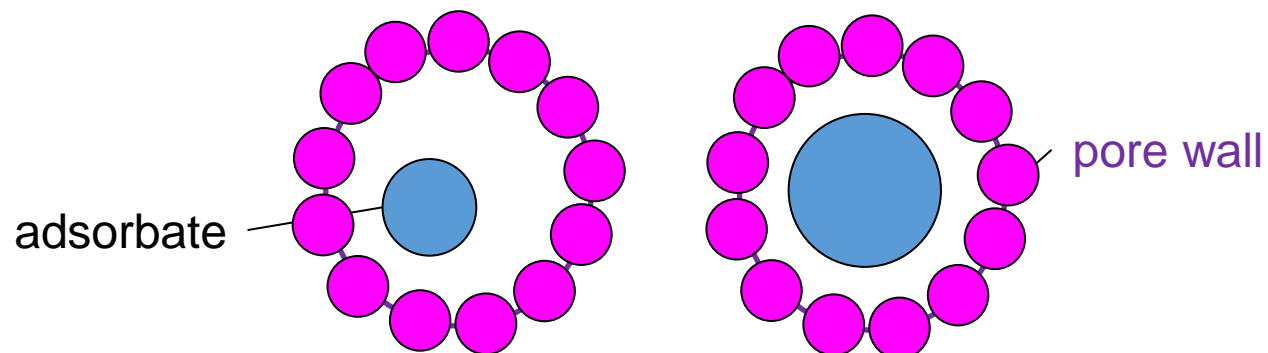
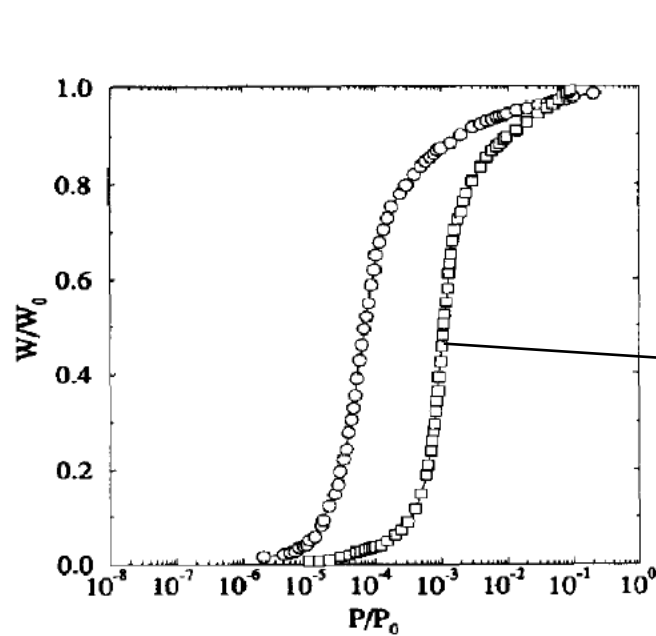# EXAMPLE OF MICROPORE SIZE DISTRIBUTION

Spherical pore model: 1,3 nm

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.

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

Slit pore model: 0,8 nm

- Importance of geometry!
- Improved model assumes Langmuir isotherm instead of linear isotherm.
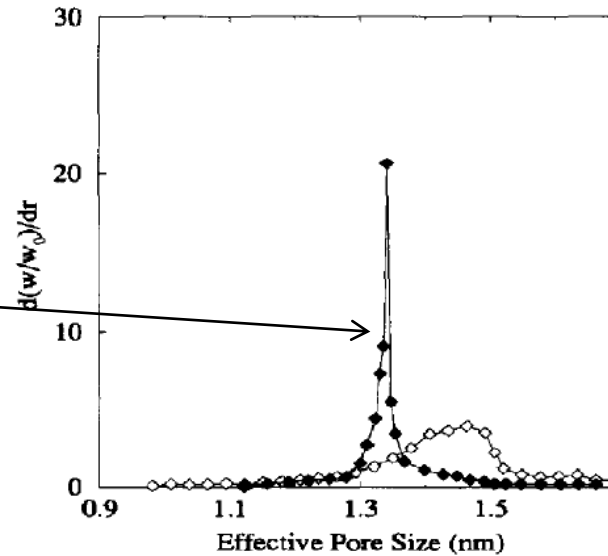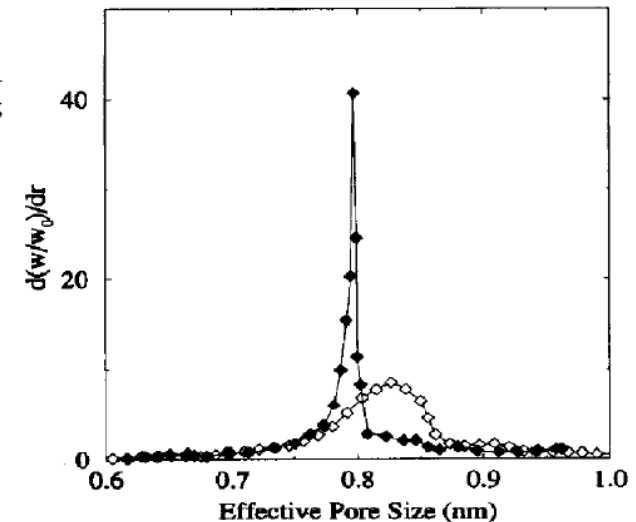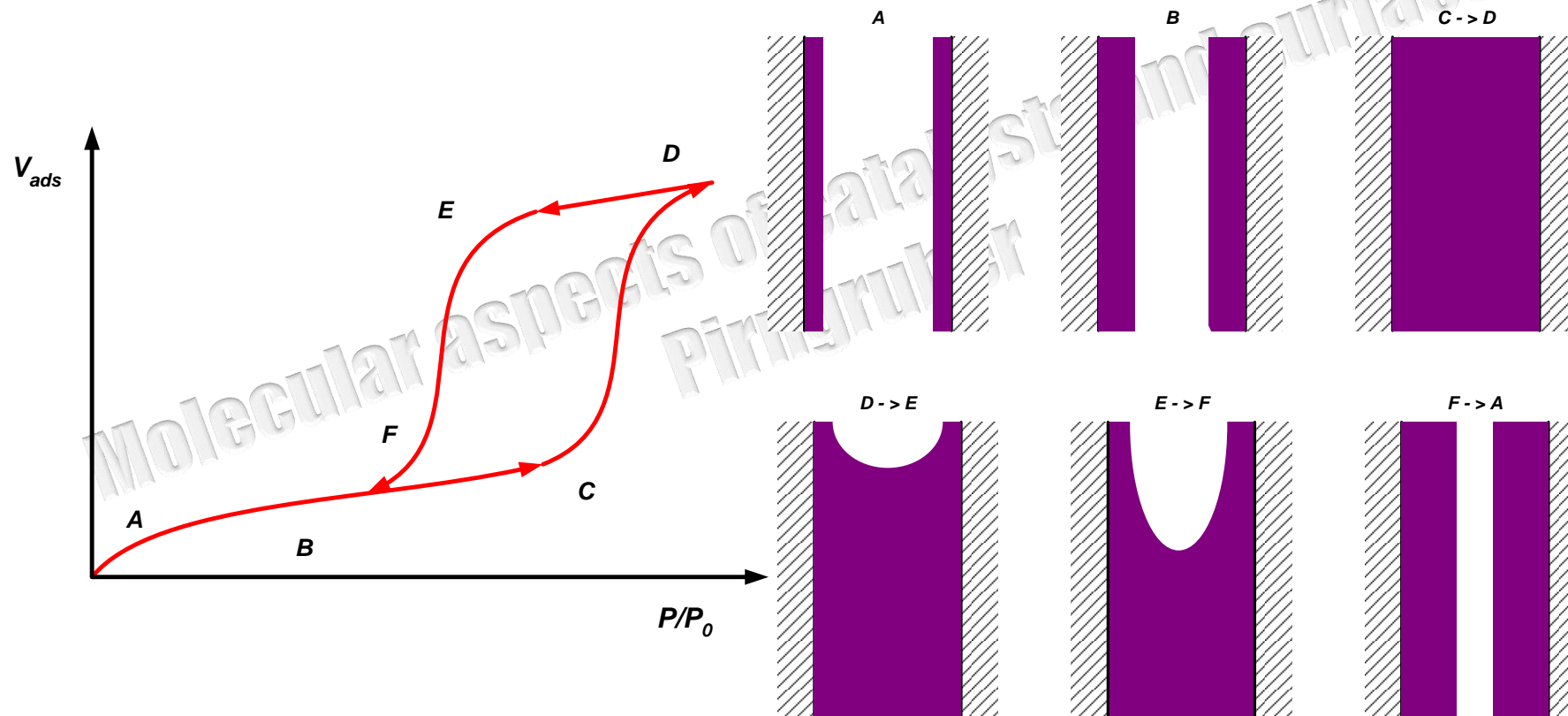
Cheng, Yang, Chem. Eng. Sci. 1994, 49, 2599.

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

- via the theory of capillary condensation

- 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.

pressure difference Δp
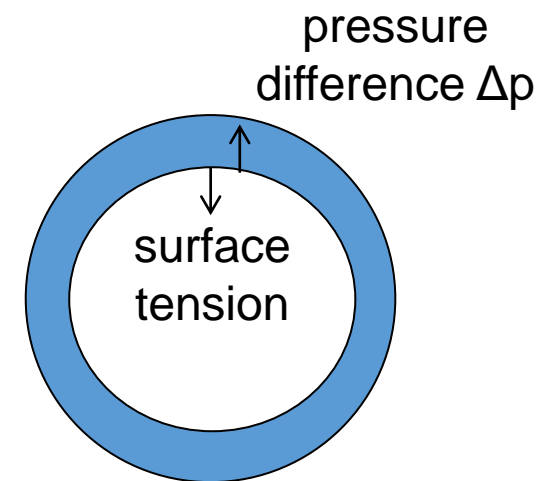
surface tension

- Mathematic formalism
  - Work against interfacial tension = change in free enthalpy

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

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

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

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

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

$$RT \ln \frac{p_{cap}}{p_{sat}} = -\frac{dA}{dV_{cap,g}} V_m \gamma$$
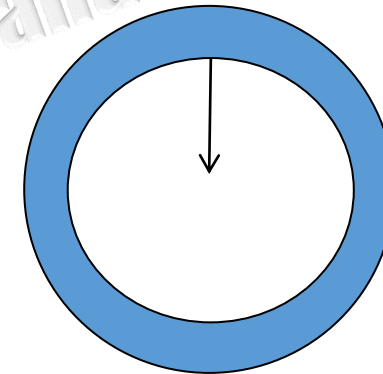
$$\mu_{capliq} = \mu_0 + RT \ln \frac{p_{cap}}{p_0}$$

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

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

- 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.

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

$2r_p$

$2(r_p - t)$

$p \uparrow$

$p \uparrow$
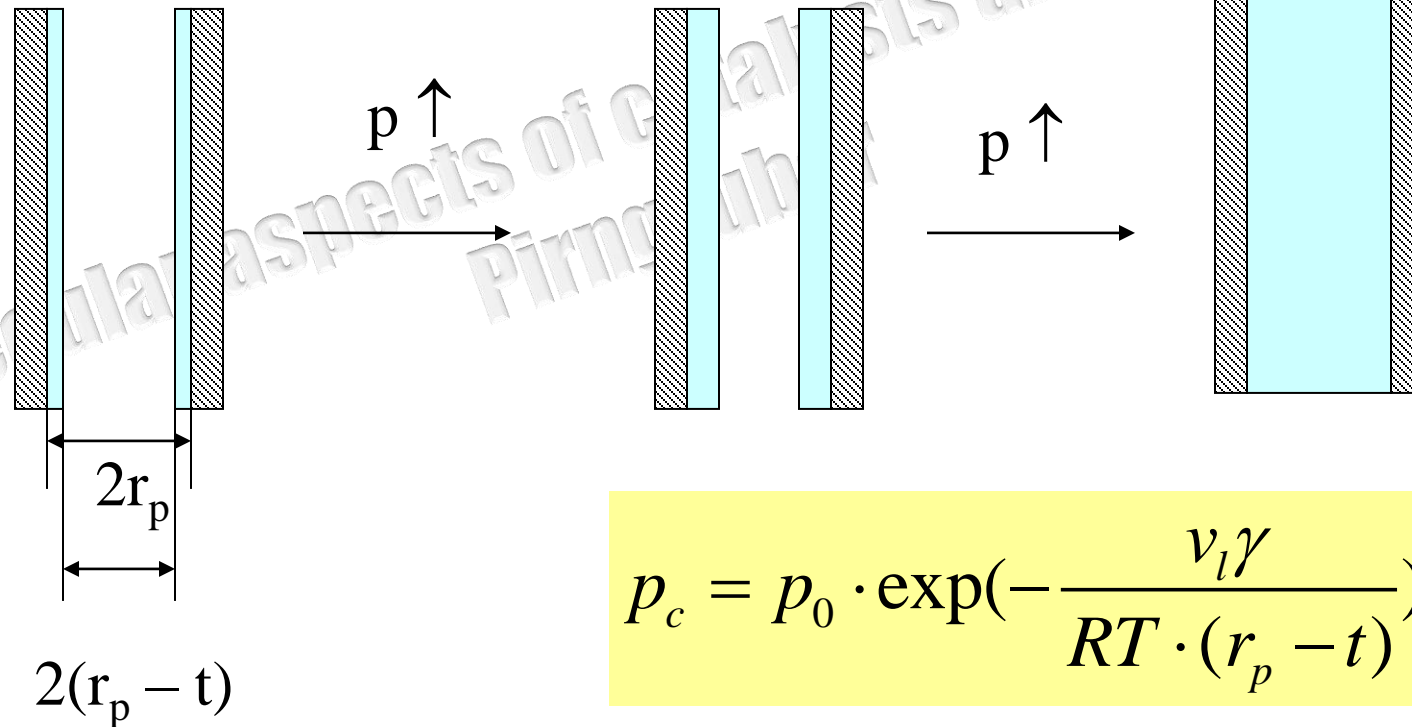
USE OF KELVIN EQUATION FOR PORE SIZE DISTRIBUTION ANALYSIS – BJH MODEL

p_4 – capillary condensation in largest pore
all pores filled
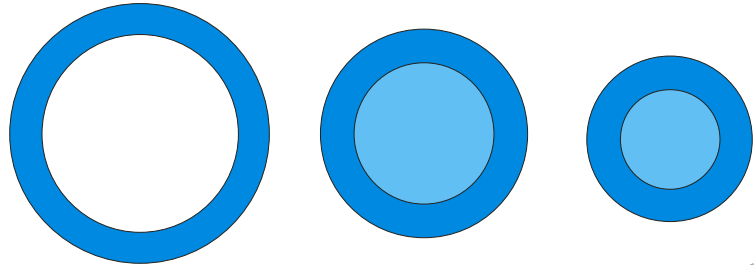
p_3 – capillary condensation in 2nd largest pore
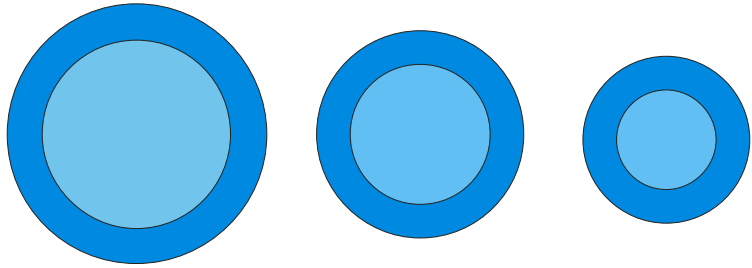increase of layer thickness in largest pore
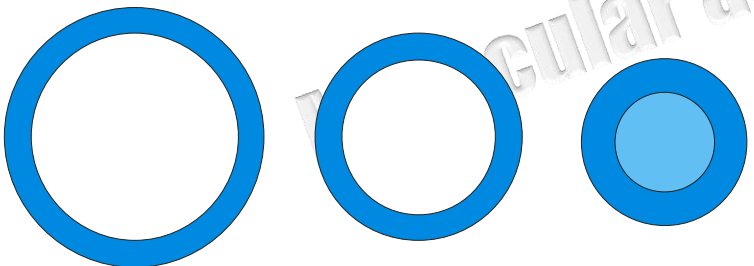
p_2 – capillary condensation in smallest pore
increase of layer thickness in open pores
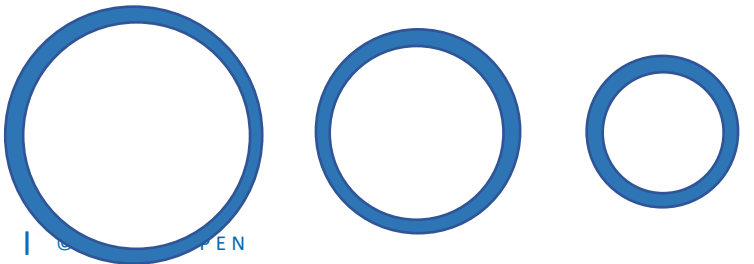
p_1 – all pores empty,
t-layer adsorbed on the pore surfaces

- Pores are filled by capillary condensation according to their pore size

- In parallel multilayer adsorption continues in the open pores

MATHEMATIC DESCRIPTION - BJH

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

$$\Delta V = \frac{(r_k + \Delta t)^2}{r_p^2} \cdot V_p$$
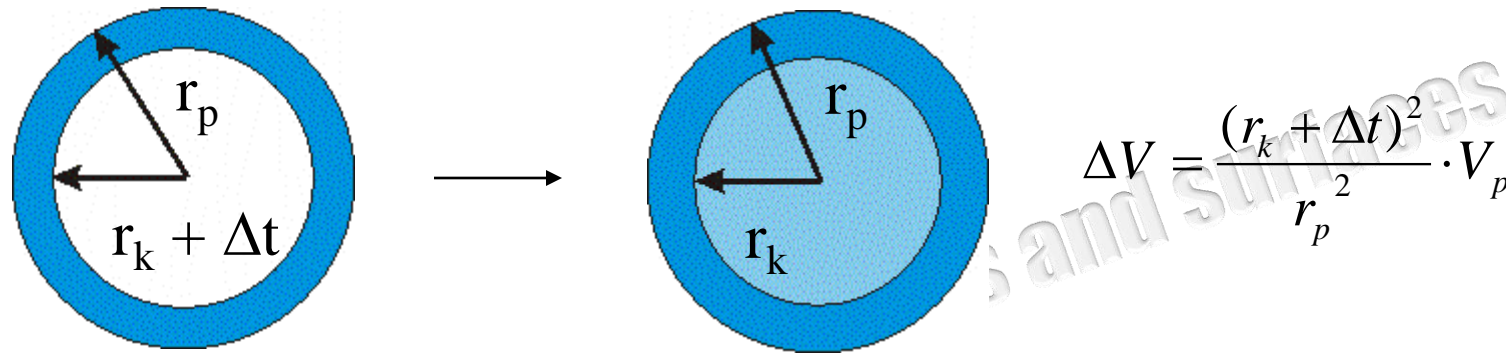
- In each pressure step $p_{n-1} \rightarrow p_n$, capillary condensation occurs from a pore of size r_{pn}

- 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.

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

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

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

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

capillary evaporation   correction term

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

$\rightarrow$ A plot of pore volume vs. pore radius is obtained.

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

$$\log \frac{p}{p_0} = \frac{-4.14}{r_k}$$
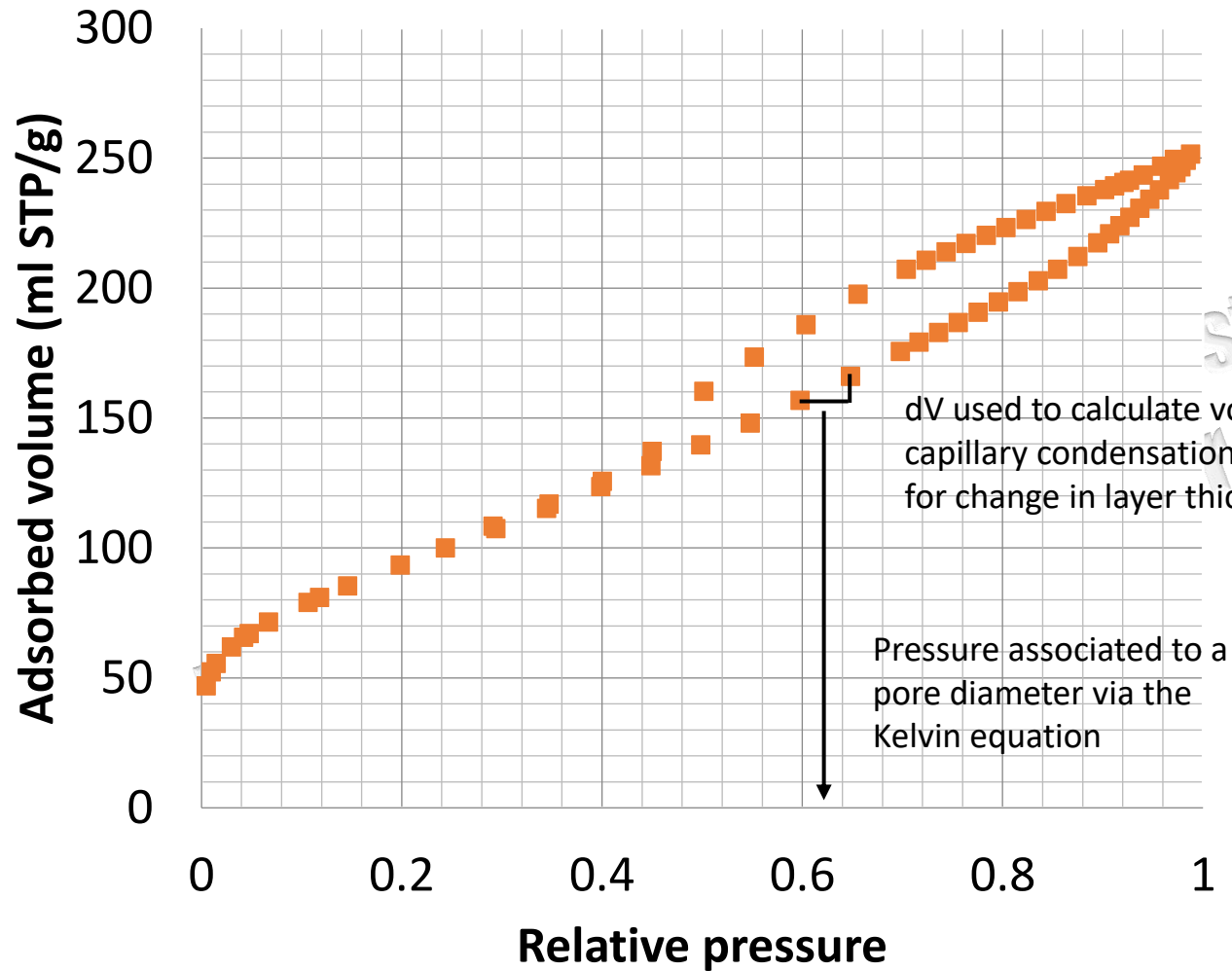
Method used to construct a plot of dV/dD as a function of the pore radius D

dV used to calculate volume in which capillary condensation occurs (after correction for change in layer thickness)

Pressure associated to a pore diameter via the Kelvin equation

- Capillary condensation usually associated with hysteresis between adsorption and desorption.

- For given pressure, two states of the pore are possible : filled or empty.

- One of these states must be metastable.

Type H1

capillary evaporation

capillary condensation

State with high density of the Adsorbed phase

State with low density of the Adsorbed phase

Vol_{ads} (cm3/g)

p/p_0
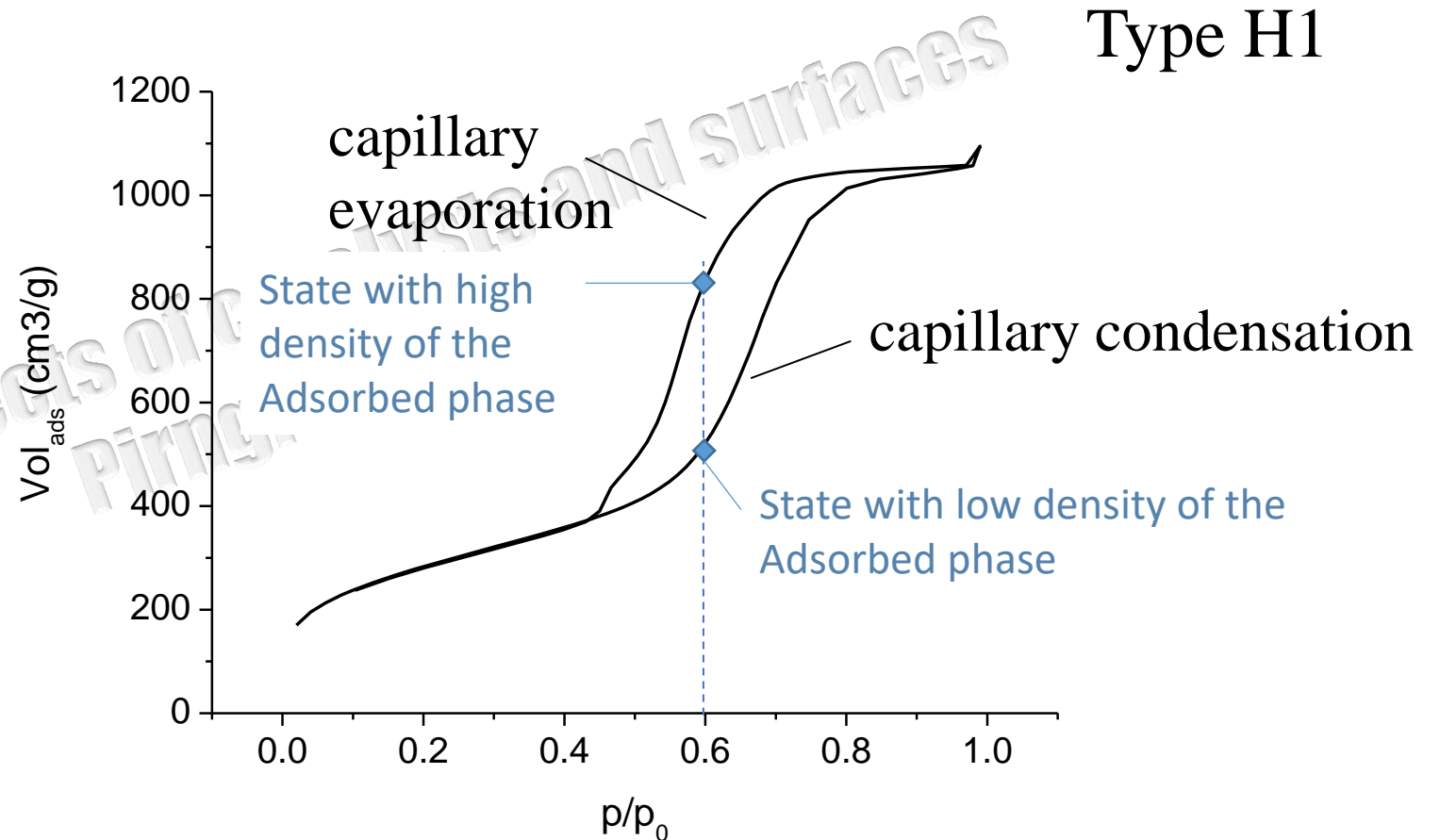
HYSTERESIS AND METASTABILITY

Adsorption branch
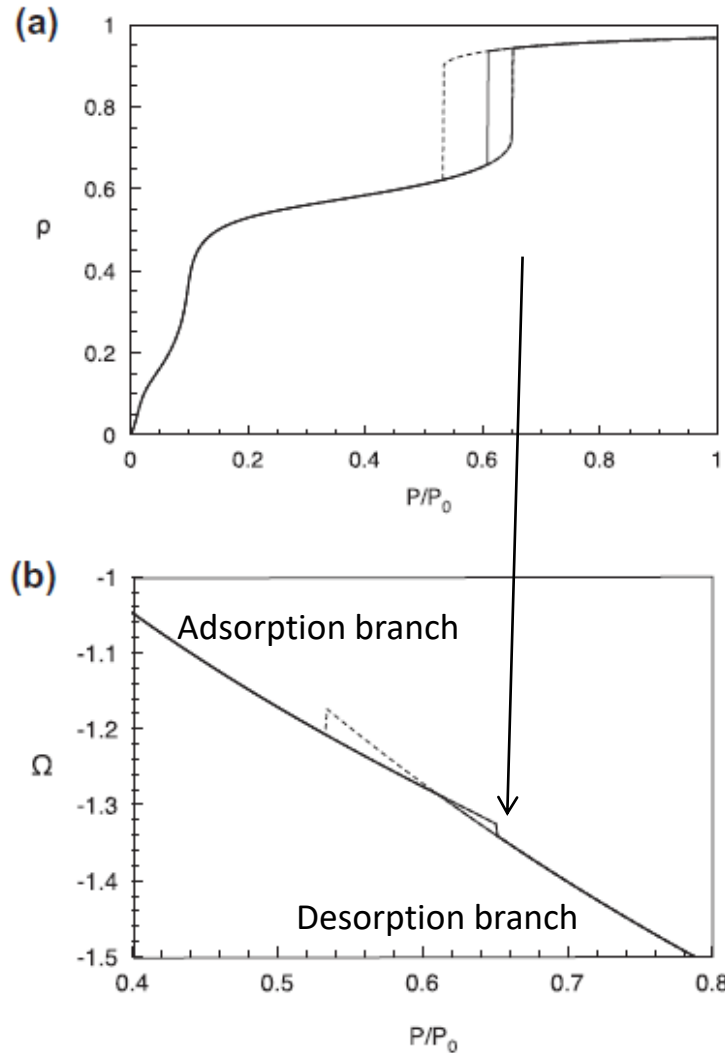
Desorption branch

- In the region of hysteresis, the thermodynamic potential of the desorption is lower than that of the adsorption branch.
- Adsorption branch (empty pore) is a metastable state.
- Desorption branch (filled pore) is in thermodynamic equilibrium.
- Reason for metastability in adsorption branch
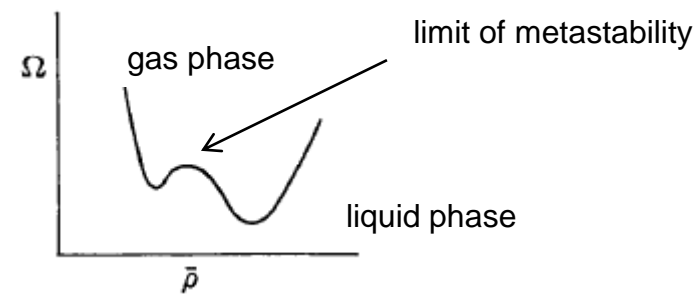 - barrier of nucleation for the formation of a liquid bridge across the pore
  - condensation occurs when limit of metastability is reached

gas phase   limit of metastability

liquid phase

Monson, MMM, 2012.

Peterson, JCS Farad 2, 1986.

INK-BOTTLE PORES

Figure 10.7. Nitrogen isotherms at 77 K for xerogel (circles), acid-washed xerogel (squares; HCl, pH2, 24 h) and alcogel (triangles) (Kenny and Sing, 1994).

Type H2

Adsorbent:
xerogel and
alcogel

r_{des}

- In desorption the evaporation from the pore neck is determining.

- Whole pore will only be fully emptied, when the capillary evaporation pressure for the pore neck is reached.

- Sudden drop in the desorption isotherm – type H2

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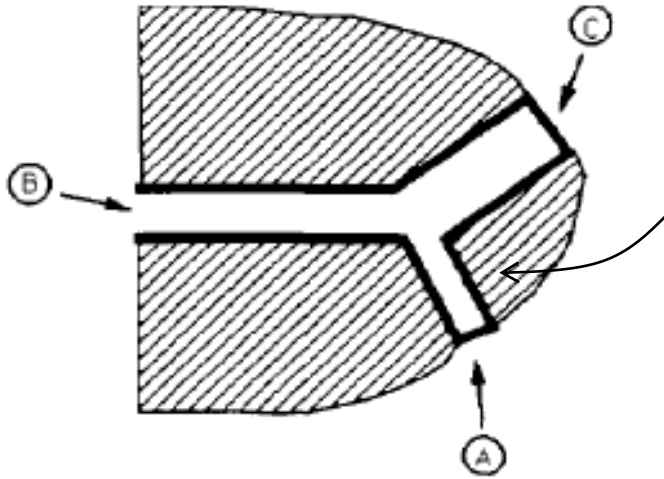
Order of capillary evaporation:
C before B and A, but
N_2 can only desorb from pore C if pore B has already been emptied.

Seaton, ChemEngSci, 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.

EXAMPLE OF BJH PORE SIZE DISTRIBUTION

- Alumina supports
  - Significant differences between PSD from adsorption and desorption
  - Analysis of adsorption branch yields larger pores than the desorption branch.
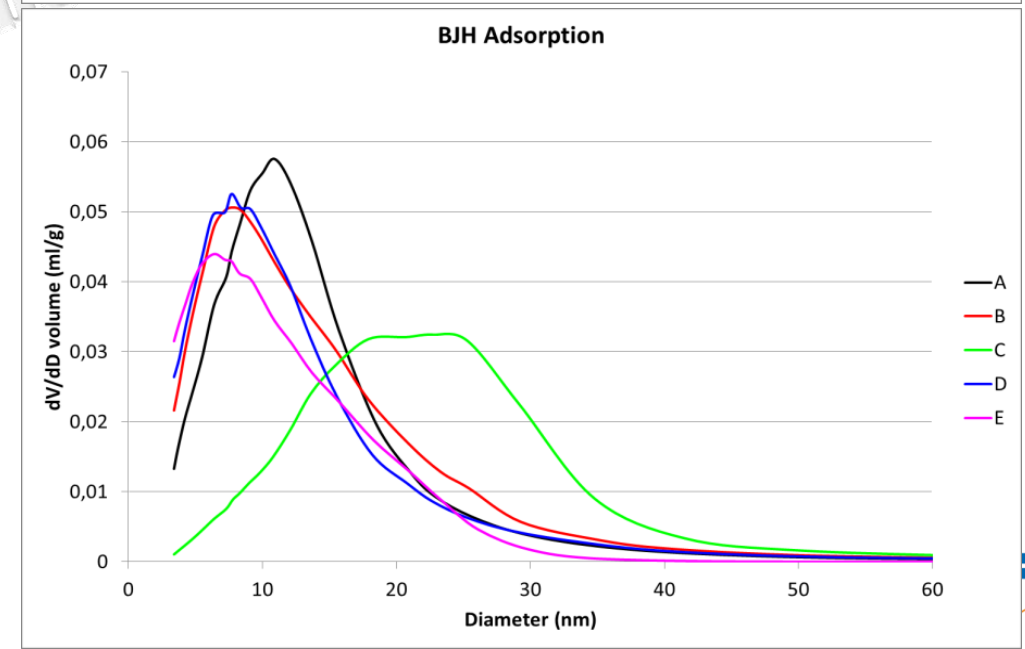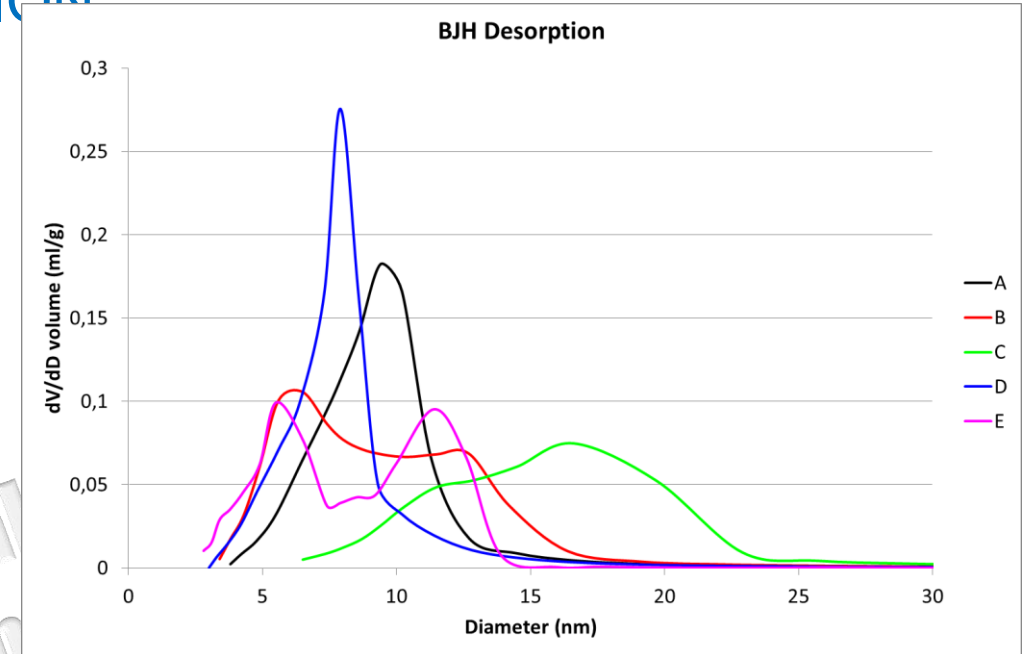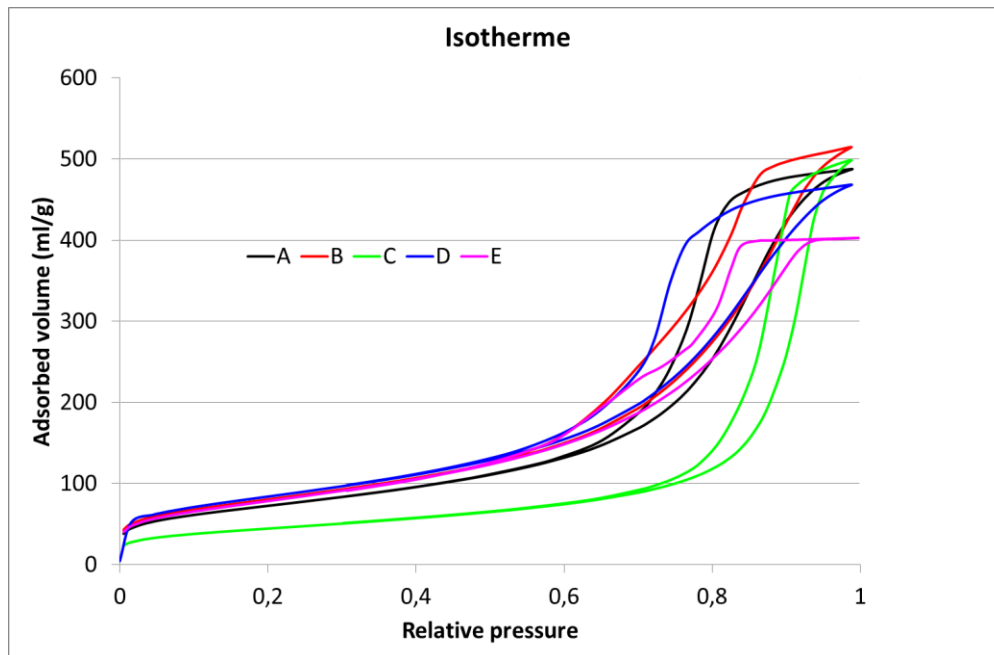
PORE SIZE ANALYSIS WITH THE BJH-MODEL

- Adsorption branch gives the pore size distribution.
- Desorption branch gives the neck size distribution.
  - May also be influenced by percolation effects (pore network).
- BJH model is not thermodynamically consistent
  - Model separates the adsorbed film and the capillary condensate – not a realistic picture
  - Fluid-wall interactions are neglected
  - Kelvin equation not valid any more in highly confined space (small pores)
- One should speak about a BJH-value rather than pore diameter.
- Alternative methods exist
  - Density Functional Theory
  - Broekhoff de Boer
  - Derjaguin – concept of disjoining pressure
    - surface tension concept that takes interaction with solid into account

FORCED CLOSURE OF THE HYSTERESIS

- N_2 ads/des hysteresis at 77K always closes at $p/p_0 \sim 0.43$. WHY?

- For small pores the difference between a filled liquid like state and an empty gas like state vanishes, the pore fluid becomes supercritical, no metastability possible any more.

- For pores which undergo capillary condensation at $p/p_0 < 0.43$, N_2 is supercritical at 77 K $\rightarrow$ isotherm necessarily closes at this pressure.

- Steps in the desorption isotherm at $p/p_0 \sim 0.43$ produce an artefact in the BJH PSD.

Isotherm

Pore size distribution
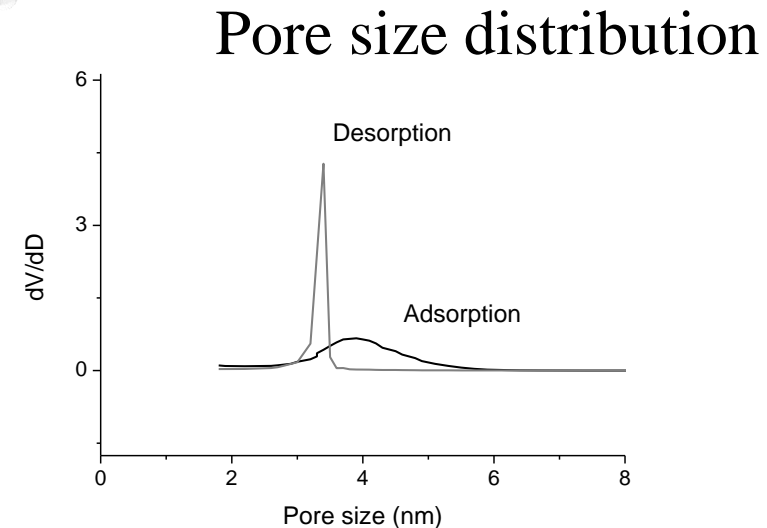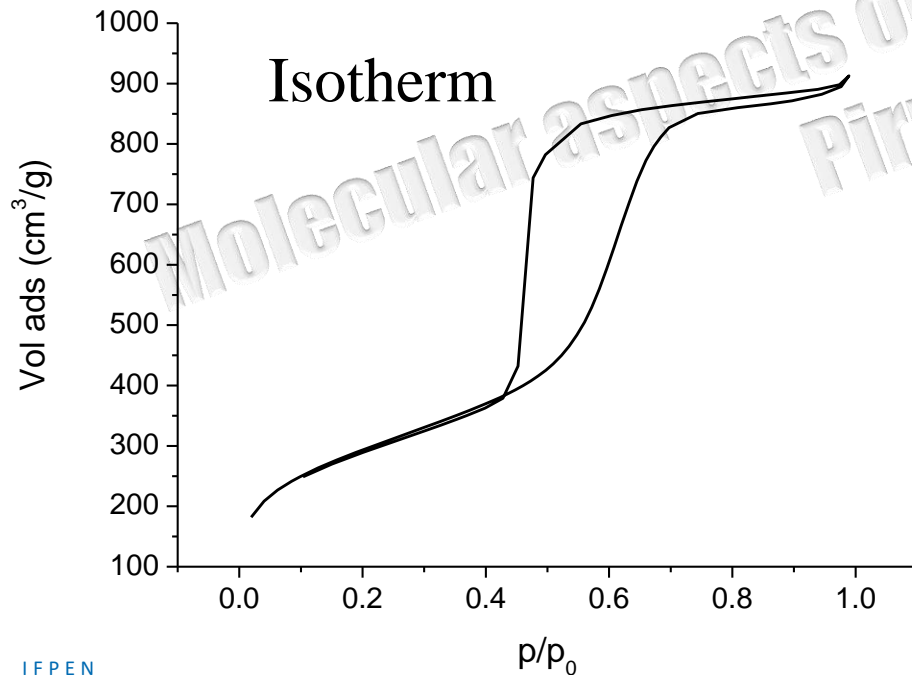
- Capillary condensation can still occur below $p/p_0 = 0,4$, but it happens without hysteresis.
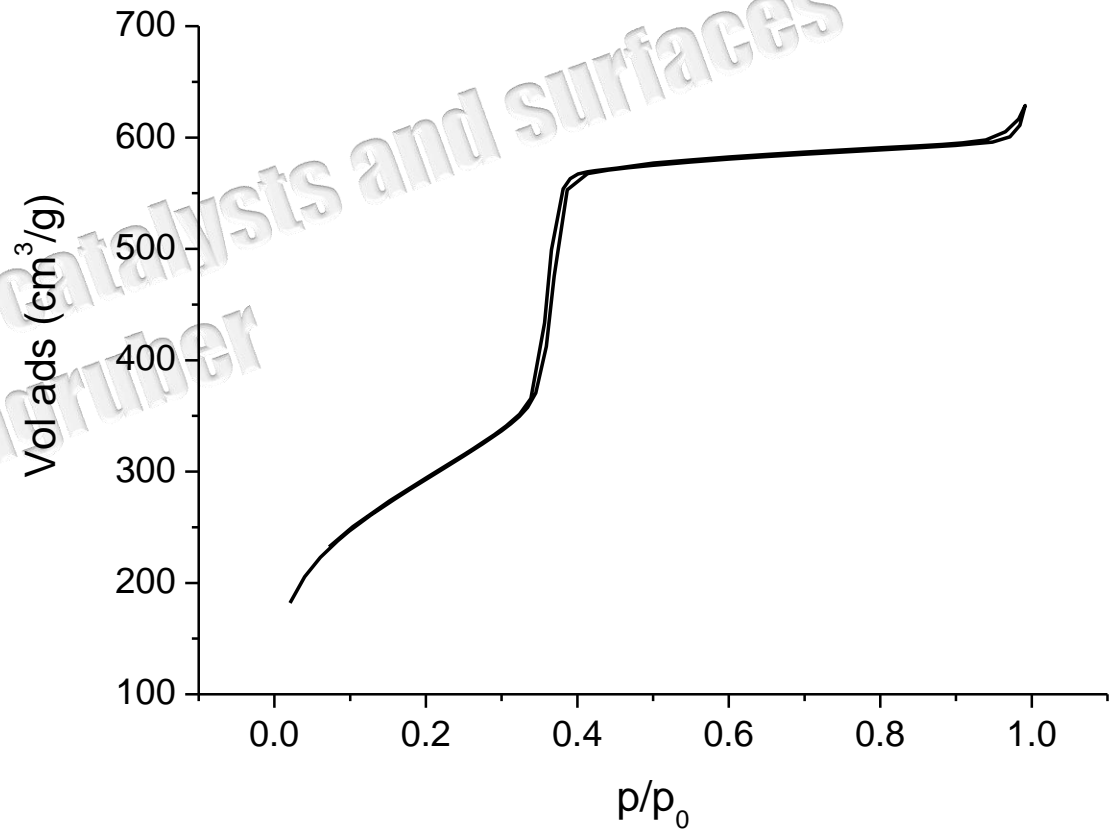
DENSITY FUNCTIONAL THEORY

- Non local Density Functional Theory (NLDFT) is becoming the state of the art in pore size/pore volume analysis.

- What is DFT?

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

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

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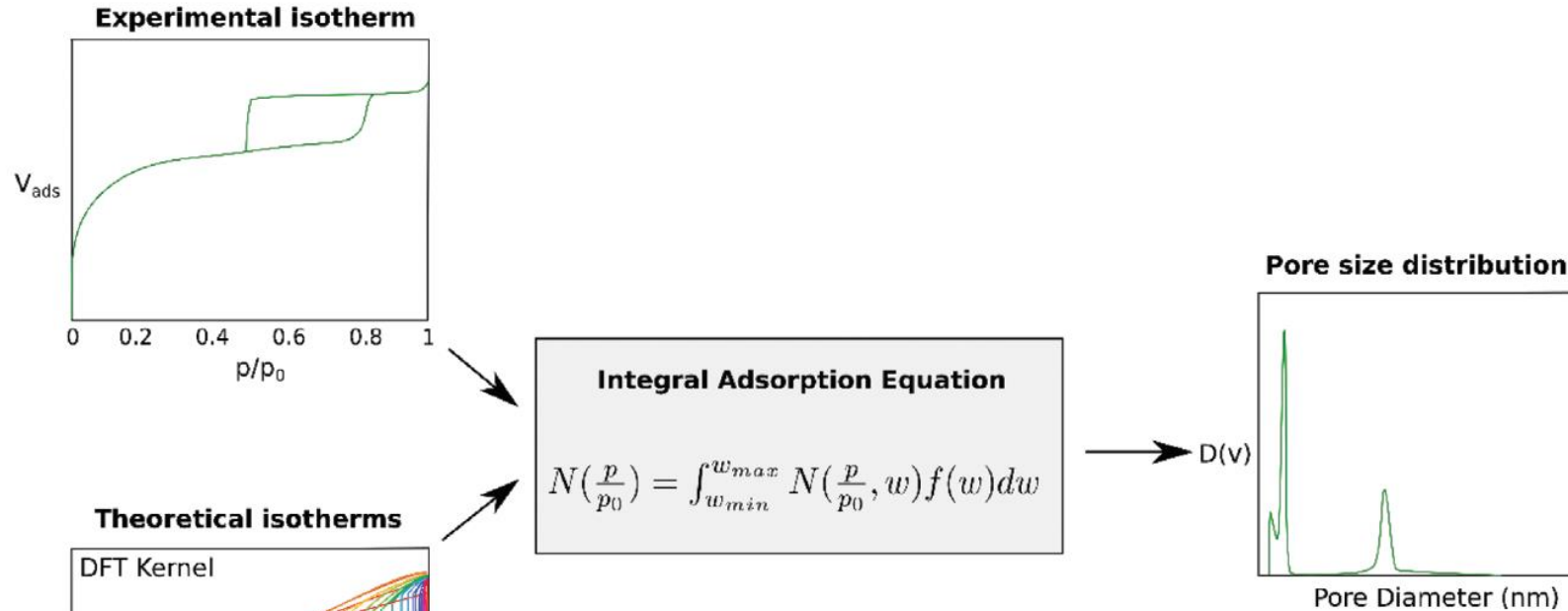- $F(\rho)$ = Helmholtz energy of the system due to fluid-fluid interactions, in the absence of an external field
- $V(r)$ = external potential at position r
- μ = chemical potential

EXPRESSION FOR THE GRAND POTENTIAL

Ideal gas

Excess energy (non-ideality)

$$\Omega[\rho(\boldsymbol{r})] = k_B T \int \rho(\boldsymbol{r}) \left[ln\left(\Lambda^3(\boldsymbol{r})\right) - 1 \right] d\boldsymbol{r} + k_B T \int d\boldsymbol{r}\, \Phi\left(\{\bar{n}_\alpha\}(\boldsymbol{r})\right)$$

$$+ \frac{1}{2} \int d\boldsymbol{r} \int \rho(\boldsymbol{r})\rho(\boldsymbol{r}')\phi_{att}(|\boldsymbol{r} - \boldsymbol{r}'|) d\boldsymbol{r}' - \int \rho(\boldsymbol{r})\left[\mu - \phi_{ext}(\boldsymbol{r})\right] d\boldsymbol{r}$$

Fluid-fluid interaction

External potential

- The part relevant for pore size analysis is the external potential Φ_{ext}
  - Solid-fluid interaction
  - Effet of pore size and pore geometry (confinement)
    - Similar to the HK, SF models of micropore size analysis

PORE SIZE ANALYSIS WITH DFT

Experimental isotherm

V_{ads}

0   0.2   0.4   0.6   0.8   1

p/p_0

Theoretical isotherms

DFT Kernel

V_{ads}

10^{-8} 10^{-6} 10^{-4} 10^{-2} 1

p/p_0

Integral Adsorption Equation

$$N\left(\frac{p}{p_0}\right) = \int_{w_{min}}^{w_{max}} N\left(\frac{p}{p_0}, w\right) f(w)\, dw$$

$D(v)$

Pore size distribution

Pore Diameter (nm)

- 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.

NLDFT IS BIG STEP FORWARD, …

- If appropriate kernels are used, NLDFT yields the same pore size distribution when analyzing the adsorption and the desorption branch.

- DFT is able to account for the delayed condensation in the adsorption branch.

- Pore size is larger than obtained by BJH.

- If PSDs of adsorption and desorption branch do not superpose : pore network effects affect the desorption branch (typical for H2 isotherms)
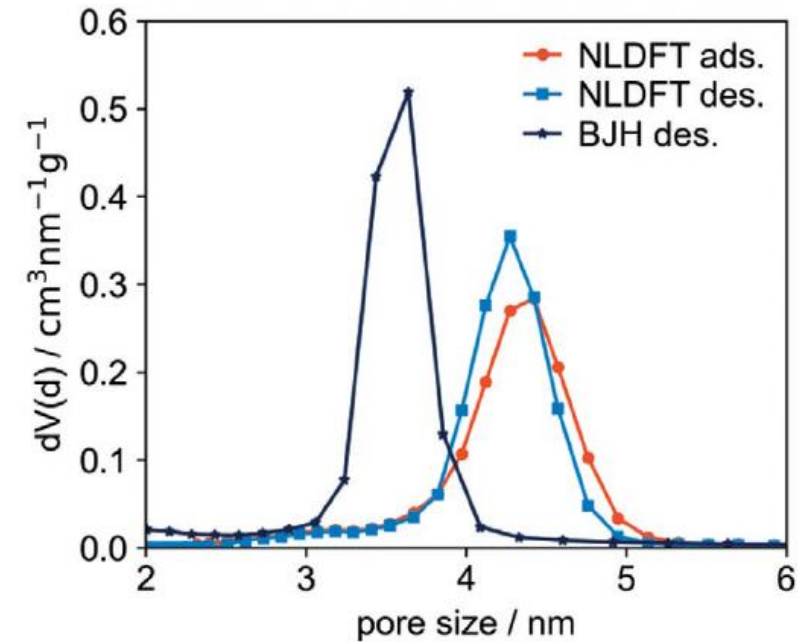

Figure 11. Comparison of mesopore size distribution of the mesoporous zeolite Y calculated with the BJH method and NLDFT using the adsorption and desorption branch of the Ar (87 K) isotherm by applying a dedicated metastable NLDFT adsorption branch kernel and an equilibrium NLDFT desorption branch kernel, respectively.

Schlumberger, Thommes, Adv Mater Interfaces 2021, 8, 2002181
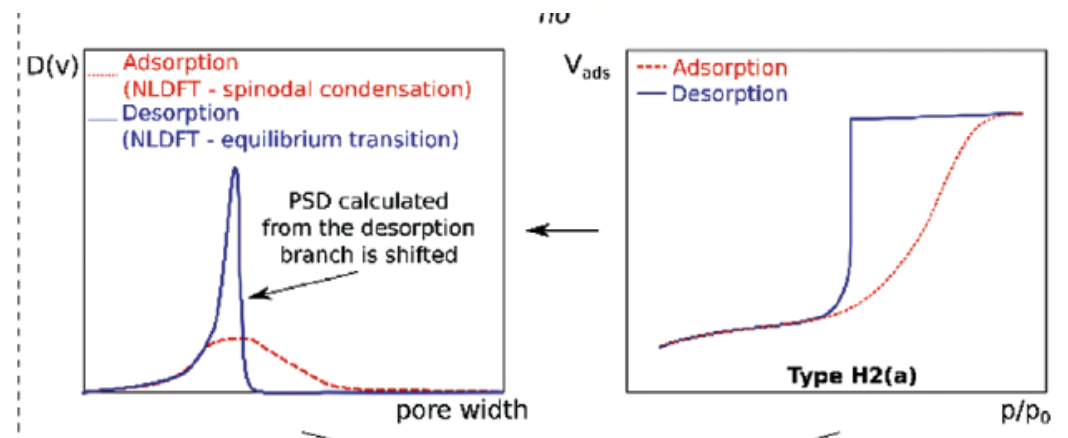
, BUT BE CAREFUL WHEN USING DFT

- Geometry effect:
  - For a given pore size, the kernel of isotherms also depends on pore geometry
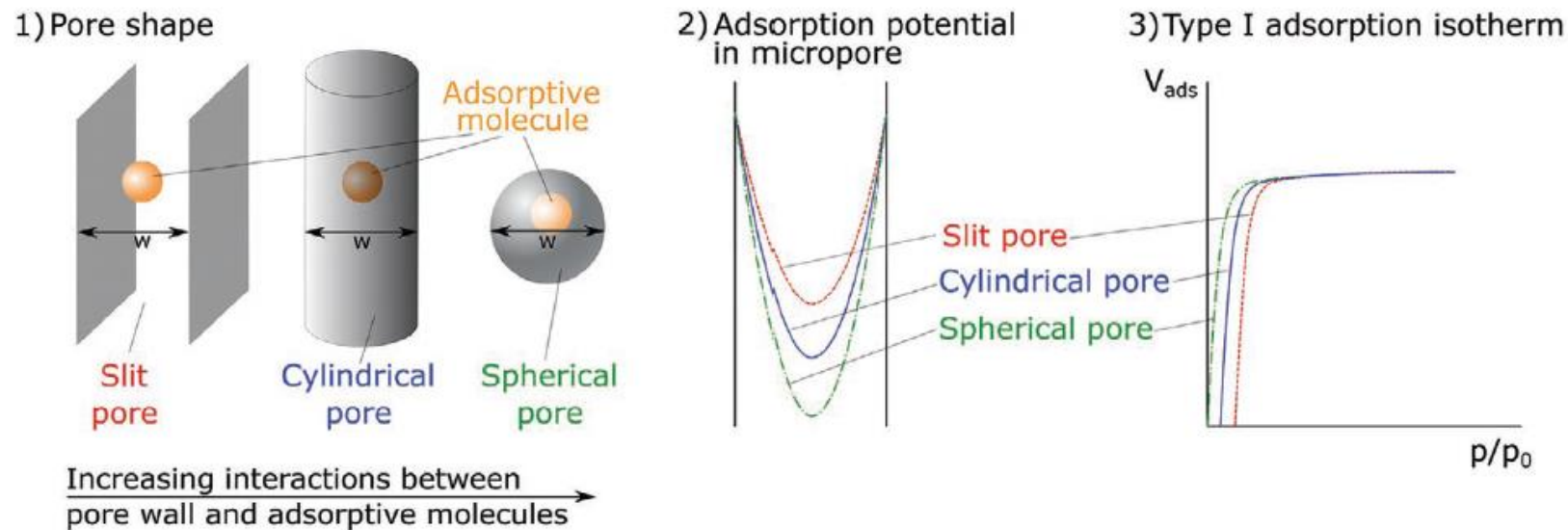 - If you apply a Kernel for spherical pores to cylindrical pores, the result will be wrong

Figure 14. Schematic illustration of pore geometry effects on the adsorption potential of fluid confined in a micropore. 1) Schematic illustration of a slit, cylindrical, and spherical micropore. 2) Adsorption potential of a slit, cylindrical, and spherical micropore. 3) Resulting Type I adsorption isotherms depending on the pore shape.

, BUT BE CAREFUL WHEN USING DFT

- The forced closure of the isotherm still produces an artefact in the PSD obtained from the desorption branch.

Schlumberger, Thommes, Adv Mater Interfaces 2021, 8, 2002181
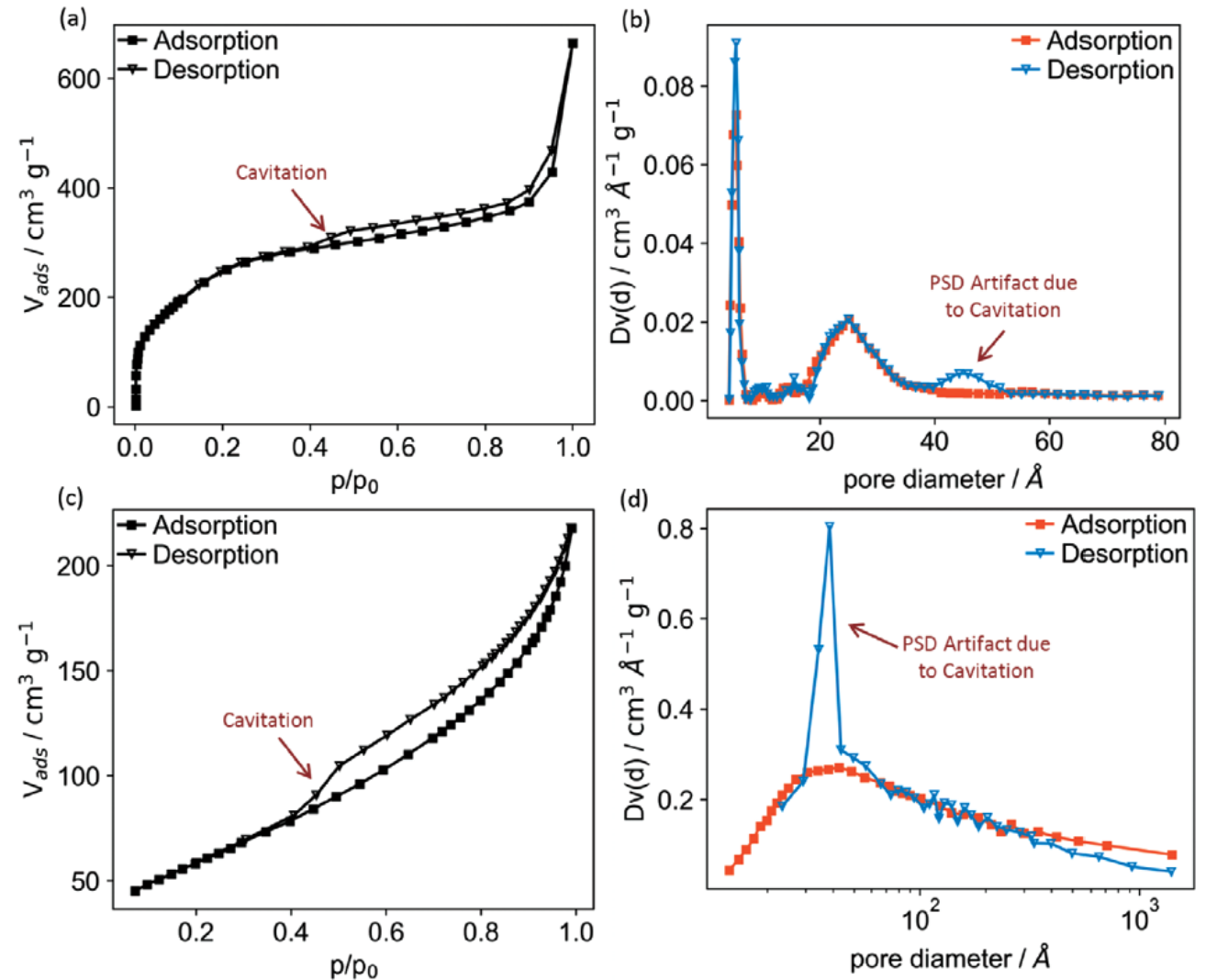
TO WRAP UP

- State of the art of pore size analysis
  - Use Ar isotherms at 87 K (instead of N2 at 77 K)
  - Use an appropriate NLDFT kernel for pore size analysis
    - Commercial software offers many possibilities, but is black-box
    - Choosing the right one is not trivial
  - If PSD from adsorption and desorption branch do not superpose you are dealing with pore network effects (ink-bottle pores, percolation, etc.)

MERCURY POROSIMETRY

ANALYSIS OF MACROPORES

- N$_2$ physisorption only detects pores of up to ~100 nm. Larger pores are not seen.

- For isotherms, which do not reach a plateau at p/p$_0$ = 1, part of the pore volume is not detected.

- For larger pores (macropores), Hg porosimetry must be used.
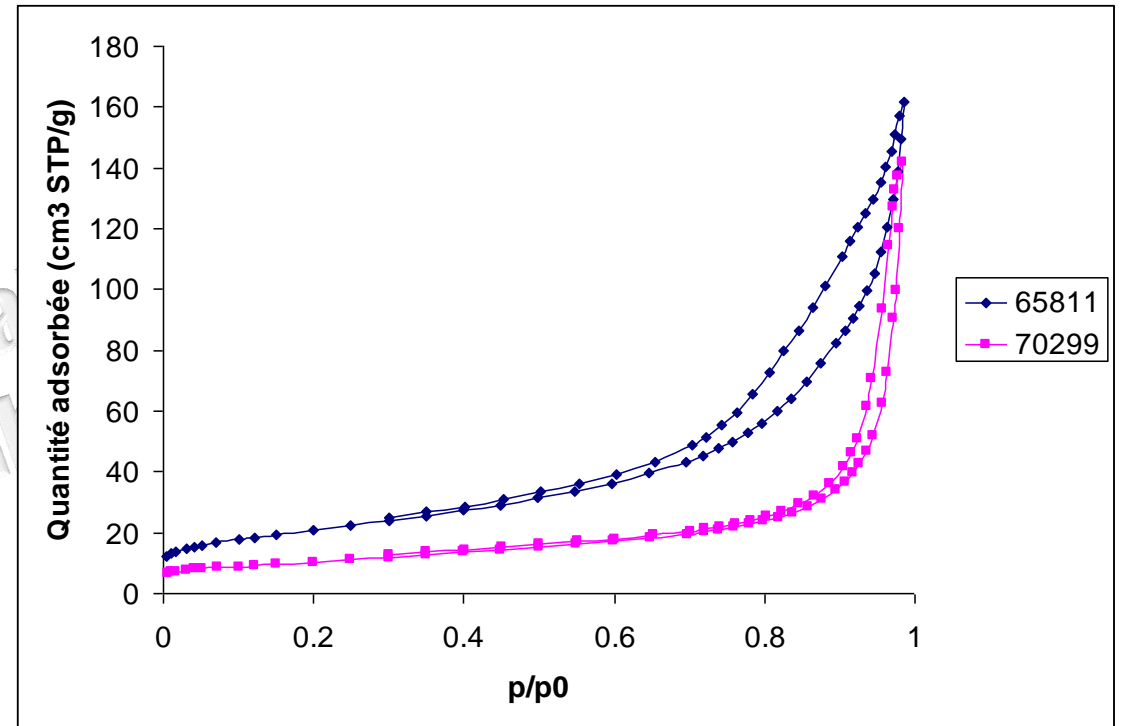
PRINCIPLE OF MERCURY POROSIMETRY

- Hg is a non-wetting fluid, must be forced by pressure to enter into small pores.

- The pressure is related to the pore size by the Washburn equation.

- $P * r = -2\gamma \quad \cos\theta$
  - P = pressure
  - R = pore radius
  - γ = surface tension of Hg (480 mN/m)
  - θ = contact angle with surface, typically 140°C
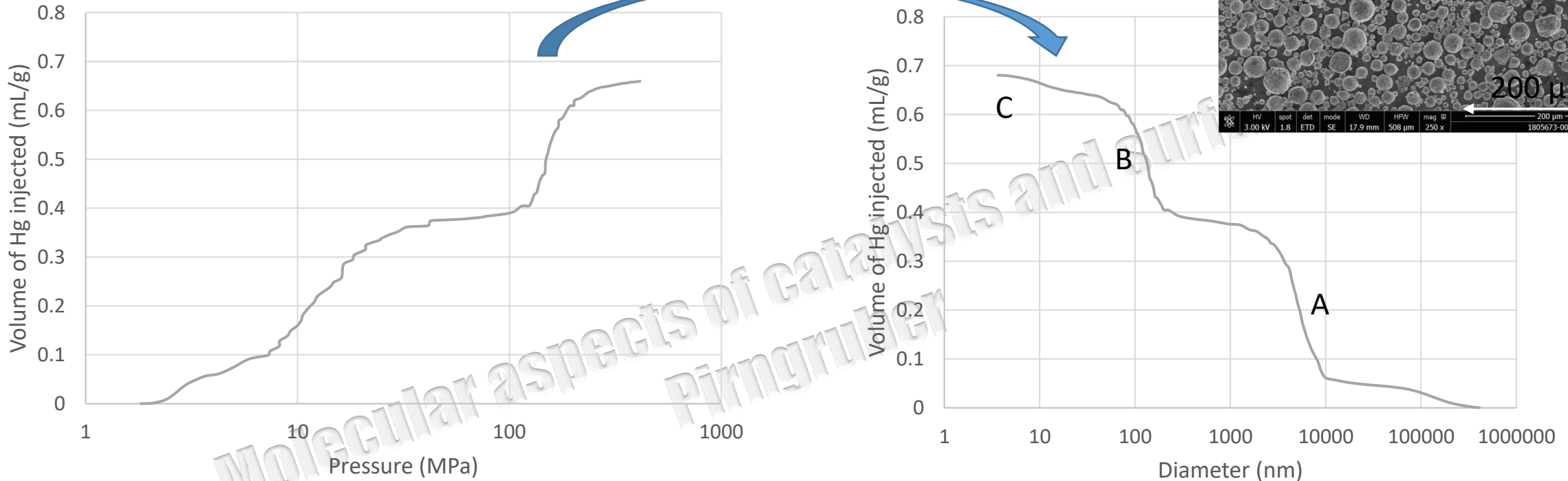
- Hg does not access pores smaller than 4 nm
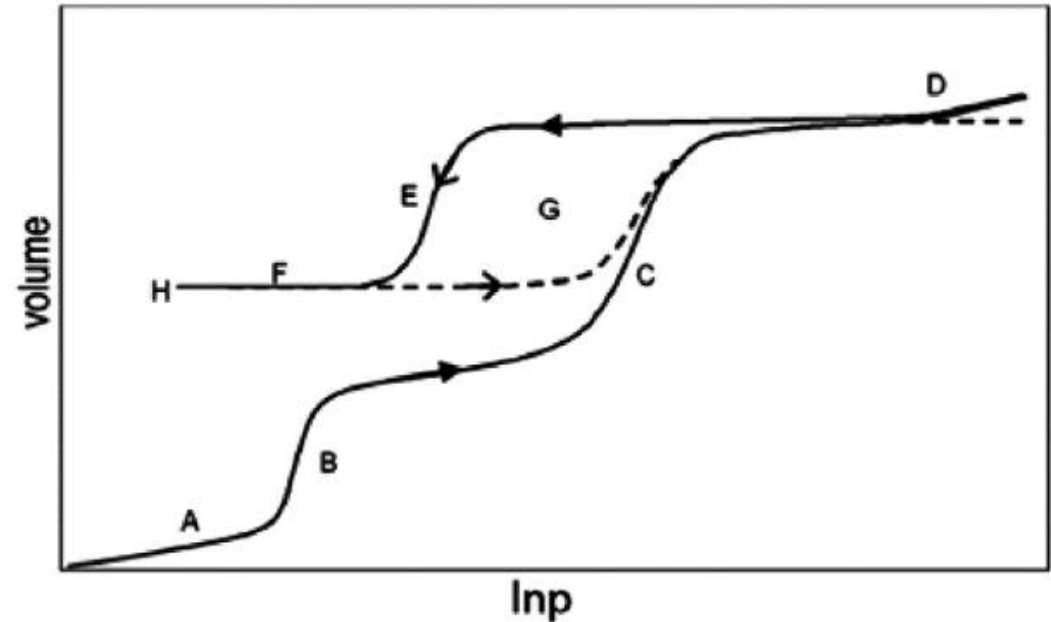
A : Compression of powder
B : intrusion in interparticle voids
C : filling of pores
D : limit of accessible pores
E : extrusion (with hysteresis)
F : some Hg remains entrapped in the solid

EXAMPLE OF MERCURY INTRUSION CURVE

Atomized zeolite particles with binder

Washburn equation

200 µm

- A = intrusion into interparticles space (~5 µm)
- B = intrusion into the particles
  - pores of ~100 nm created by the agglomeration of zeolite crystals having about this size
- C = intrusion into the mesopores of the zeolite crystals

$$\left| \begin{matrix} \mathbf{M} \\ \mathbf{A} \\ \lambda\mathbf{L} \end{matrix} \right| x_d = \left| \begin{matrix} v \\ n \\ 0 \end{matrix} \right|, \; x_d \geq 0$$

● Fit the N2/Ar isotherm and the Hg intrusion with a single pore size distribution

Unified method
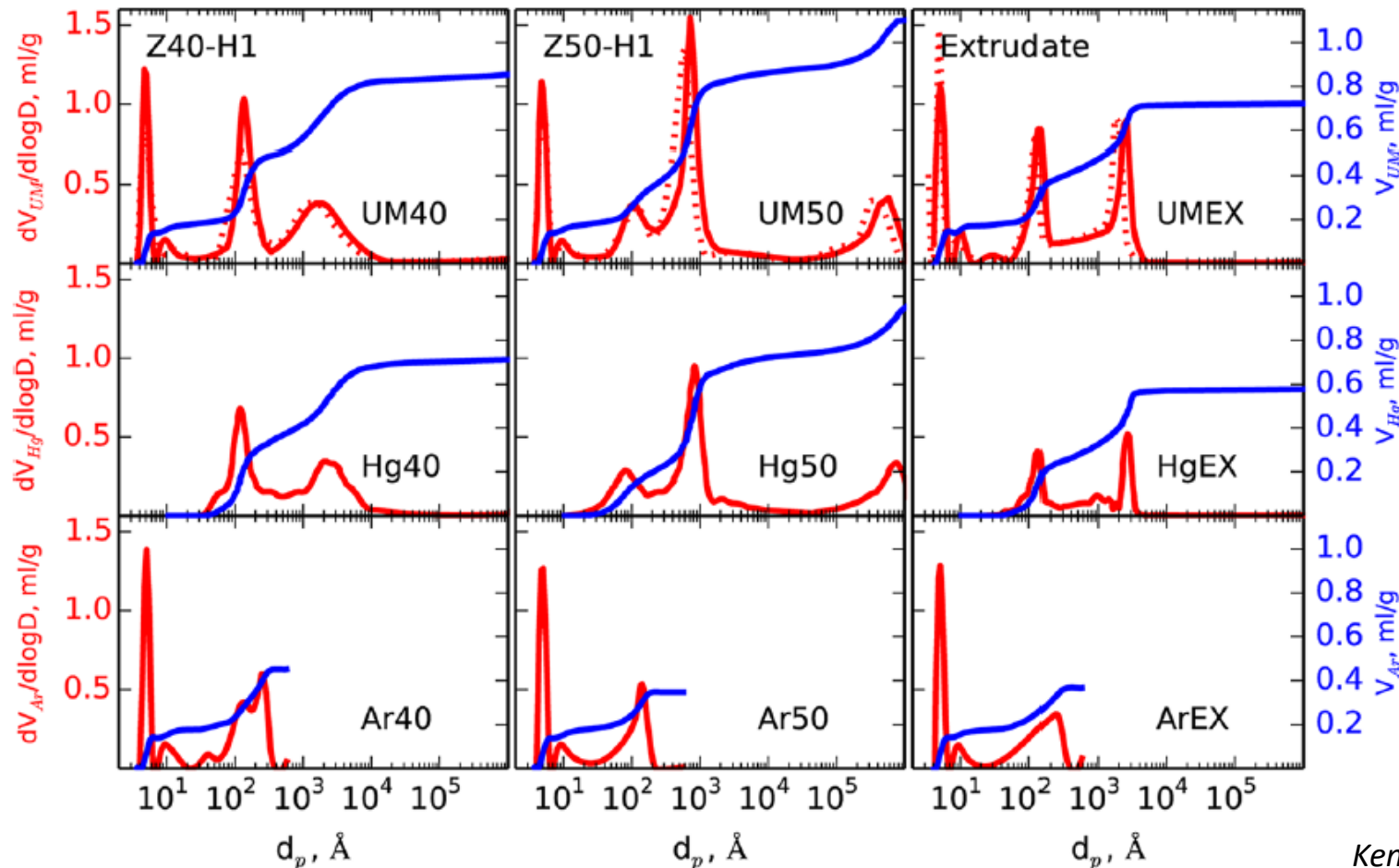
Hg

Ar

Kenvin et al., Langmuir 2015, 31, 1242

LITERATURE

- Review articles discussing 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.
  - K. Cychosz, R. Guillet-Nicolas, J. Garcia-Martinez, M. Thommes, Chem. Soc. Rev. 46 (2017) 389.
  - Schlumberger, Thommes, Adv Mater Interfaces 8 (2021) 2002181

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