



*1er Simposio sobre Adsorción, Asorbentes y sus Aplicaciones,  
San Luis, Argentina, 24-27 Febrero 2009*



# Fisisorción de gases: la herramienta básica para caracterizar adsorbentes (área superficial, microporos)

Jean Rouquerol, Sandrine Bourelly, Françoise Rouquerol  
Philip Llewellyn y Renaud Denoyel



Laboratoire Chimie Provence, Site MADIREL, CNRS-Université de Provence, Marseille



Jean  
Rouquerol



Françoise  
Rouquerol



Sandrine  
Bourelly



## Los co-autores de esta charla



Philip  
Llewellyn

Renaud  
Denoyel





# Gas physisorption: the basic tool to characterize adsorbents (surface area, micropores)



## *Outline*

- ★ Introduction: why the basic tool ?
- ★ Landmarks and basic assumptions of the BET method
- ★ Issues raised by the BET method
- ★ The micropore filling : comments on t-method,  $a_s$ -method and the calorimetric approach
- ★ Conclusion: a few rules to keep in mind

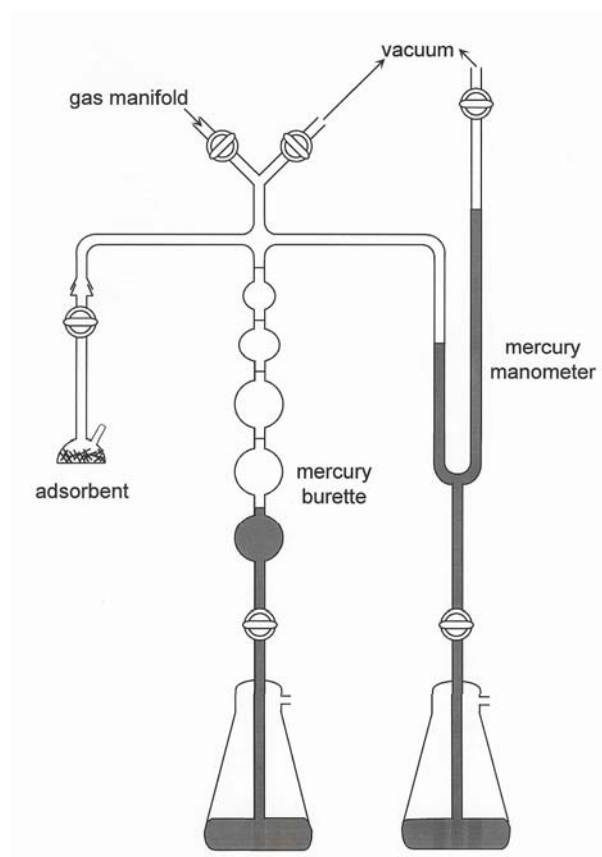


## Why is gas physisorption the basic tool to characterize adsorbents?

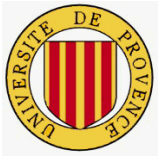
- ★ Essentially, because it makes sense to characterize a material to be used as an adsorbent...after its adsorption properties
- ★ Also, because gas adsorption techniques are now quite convenient to use, with modern equipment



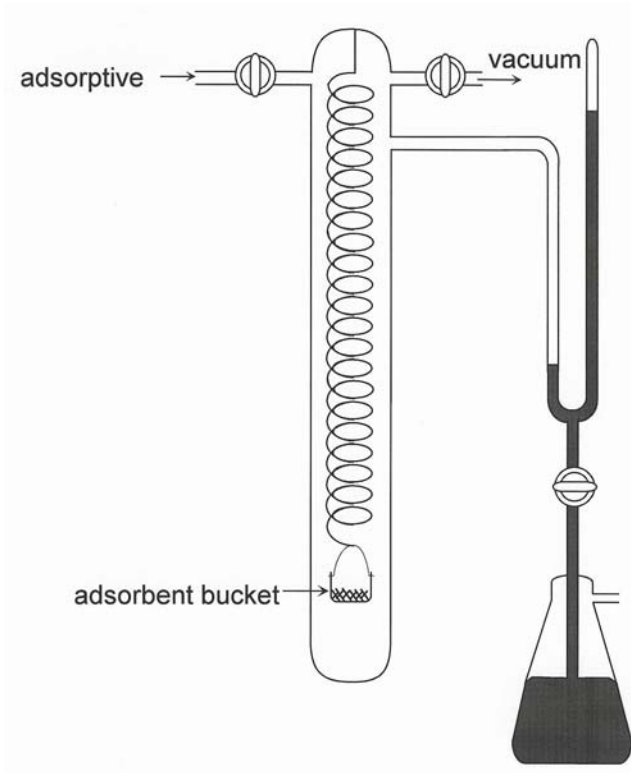
Up to the 80<sup>ies</sup>, the basic adsorption equipment was most demanding in time and attention:  
1/ The BET apparatus



The standard volumetric « BET » set-up made use of **glass** and **mercury**, was manually operated (up to 40 greased stopcocks in sophisticated models) and requested reading of mercury level with **cathetometer**



Up to the 80<sup>ies</sup>, the basic adsorption equipment was most demanding in time and attention:  
2/ The Mac Bain balance

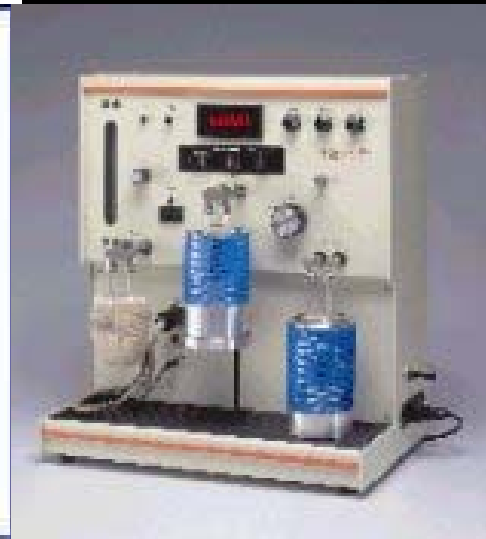
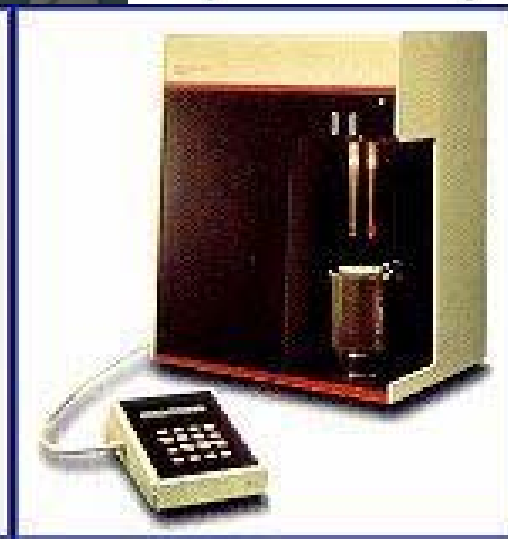


The Mac Bain and Bakr adsorption balance not only made use of glass and mercury, but also of a most sensitive and fragile **fused silica spring**. Here, Two levels had to be followed by a cathetometer: that of the mercury and that of the sample





# To-day, automated equipment is the rule



Laboratoire Chimie Provence, Site MADIREL, CNRS-Université de Provence, Marseille



# Why gas physisorption is the basic tool to characterize adsorbents?



- ★ Essentially, because it makes sense to characterize a material to be used as an adsorbent...after its adsorption properties
- ★ Also, because gas adsorption techniques are now quite convenient to use, with modern equipment
- ★ Finally, because the interpretation of the adsorption data is well developed (and still improves, with help of modelling!)





# Gas physisorption: the basic tool to characterize adsorbents (surface area, micropores)

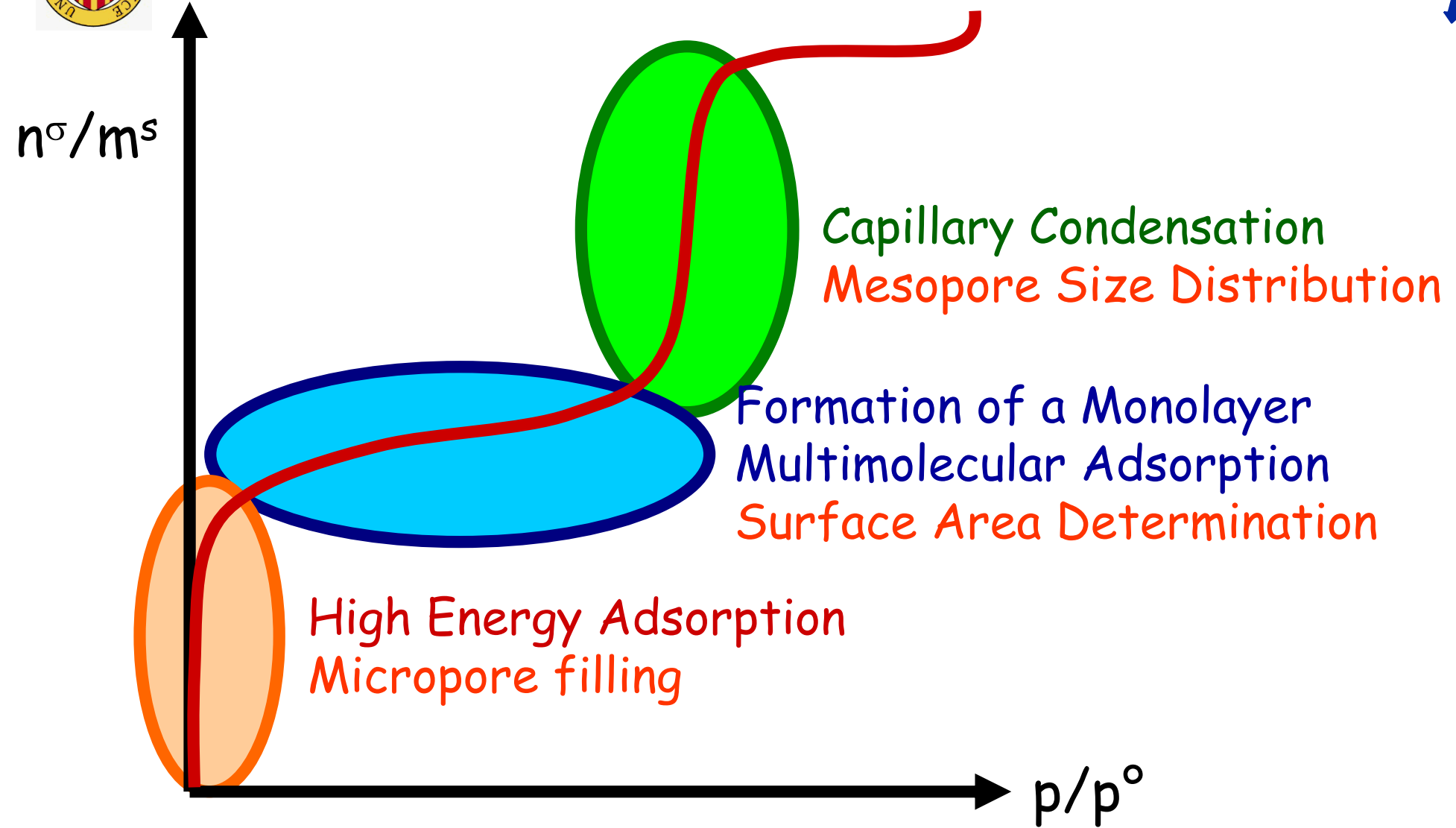


## *Outline*

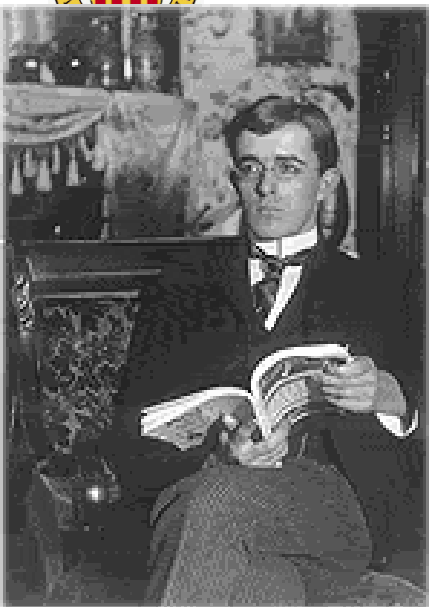
- ★ Introduction: why the basic tool ?
- ★ Landmarks and basic assumptions of the BET method
- ★ Issues raised by the BET method
- ★ The micropore filling : comments on t-method,  $a_s$ -method and the calorimetric approach
- ★ Conclusion: a few rules to keep in mind



# The adsorption *isotherm* of a vapour

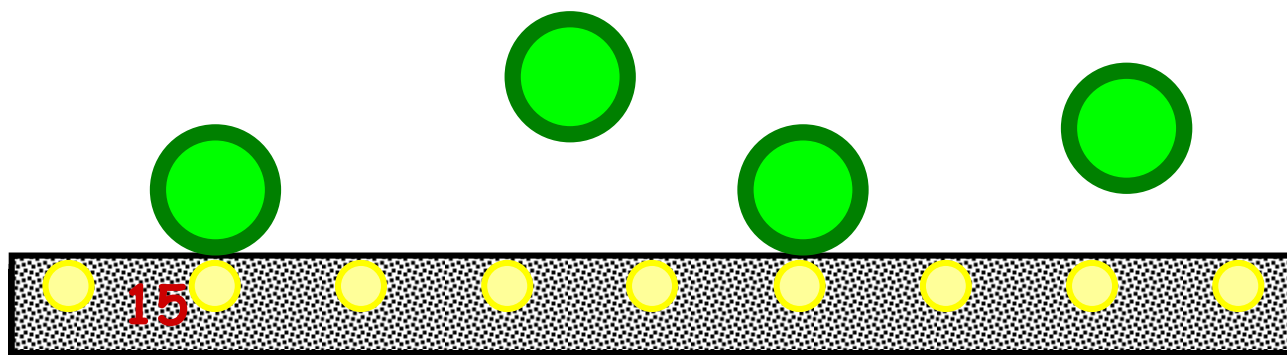
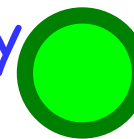


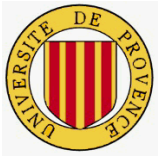
# Irving Langmuir, 1881-1957



Aims to explain **chemisorption** giving rise to **type I isotherm with plateau**

- All sites are energetically identical
- Gas sticks to the surface : 1 layer only possible
- No lateral interactions





# Kinetic derivation of Langmuir Equation



⊗ Rate of **Condensation** :  $\mu$   $\mu = \alpha.p(1 - \theta)$

⊗ Rate of **Evaporation** :  $\nu$   $\nu = \beta.\theta.e^{-E/RT}$

⊗ Fraction of surface covered :  $\theta = \frac{\Gamma}{\Gamma_m}$

$E$  : Energy of activation of the desorption = - Energy of adsorption

$\alpha$  : Adsorption coefficient on a bare surface

$\beta$  : Desorption coefficient from a covered surface

$\Gamma$  : Concentration of molecules at the surface

$\Gamma_m$  : Concentration of molecules at the surface in a complete monolayer

$$n^\sigma = n_m^\sigma \frac{bp}{1 + bp}$$

# The BET team

S. Brunauer, P.H. Emmett. E. Teller (1938). Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60, 309-319.



Stephen Brunauer  
1903-1986



Photo by The Broekner Studio, Pittsburgh, Pa.

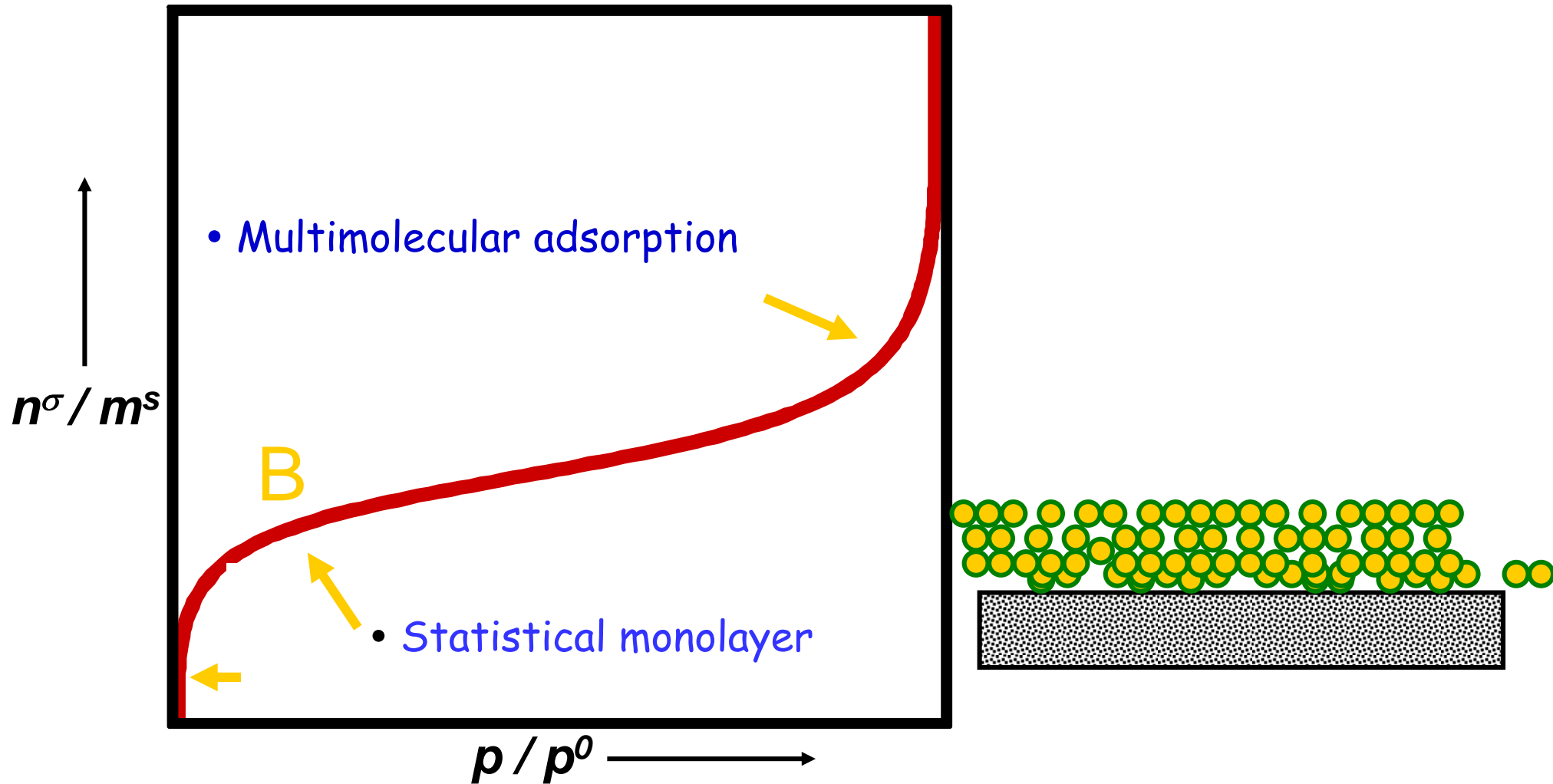
*Paul H. Emmett*

Paul H Emmett  
1899-1985



Edward Teller  
1908-1957

# Adsorption on a purely non-porous sample





# The BET team

S. Brunauer, P.H. Emmett. E. Teller (1938). Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60, 309-319.



Stephen Brunauer  
1903-1986



Photo by The Broekner Studio, Pittsburgh, Pa.

*Paul H. Emmett*

Paul H Emmett  
1899-1985



Edward Teller  
1908-1957



# Brunauer Emmett et Teller (BET) theory



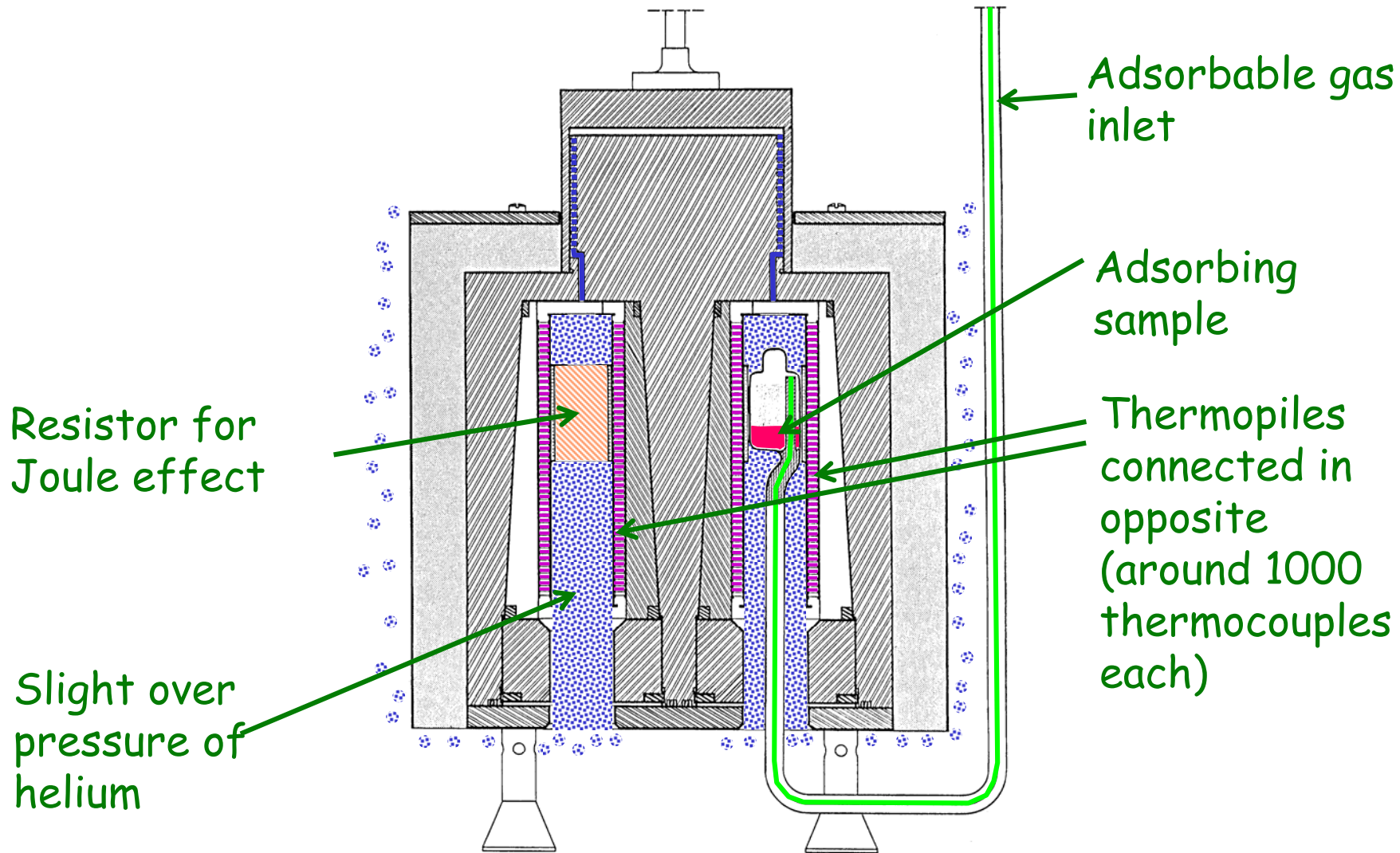
## Assumptions

1. One type of "adsorption site" with constant molar energy of adsorption  $E_1$  on 1<sup>st</sup> layer

### *Comments:*

- "Sites" not needed; leads to inconsistency with assumption that molecules are close-packed.*
- Calorimetry does not show  $E_1 = \text{constant}$*

# Adsorption calorimetry at liquid N<sub>2</sub> or Ar temperature





# The Gas Adsorption Calorimeter in its Liquid Cryostat



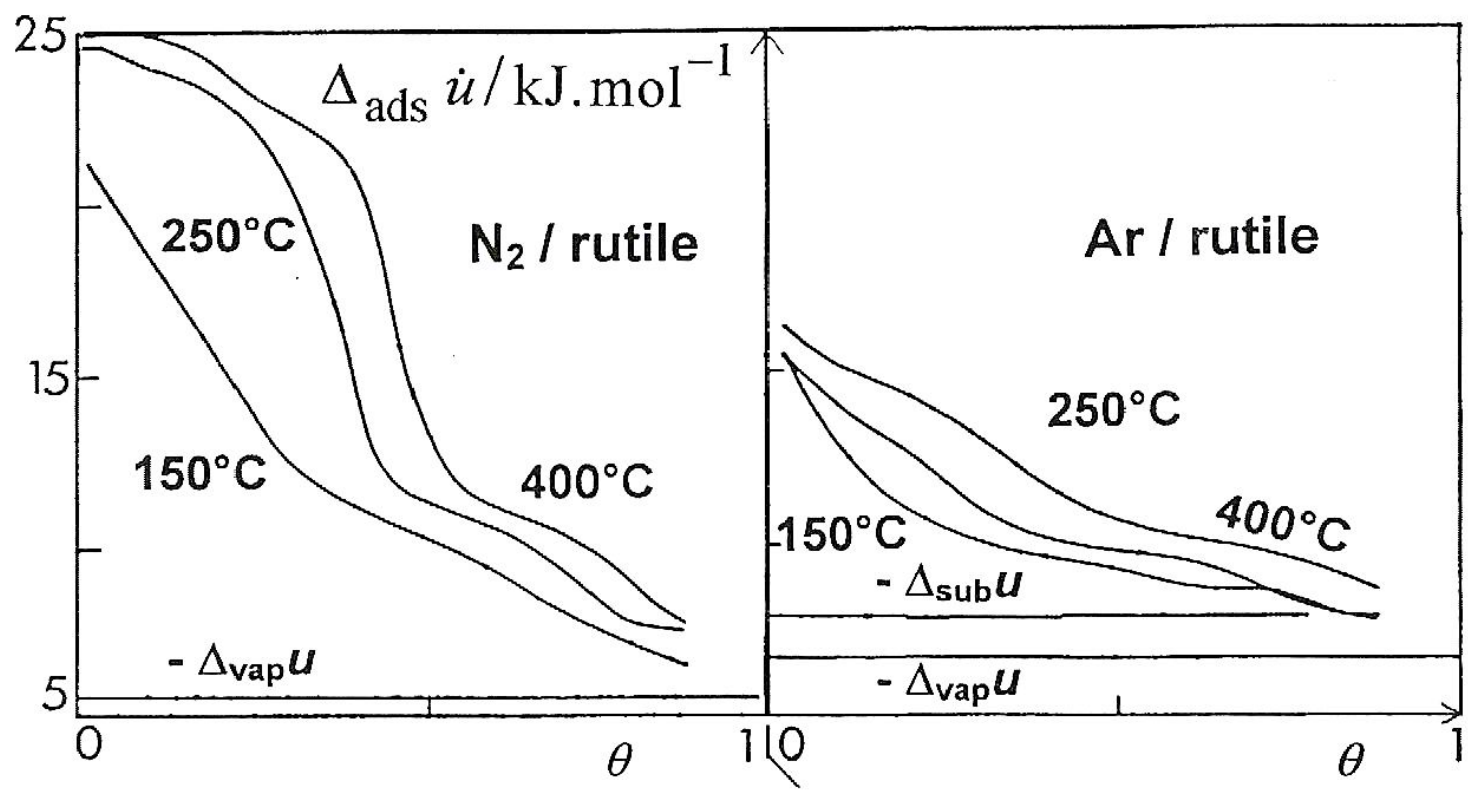
Completely immersed in either liquid nitrogen or liquid argon

Helium gas (flow rate  $1 \text{ ml.mn}^{-1}$ ) carefully cooled in « aluminum tower » (3 m cooling path).





Is  $\Delta_{\text{ads}}H$  constant during completion of monolayer ?



Direct calorimetric measurements show that, even in the absence of microporosity,  $\Delta_{\text{ads}}H$  varies much, even with argon, as soon as « active sites » are on the surface (here, hydroxyls and Ti<sup>+++</sup>cations)



# Brunauer Emmett et Teller (BET) theory



## Assumptions

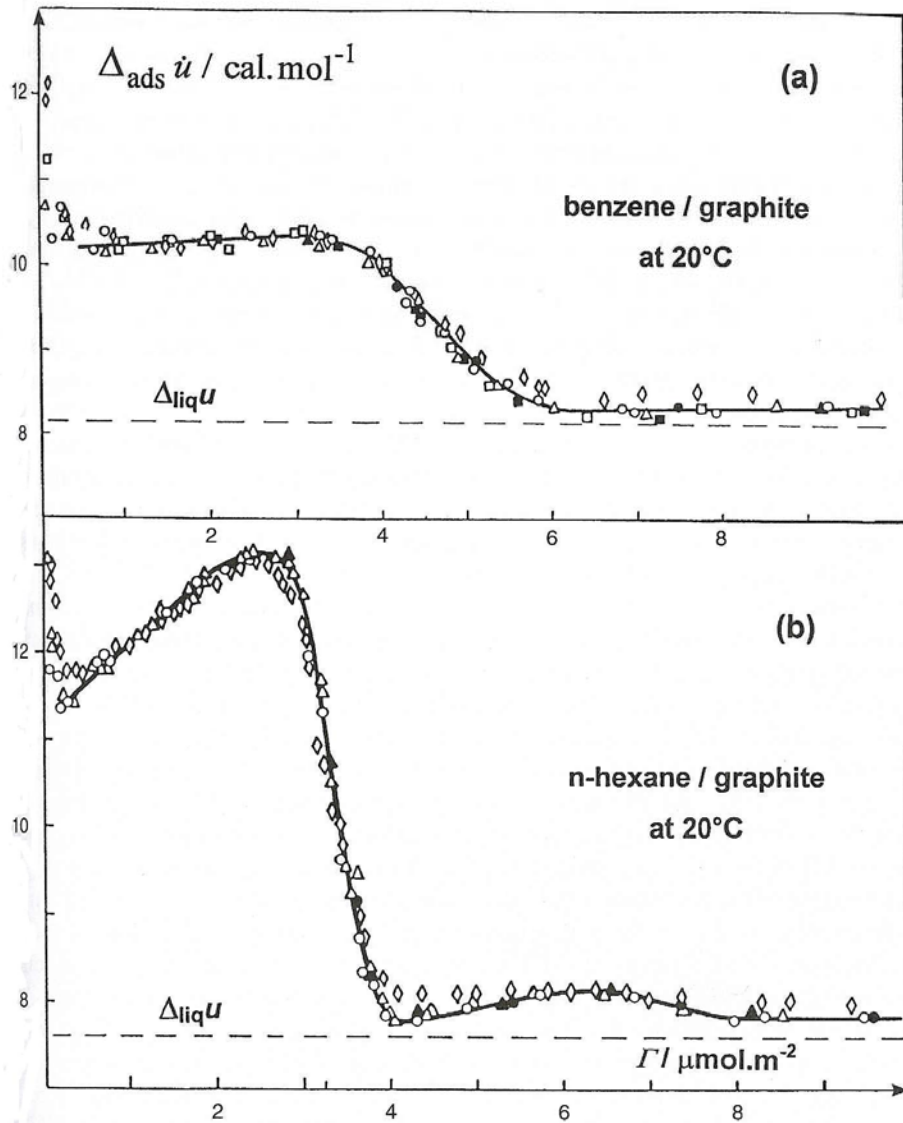
1. One type of "adsorption site" with constant molar energy of adsorption  $E_1$  on 1<sup>st</sup> layer
2. No lateral interactions

### *Comments:*

- Again, an oversimplification (see calorimetry)*



# During formation of 1st layer, should we ignore the "lateral interactions" ? (A.A.Isirikian and A.V.Kiselev, 1962)



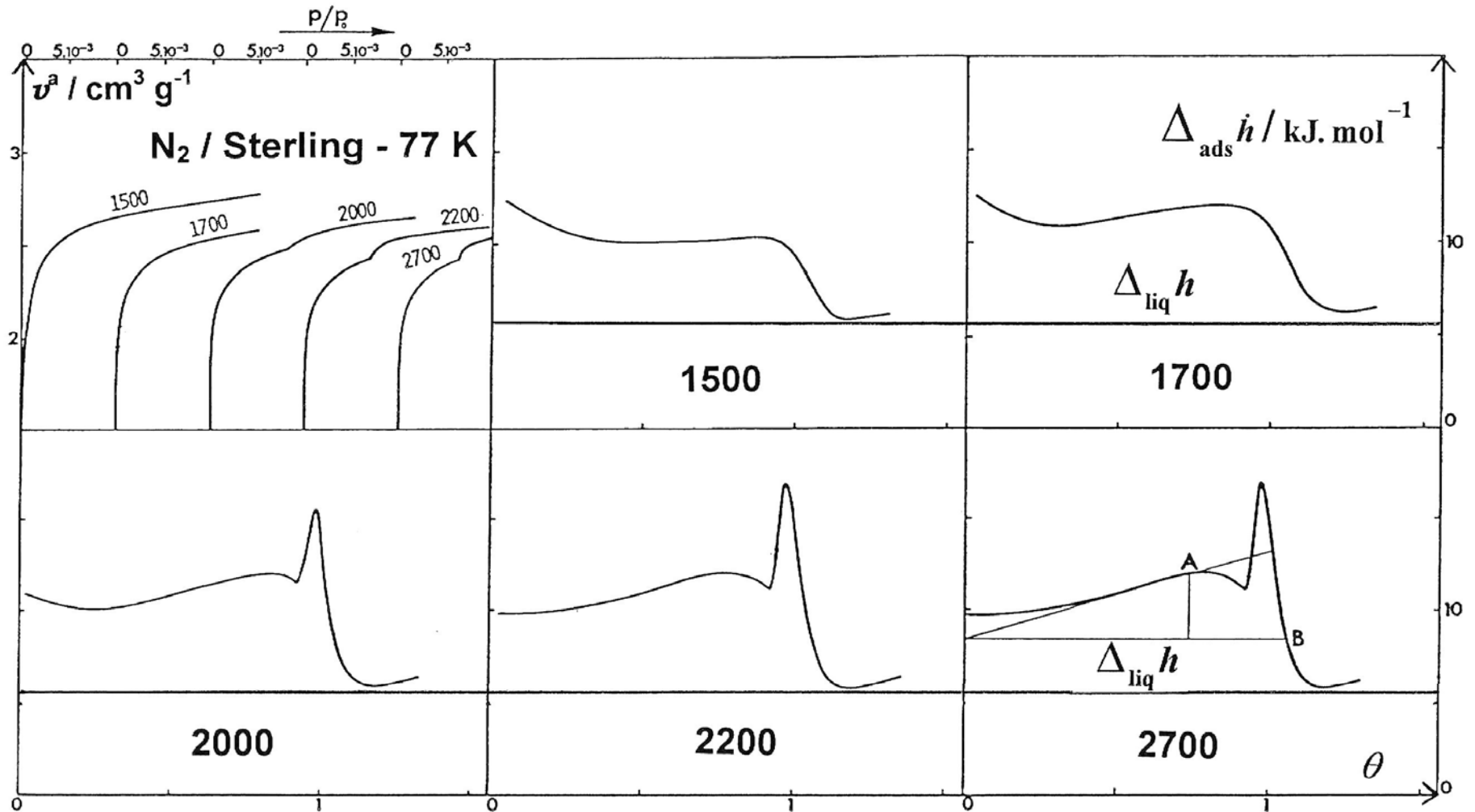
Highly homogeneous graphite allows to **avoid** screening or compensation by **other effects**

**Benzene** adsorbs flat, hence negligible « lateral » interactions

**N-hexane** adsorbs normal to the surface, hence large interactions between adsorbed molecules

Conclusion: difficult to ignore...but difficult to take into account

During formation of 1st layer, should we ignore the "lateral interactions" ? (Grillet *et al.* 1979)





# Brunauer Emmett et Teller (BET) theory



## Assumptions

1. One type of "adsorption site" with constant molar energy of adsorption  $E_1$  on 1<sup>st</sup> layer
2. **No lateral interactions**

### *Comments:*

- Again, an oversimplification (see calorimetry)*
- But a bright oversimplification: in some respect, neglecting simultaneously "lateral interactions" ( $\Delta_{ads}H$  increases) and the role of heterogeneities ( $\Delta_{ads}H$  decreases) leads to some compensation*



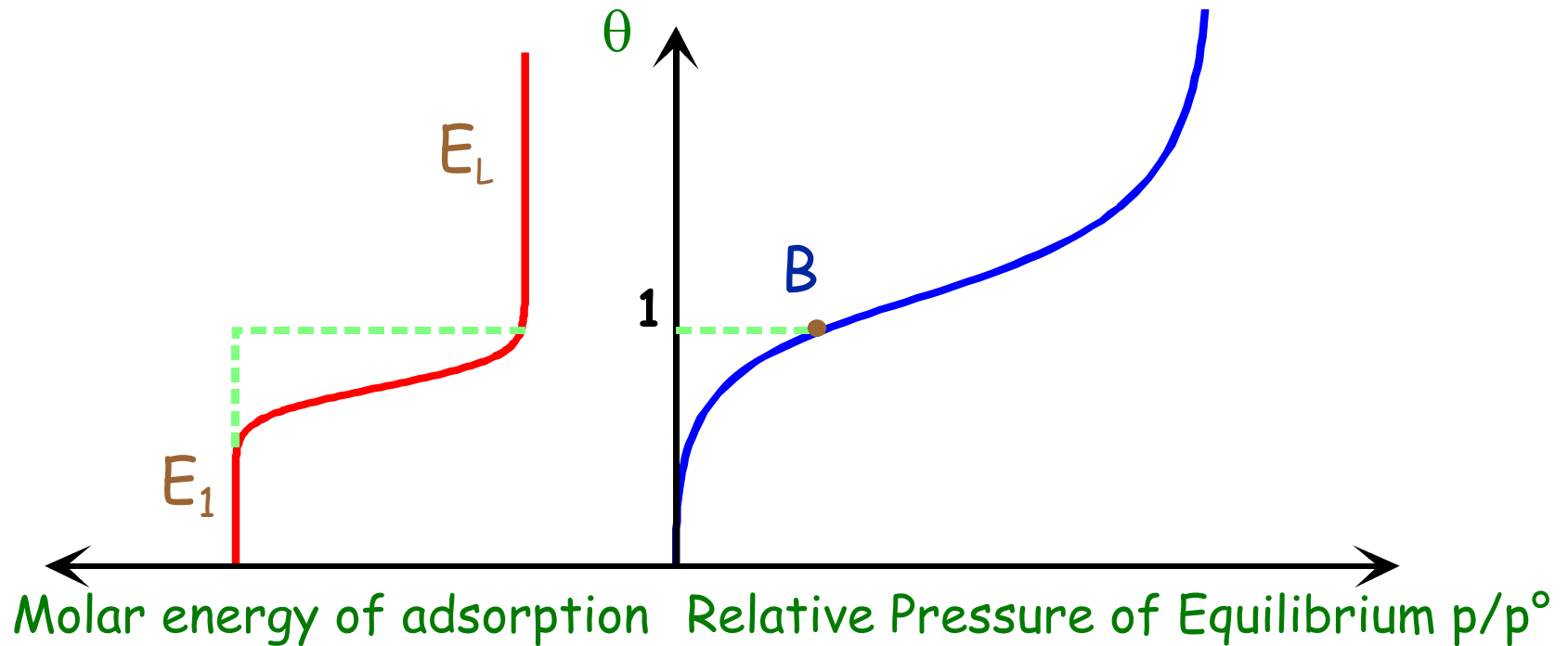
# Brunauer Emmett et Teller (BET) theory



## Assumptions

1. 1 type of "adsorption site" with constant molar energy of adsorption  $E_1$  on 1<sup>st</sup> layer (*"sites" not needed; leads to inconsistency. Calorimetry does not show  $E_1 = \text{constant}$* )
2. no lateral interactions (*and no heterogeneities*) (*bright simplification, compensate each other*)
3. From the second layer  $E_{\text{ads}} \approx E_L$  molar liquefaction energy of the adsorptive (*confirmed by calorimetry*)
4. The second layer starts before 1st layer completed

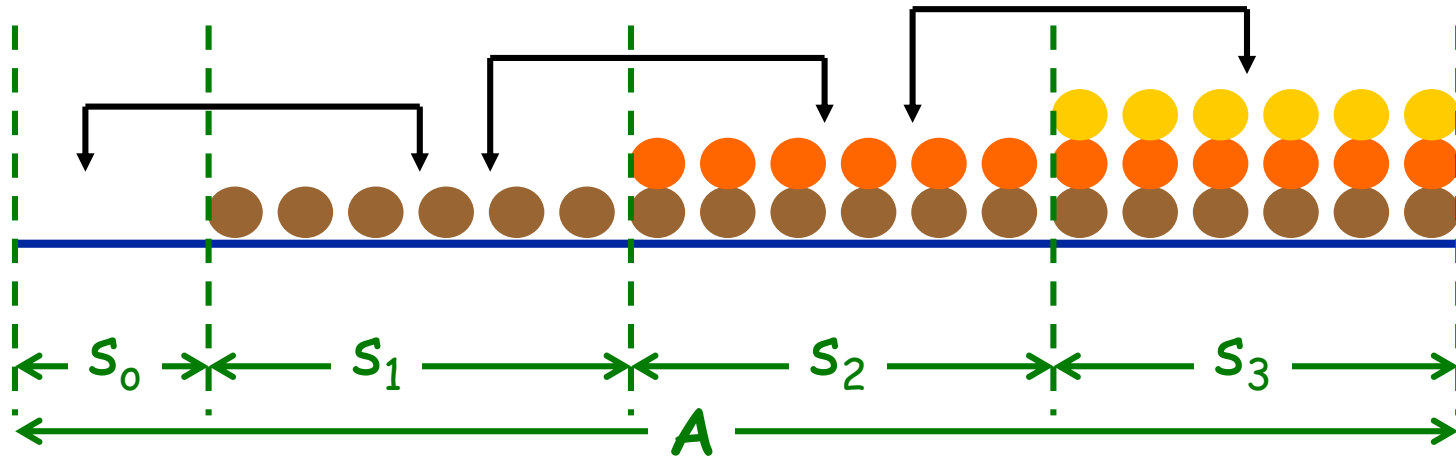
BET theory assumes multilayer starts before monolayer is completed (*correct*)



$E_1$  = Molar energy of adsorption for the first adsorbate layer

$E_l$  = Molar energy of liquefaction of the adsorptive at the temperature of adsorption

# Basic assumptions used in BET theory



surface  $s_0$  covered by 0 adsorbed layer

...  $s_1$  ... 1

... ...

...  $s_i$  ...  $i$

total surface  $A = s_0 + s_1 + \dots + s_i + \dots$





# Brunauer Emmett et Teller (BET) Equation



→  $C \approx \exp\left(\frac{E_1 - E_L}{RT}\right)$

→ N = maximum stacking number

$x = p/p^0 =$  equilibrium  
relative pressure

$$\frac{n}{n_m} = \frac{Cx}{1-x} \cdot \frac{1 - (N+1)x^N + Nx^{N+1}}{1 + (C-1)x - Cx^{N+1}}$$

If  $N \rightarrow \infty$

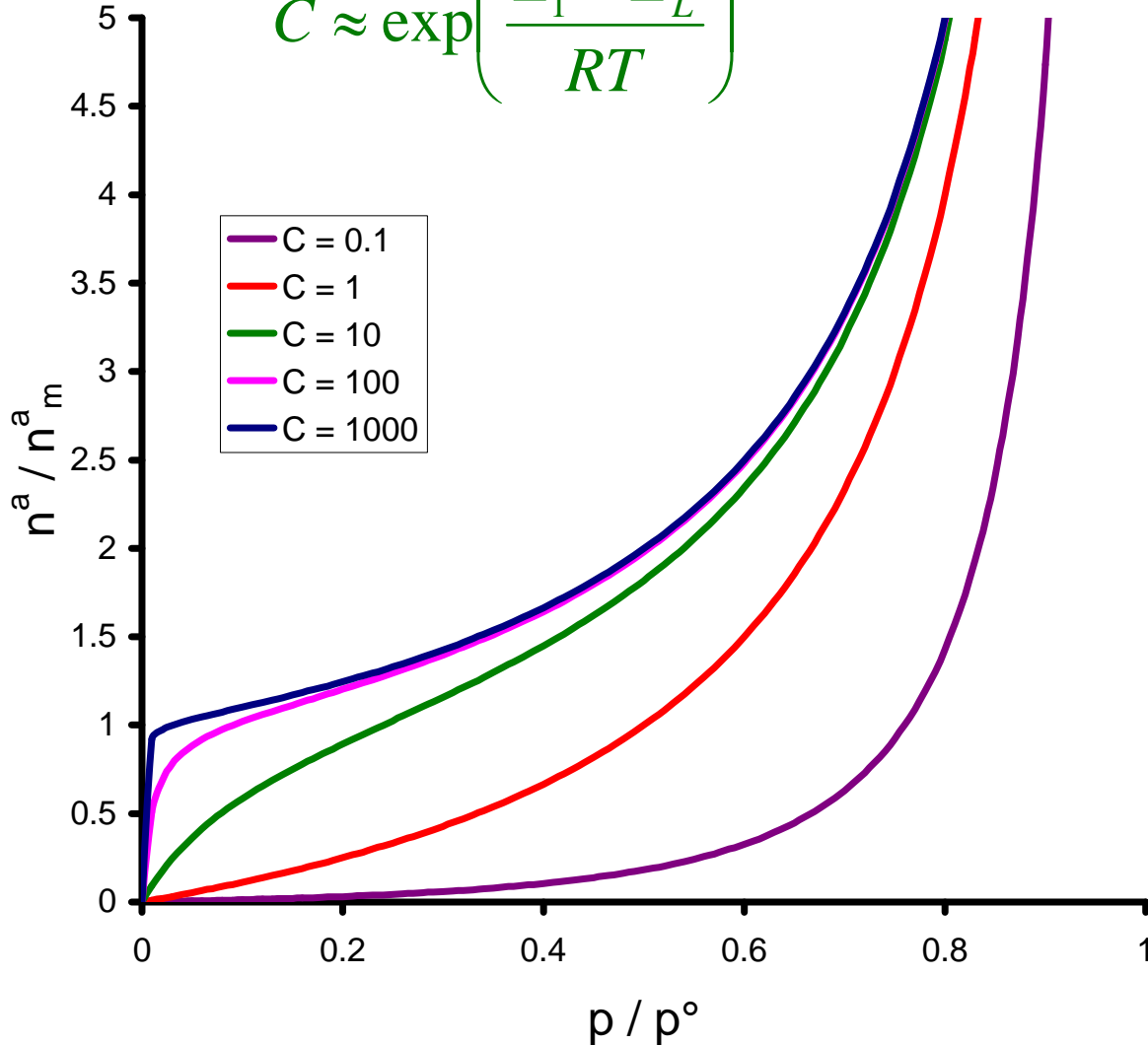
$$\frac{n}{n_m} = \frac{Cx}{(1-x)[1 + x(C-1)]}$$

Transformed BET equation

$$\frac{x}{n(1-x)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} x$$

# Influence of the Energetic Constant "C" on the shape of a theoretical BET adsorption isotherm

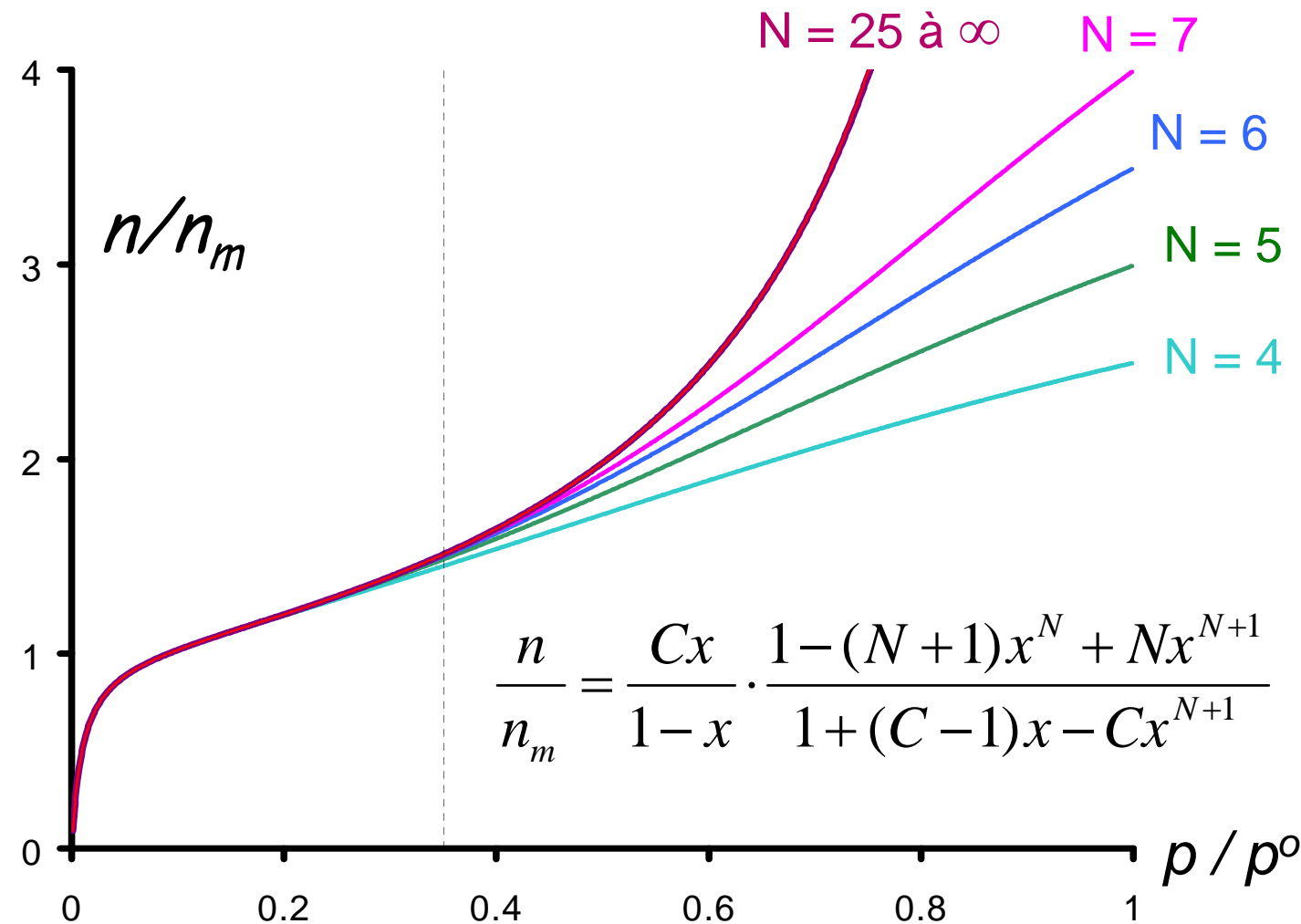
$$C \approx \exp\left(\frac{E_1 - E_L}{RT}\right)$$



Conclusion: for «  $C$  » lower than 10, most difficult to see a « knee », to determine a « point B » and to draw  $n_m$  from the BET equation

$$\frac{n}{n_m} = \frac{Cx}{(1-x)[1+x(C-1)]}$$

# Influence of the maximum stacking number N on the shape of a theoretical BET adsorption isotherm



Conclusions:

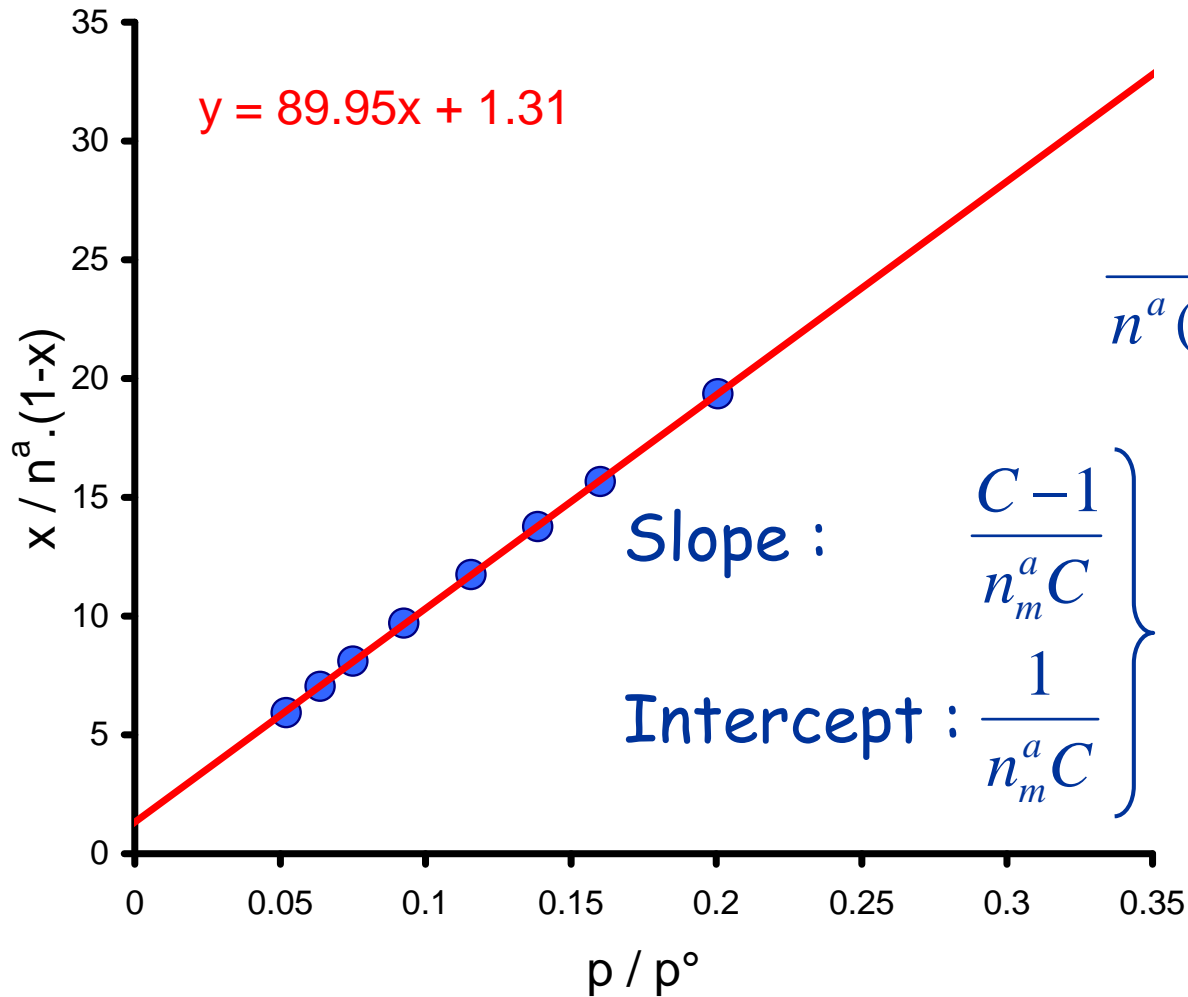
1/ Up to  $p/p_0 = 0.35$ , BET assumption that

$N = \infty$  provides same curve as  $N=4$

2/ No objection to applying BET equation for mesoporous solid

# Treatment of the isotherm by the BET method

exemple : alumina NPL / N<sub>2</sub> / 77 K



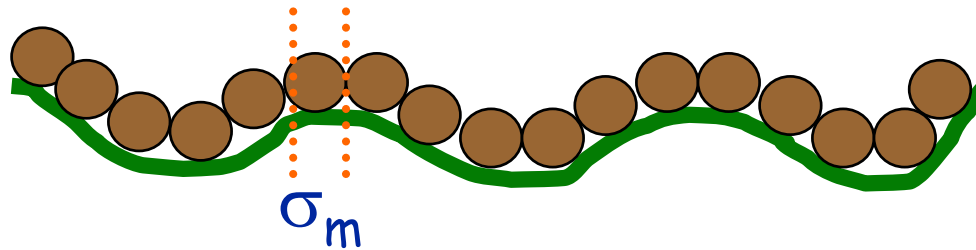
$$\frac{x}{n^a(1-x)} = \frac{1}{n_m^a C} + \frac{C-1}{n_m^a C} x$$

Slope :  $\frac{C-1}{n_m^a C}$

Intercept :  $\frac{1}{n_m^a C}$

$$\left. \begin{array}{l} \text{Slope : } \frac{C-1}{n_m^a C} \\ \text{Intercept : } \frac{1}{n_m^a C} \end{array} \right\} \begin{array}{l} n_m^a = \frac{1}{S+I} \approx 0.011 \\ C = \frac{S}{I} + 1 \approx 70 \end{array}$$

# Principle of the measurement of the specific surface area

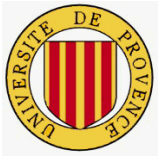


$n_m^a$  = quantity of substance required to cover the surface with a monomolecular layer

$\sigma_m$  = area occupied by a single molecule on the surface in the monolayer

## Assumptions

- \* adsorbed molecules treated as spheres of radius  $r$  occupying area  $\sigma_m$  in the completed monolayer
- \* monolayer supposed to be hexagonal compact and liquid (density  $\rho$  at the temperature of adsorption) (*inconsistent with the "adsorption sites" of the starting assumptions, borrowed from Langmuir*)



# Gas physisorption: the basic tool to characterize adsorbents (surface area, micropores)



## *Outline*

- ★ Introduction: why the basic tool ?
- ★ Landmarks and basic assumptions of the BET method
- ★ **Issues raised by the BET method**
- ★ The micropore filling : comments on t-method,  $a_s$ -method and the calorimetric approach
- ★ Conclusion: a few rules to keep in mind



# Issues for the application of the BET method

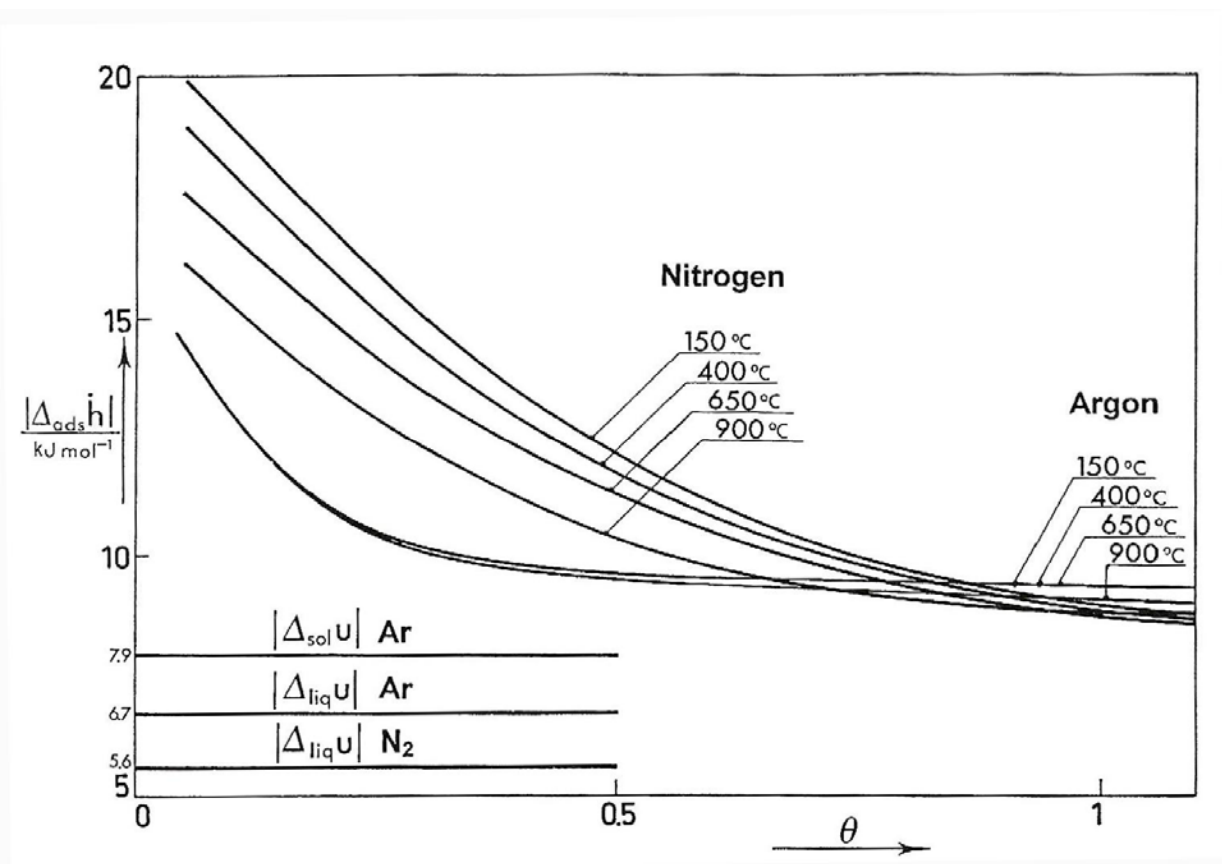
- 1/ Do we know the "true" cross-sectional area " $\sigma$ " of the adsorbed molecule in the statistical monolayer ?
  - 2/ Should we use the BET equation for microporous adsorbents ?
  - 3/ How to make  $n_m$  a highly reproducible quantity and to make the BET method as useful as possible in spite of its limitations ?
-

# Issues for the application of the BET method

1/ Do we know the "true" cross-sectional area " $\sigma$ " of the adsorbed molecule in the statistical monolayer ?

- \* If yes, why BET ( $N_2$ ) areas on non-microporous adsorbents are consistently larger than BET (Ar) surface areas ?
- \* First explanation:  $\sigma$  is OK for  $N_2$  (confirmed by Harkins and Jura, with their « absolute » immersion calorimetry method... but by a single experiment on a single  $TiO_2$  sample !), whereas Ar would be adsorbed in a loose arrangement
- Second explanation:  $\sigma$  is OK for Ar (spherical molecule), whereas ellipsoidal  $N_2$  is oriented, « standing » on the surface, depending of the interaction of its quadrupole with the surface. Interaction confirmed by calorimetry.  $\sigma$  ( $N_2$ ) probably ranges between 0.11 and 0.162 nm<sup>2</sup>

# Calorimetric determination of specific interaction of N<sub>2</sub> with OH groups



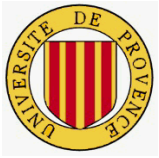
For Ar, no effect of concentration of OH groups

For N<sub>2</sub>,  $\Delta_{ads} H$  increases by 3kJ from bare to fully hydroxylated surface

Enough to explain orientation of N<sub>2</sub> molecule on surface

# Issues for the application of the BET method

- 1/ Do we know the "true" cross-sectional area " $\sigma$ " of the adsorbed molecule in the statistical monolayer?
  - 2/ Should we use the BET equation for microporous adsorbents?
  - 3/ How to make  $n_m$  a highly reproducible quantity
-



# Issues for the application of the BET method

2/Should we use the BET equation for microporous adsorbents ?

A/ We know that we should not, since microporous materials hardly fulfil basic BET assumptions:

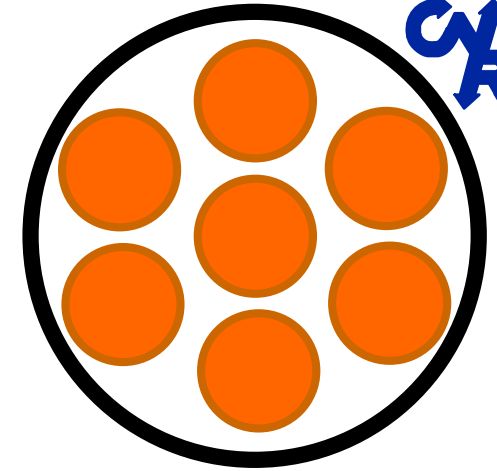
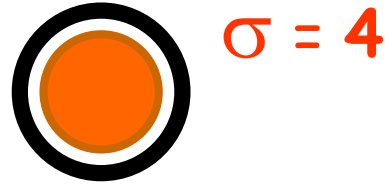
- ⌘ The adsorption surface is **never uniform**
- ⌘ **Multilayer adsorption is impossible in ultra micropores**
- ⌘ The **area covered** by an adsorbate molecule is **never known !**



# Area covered by an adsorbed molecule

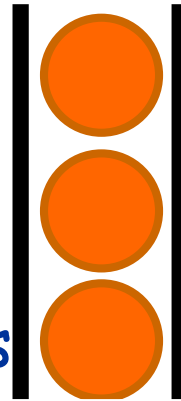


Cylindrical micropores



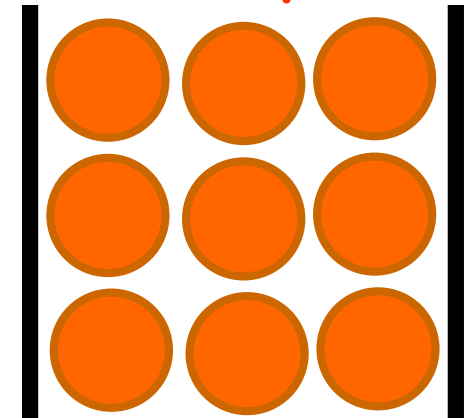
Flat surface

$\sigma = 2$



$\sigma = 0,85$

$\sigma = 0,6$



Flat, slit-shaped micropores

$\sigma$  = cross-sectional area

Ultramicropores  
(width=1 mol.diameter)

Supermicropores  
(width= 3 mol.diameter)



## 2/Should we use the BET equation for microporous adsorbents ? (continued)



B/ We like it, and find it convenient to use !

- ⌘ It provides a surface area, expressed in  $\text{m}^2$ , which **speaks to the imagination**
- ⌘ Our excuse: we **do not know in advance** whether the material is microporous or not
- ⌘ It allows to « sell » carbons with **surface areas as high as  $3700 \text{ m}^2\text{g}^{-1}$**  and MOF's with surface areas of up to  **$7000 \text{ m}^2\text{g}^{-1}$** ! ( even if no adsorbent can exist with more than  $2700 \text{ m}^2\text{g}^{-1}$ )
- ⌘ Above all, the specific surface area looks like a **universal concept** and looks **easy to assess** experimentally





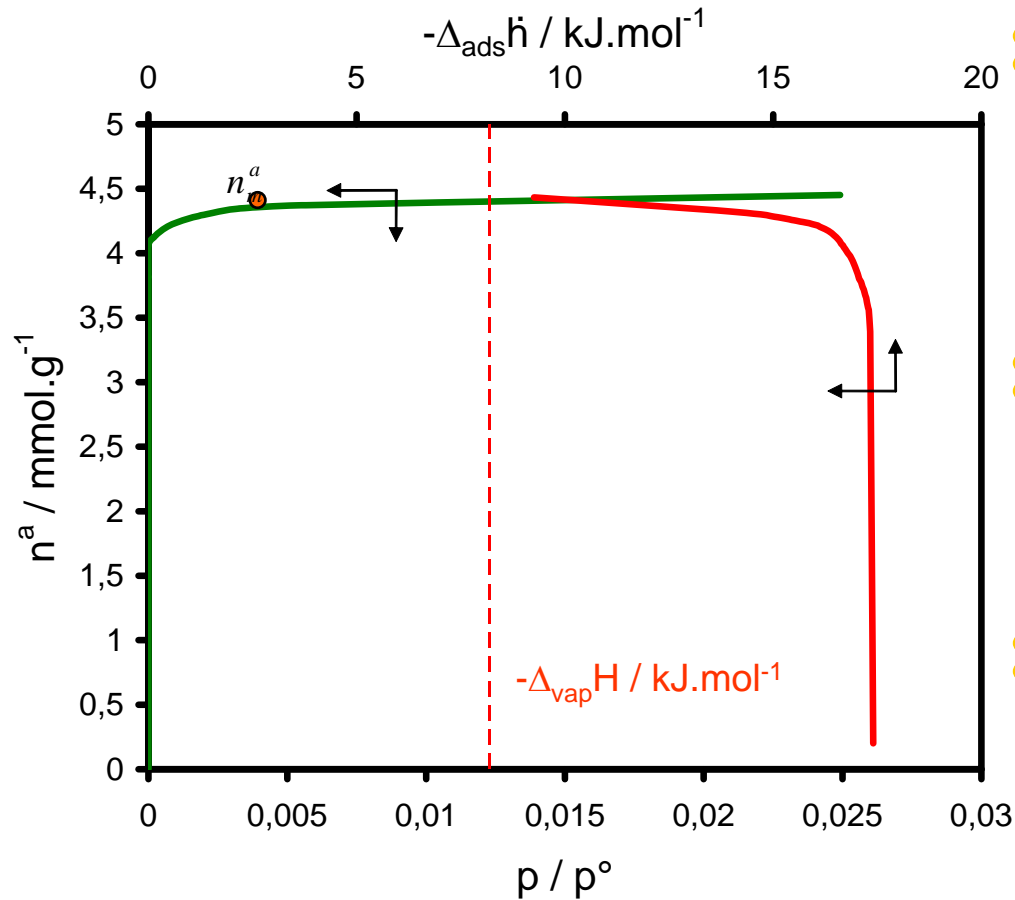
2/ Should we use the BET equation for microporous adsorbents ? *(continued)*

C/ What is therefore the **actual meaning of  $n_m(BET)$**  when micropores are present?

- It embraces the amount adsorbed to **fill the micropores** and to cover the **external surface with a monolayer**
- It corresponds to the **most strongly adsorbed portion of the adsorbate**

# Methane on Silicalite at 77 K

(Llewellyn *et al*, 1993)



- ⌘ Only direct adsorption microcalorimetry allows to assess  $\Delta_{\text{ads}} h$  during the micropore filling
- ⌘ Dramatic decrease of  $\Delta_{\text{ads}} h$  as the « BET monolayer » is completed
- ⌘ The « BET monolayer » therefore corresponds to the most strongly adsorbed portion of the adsorbate

# Issues for the application of the BET method

- 1/ Do we know the "true" cross-sectional area " $\sigma$ " of the adsorbed molecule in the statistical monolayer?
  - 2/ Should we use the BET equation for microporous adsorbents?
  - 3/ How to make  $n_m$  a highly reproducible (and useful!) quantity
-

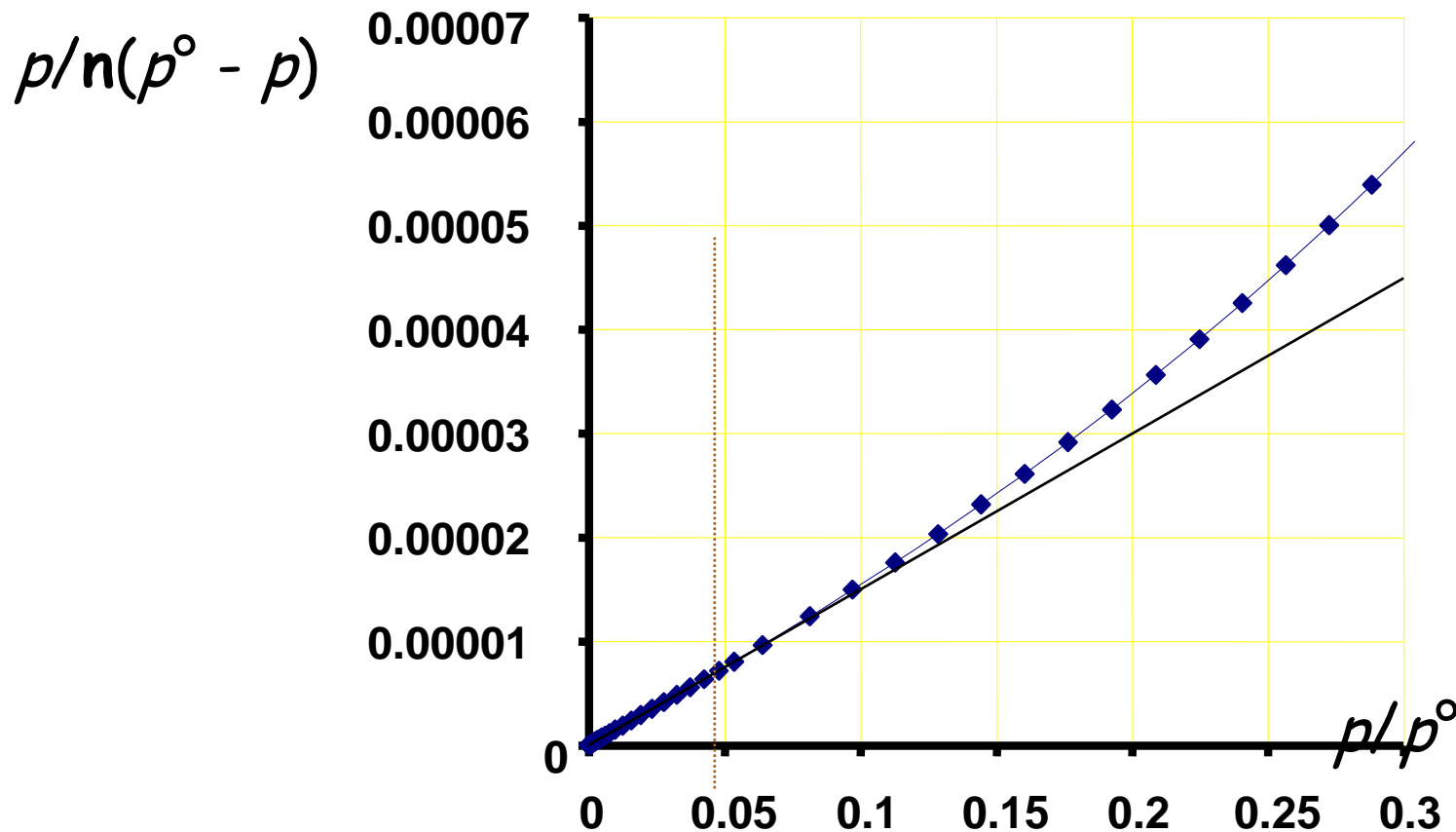


### 3/ How to make $n_m$ a highly reproducible quantity



- ⌘ Not simply a problem of isotherm determination (good equipment...and satisfactory equilibration time)
- ⌘ A problem of calculation
- ⌘ When micropores are present, (a frequent case...) always ambiguous location of *the* straight part of the BET plot
- ⌘ Which part should be selected ?

BET plot for Ar on zeolite 13 X at 87K:  
where is the linear region ?  
 $a$  (BET) ranges from 570 to 620  $\text{m}^2\text{g}^{-1}$





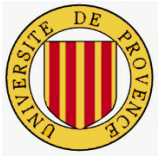
# Self-consistency criteria proposed to make the BET monolayer a reproducible quantity



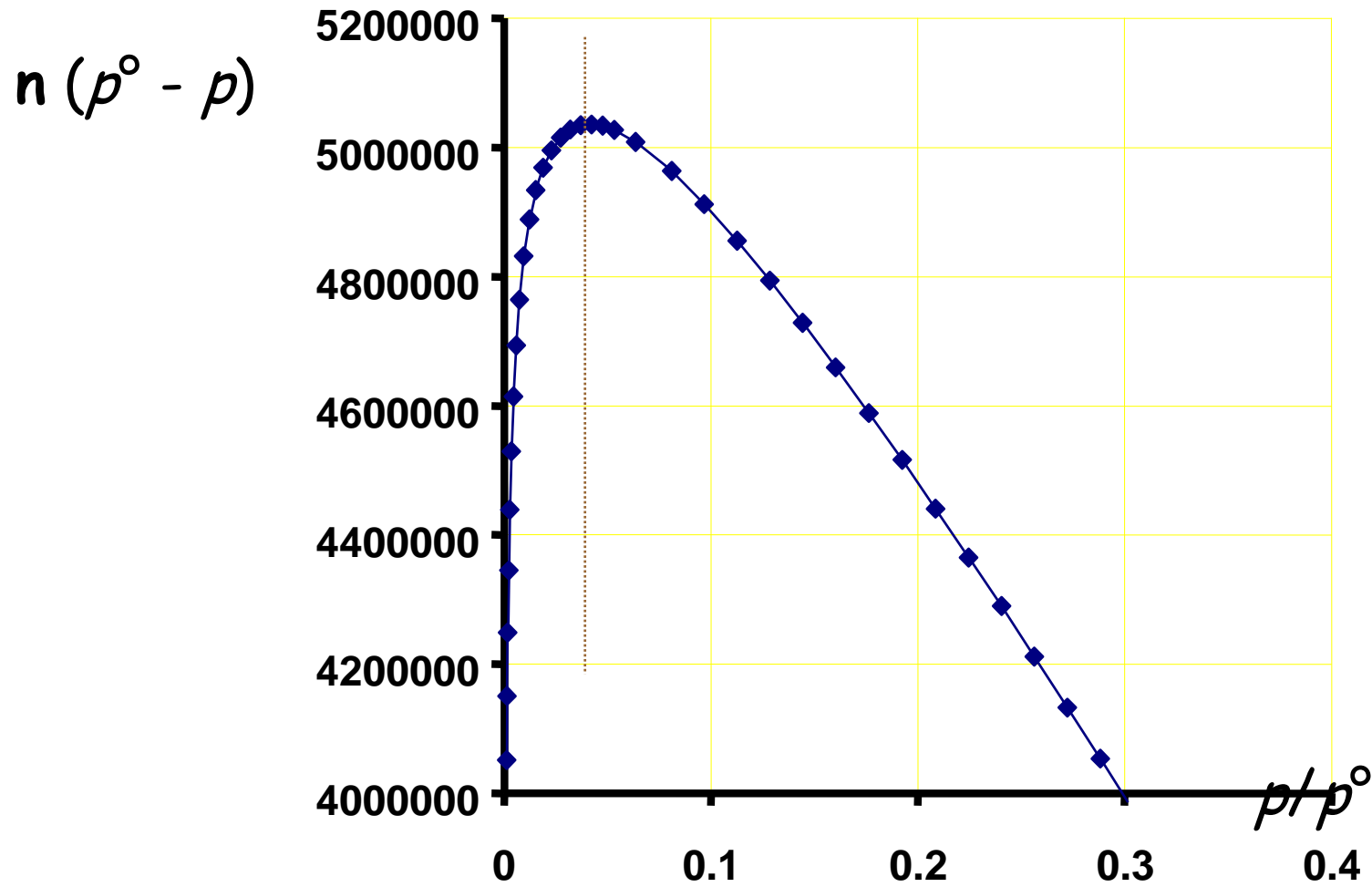
(J.Rouquerol, P.Llewellyn and F.Rouquerol, Characterization of Porous Solids VII, Elsevier, 2007, 49-56)

- 1/ The basic BET criterion: **only select straight parts** of the BET plot (inconsistent with selecting, *a-priori*, a standard pressure range)
- 2/ The straight portion selected should have a **positive intercept** on the ordinate (*ie* no negative «  $C$  », which would be meaningless)
- 3/ On the adsorption isotherm, the BET monolayer capacity should fall **within the pressure region selected** for the calculation
- 4/ The  $p/p^\circ$  for the monolayer capacity can be **re-calculated from «  $C$  »** (through the BET equation, after stating  $n^a = n^a_m$ ) and should be **close to the actual one**
- 5/ The term  $n^a (p^\circ - p)$  should **continuously increase** together with  $p/p^\circ$ : if not, the pressure range should be narrowed

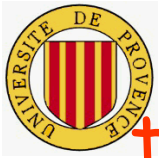
**All of the above criteria can be introduced in the software**



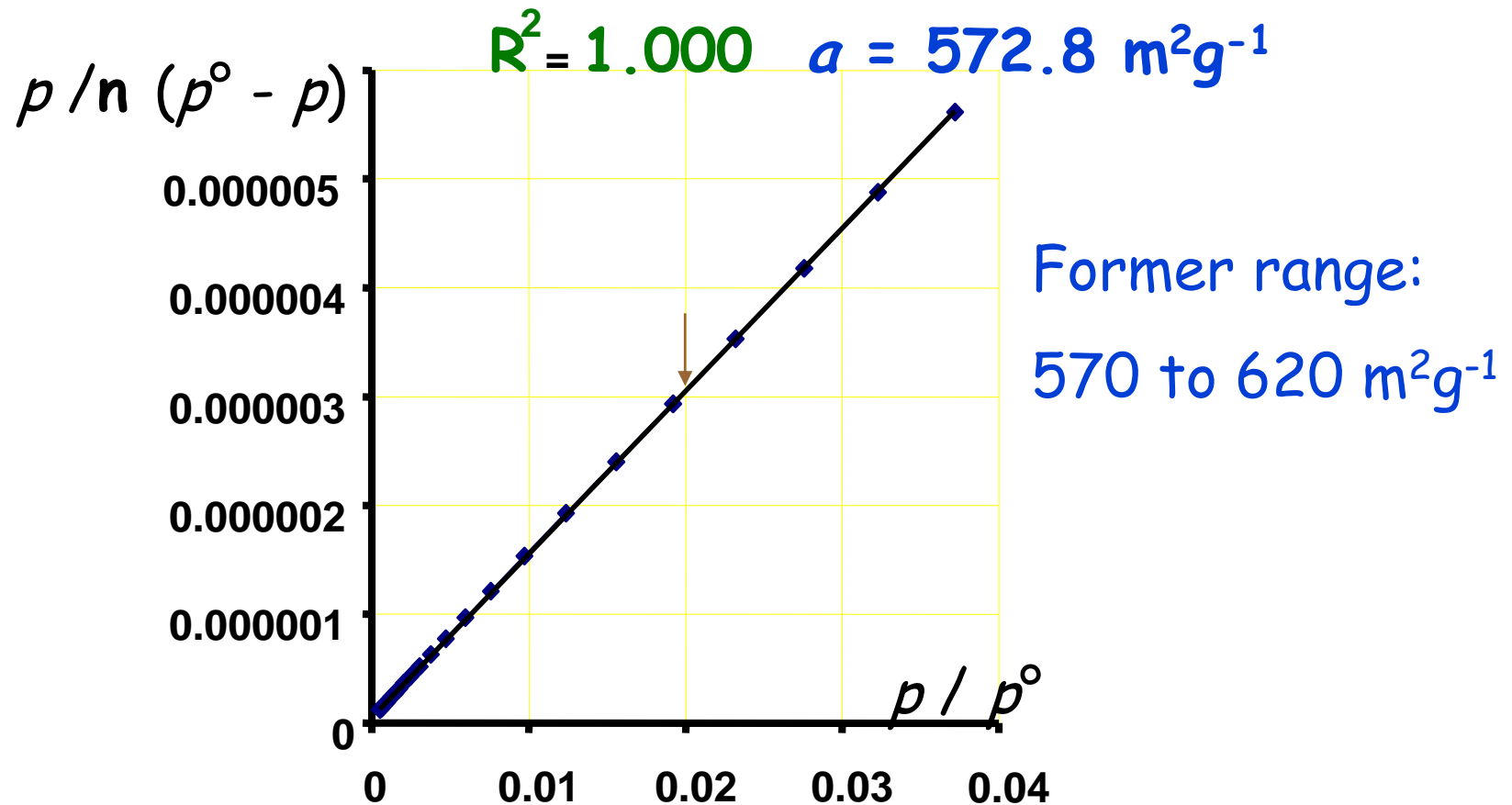
# Application of the BET equation for Ar on zeolite 13X at 87.28 K : evolution of term $n(p^\circ - p)$







# Application of the BET law to the adsorption of Ar at 87.28 K on zeolite 13X





# Gas physisorption: the basic tool to characterize adsorbents (surface area, micropores)

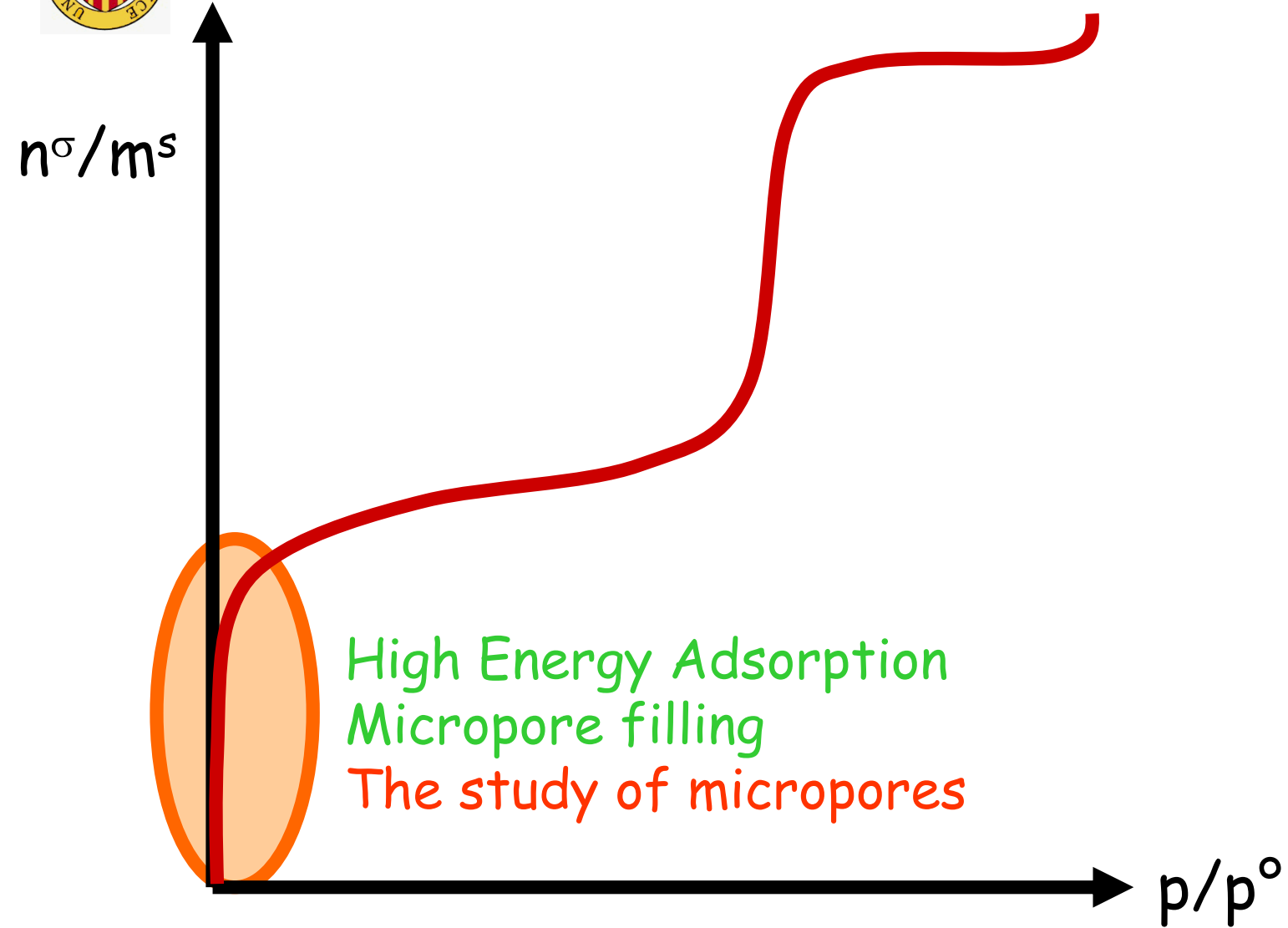


## *Outline*

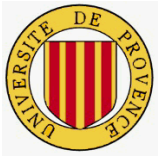
- ★ Introduction: why the basic tool ?
- ★ Landmarks and basic assumptions of the BET method
- ★ Issues raised by the BET method
- ★ The **micropore filling** : comments on t-method,  $a_s$ -method and the calorimetric approach
- ★ Conclusion: a few rules to keep in mind



# The adsorption *isotherm* of a vapour



High Energy Adsorption  
Micropore filling  
The study of micropores



# Methods to analyse type I isotherms

Dubinin's method

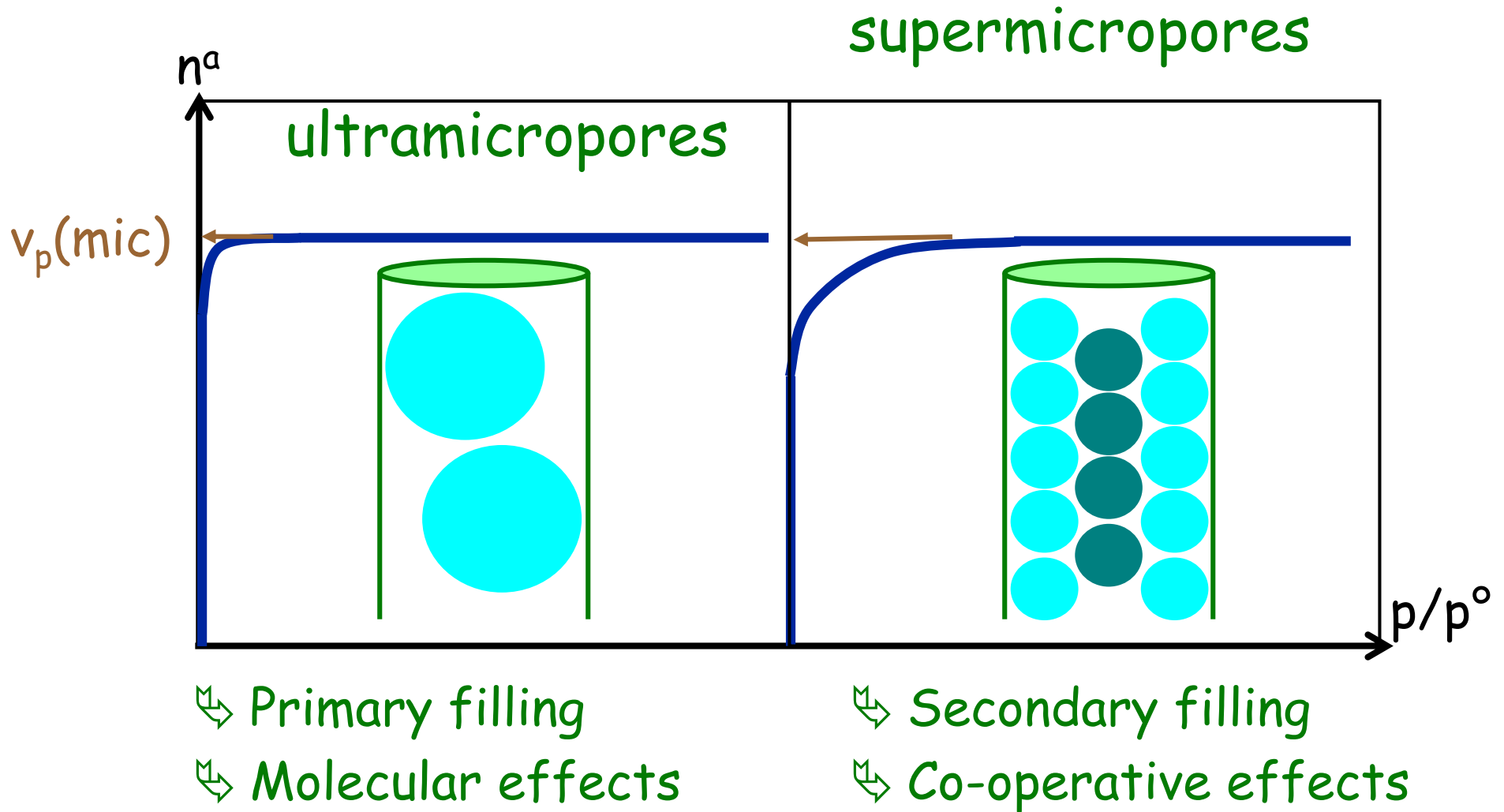
De Boer's  $t$ -method

Sing's  $a_s$  method

Horwath and Kawazoe method (HK)

Density Functional Theory (DFT)

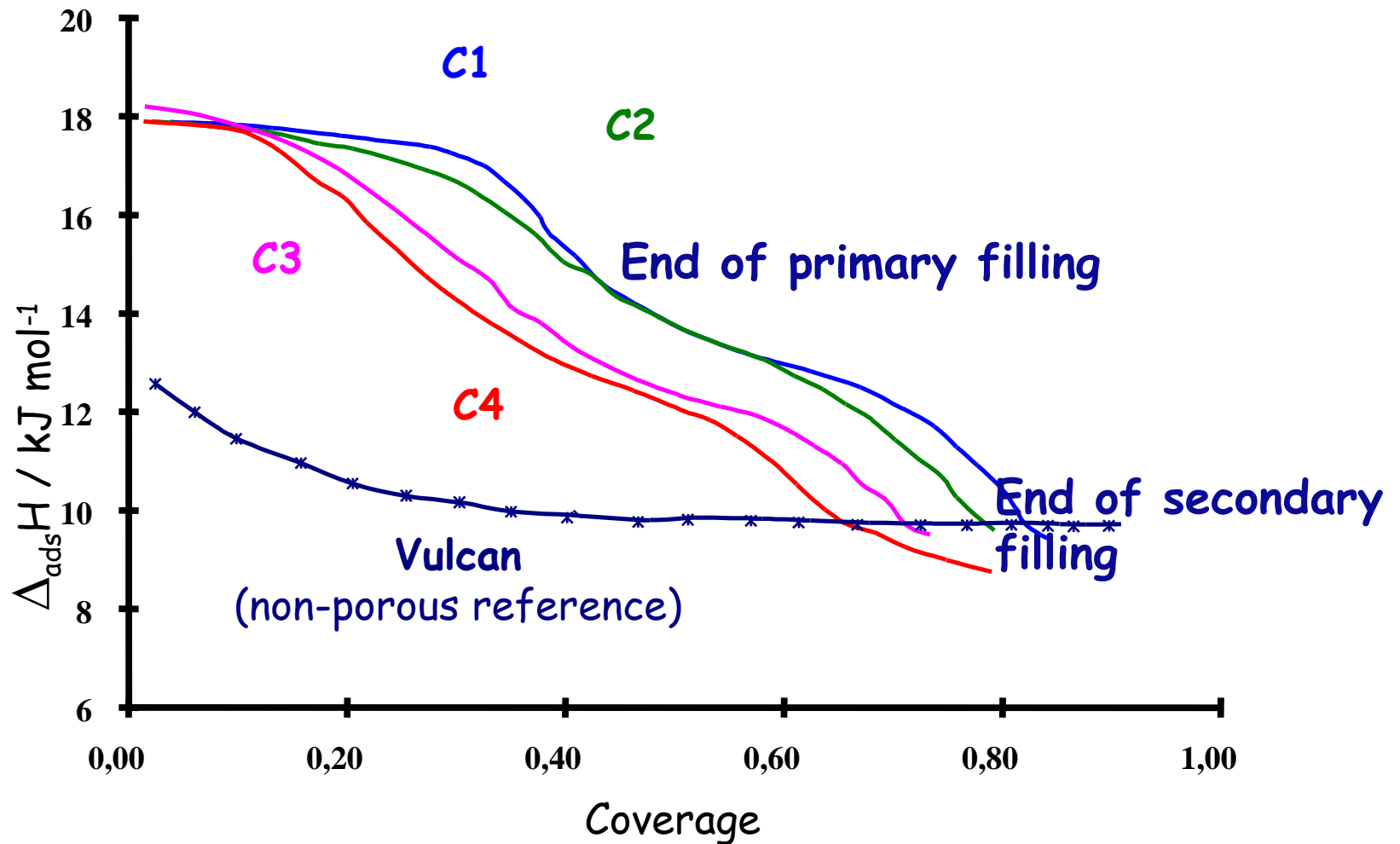
# The micropore filling mechanisms





# N<sub>2</sub> adsorption calorimetry at 77 K on microporous carbons

(Note: Ar adsorption calorimetry curves very similar, showing enhancement due to confinement, not to chemical heterogeneities)





# Jan Hendrik De Boer , 1899-1971

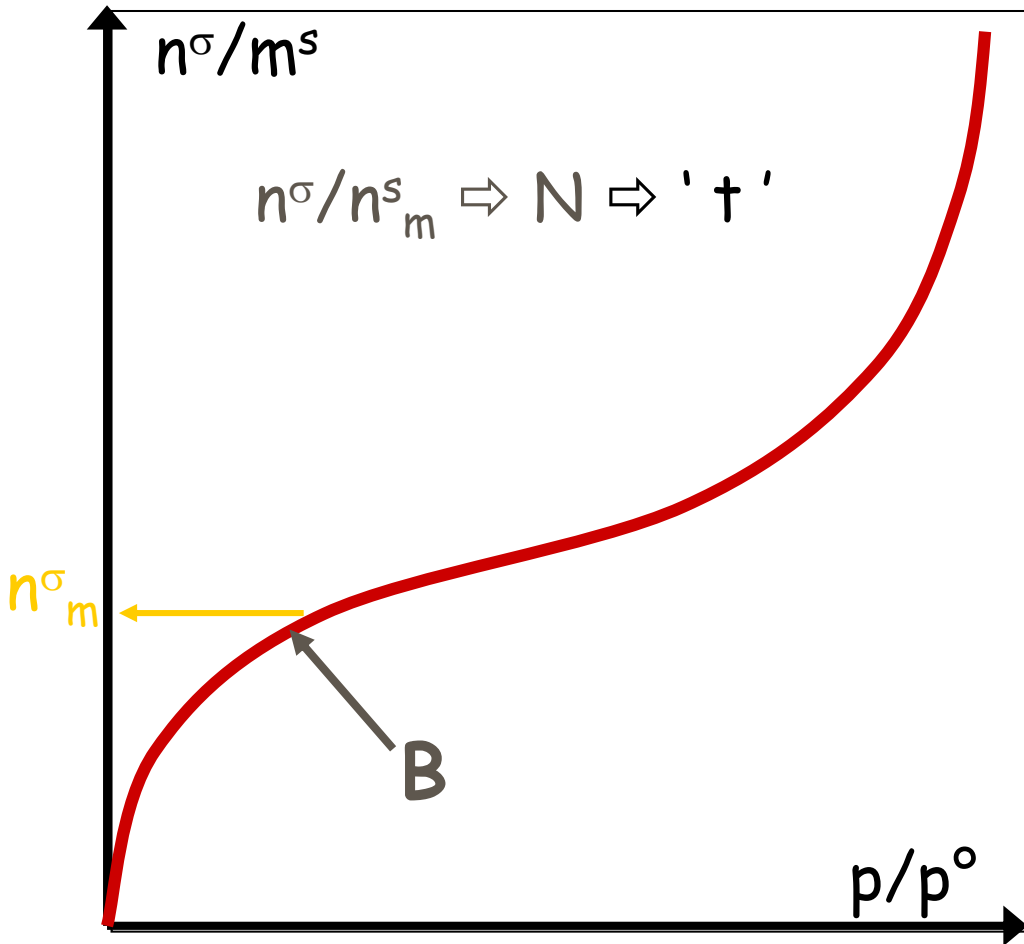


PROFESSOR DR. J. H. DE BOER

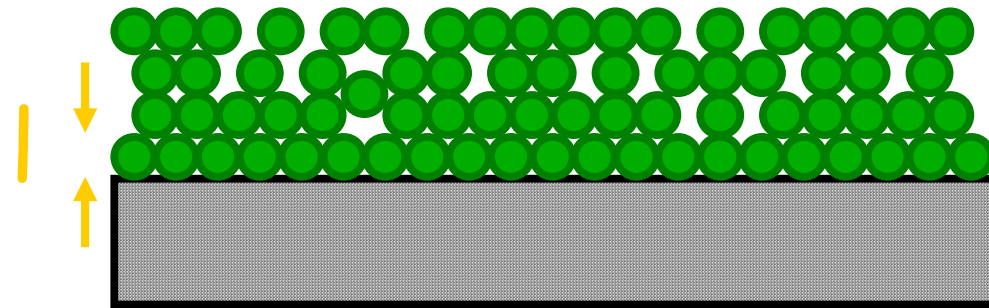
Laboratoire Chimie Provence, Site MADIREL, CNRS-Université de Provence, Marseille



# Construction of the universal 't' curve



1. Reference isotherms  
on **non-porous** oxides
  2.  $n_m^s = \text{BET monolayer}$
  3. Number of adsorbed layers  
 $N = n^s / n_m^s$
  4. Monolayer thickness "t<sub>1</sub>"  
 $t_1 (\text{N}_2) = 0.354 \text{ nm}$
  5. Thickness of adsorbed layers  
 $t = N \times t_1$
- ⇒ Universal 't' Curve



# "t" method (de Boer) [1]

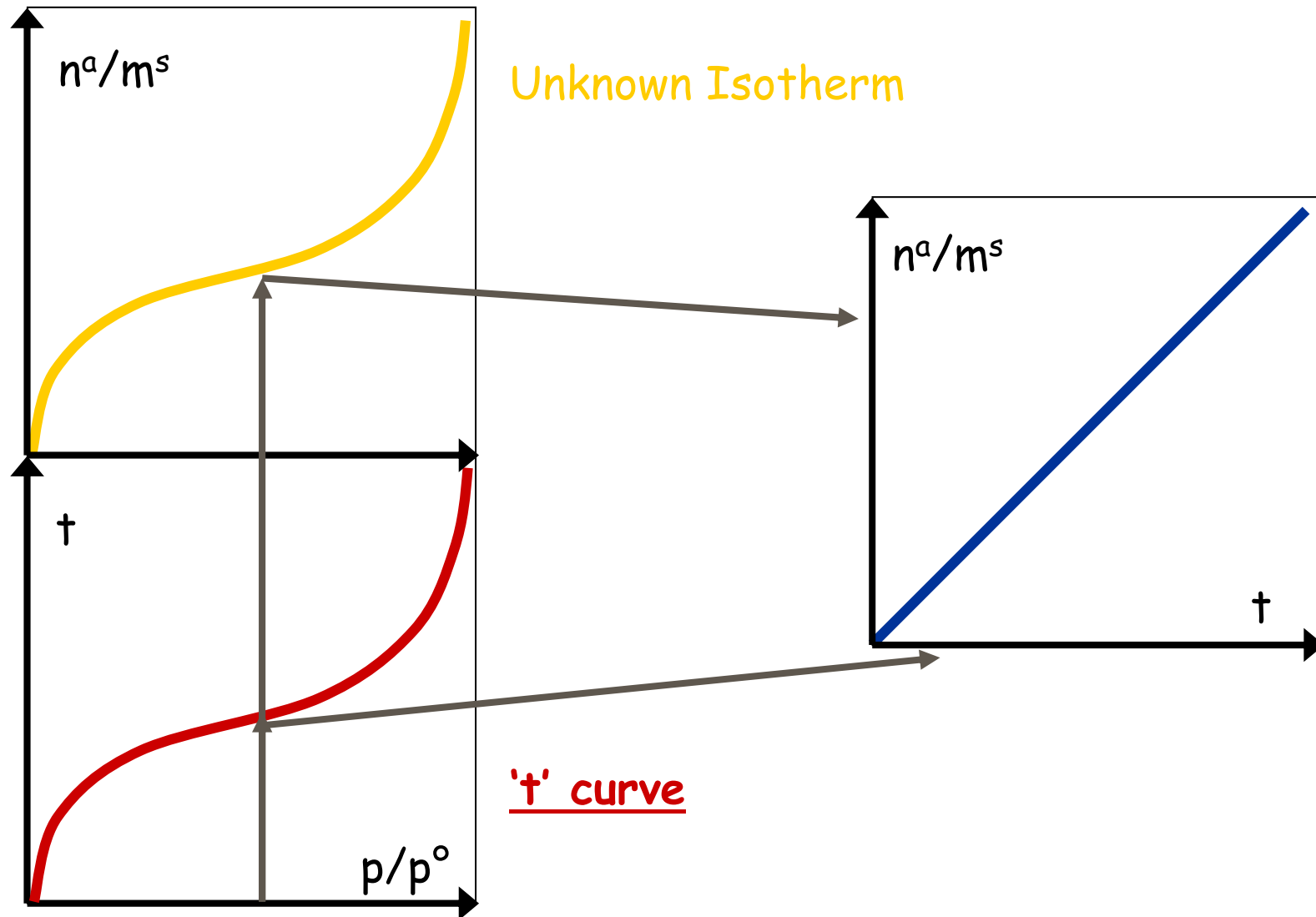
Non-porous solids → multimolecular adsorption

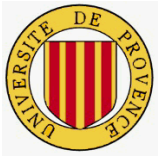
- $t$  (thickness of the adsorbed layer) increases with  $p/p^\circ$  according to a

"universal t curve" [=  $0,354 n^a/n_m = f(p/p^\circ)$ ]

- the layer (supposed liquid) covering the surface  
A occupies a volume  $V^l$  :  $V^l = A \cdot t$

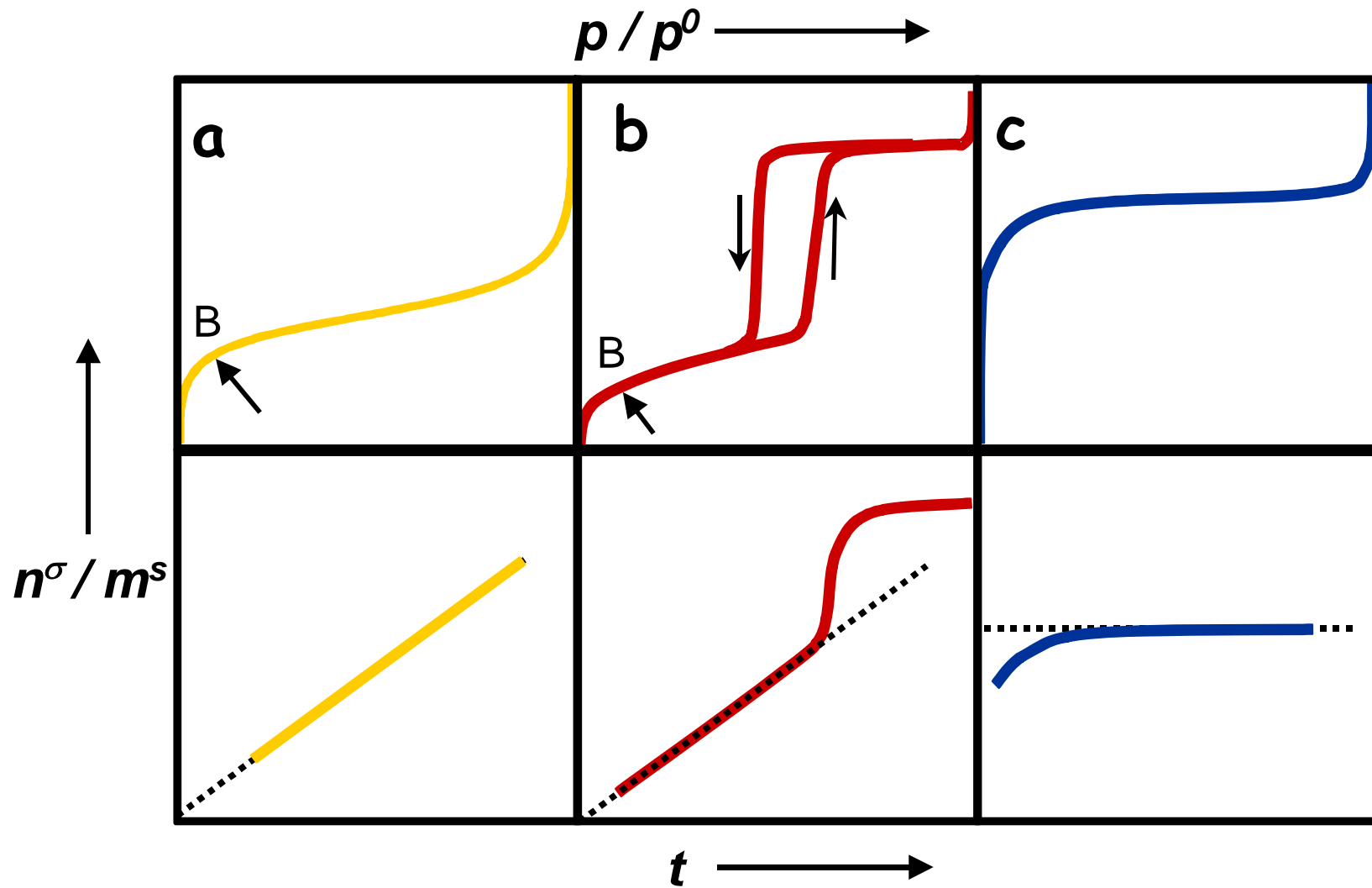
# Construction of the t-plot



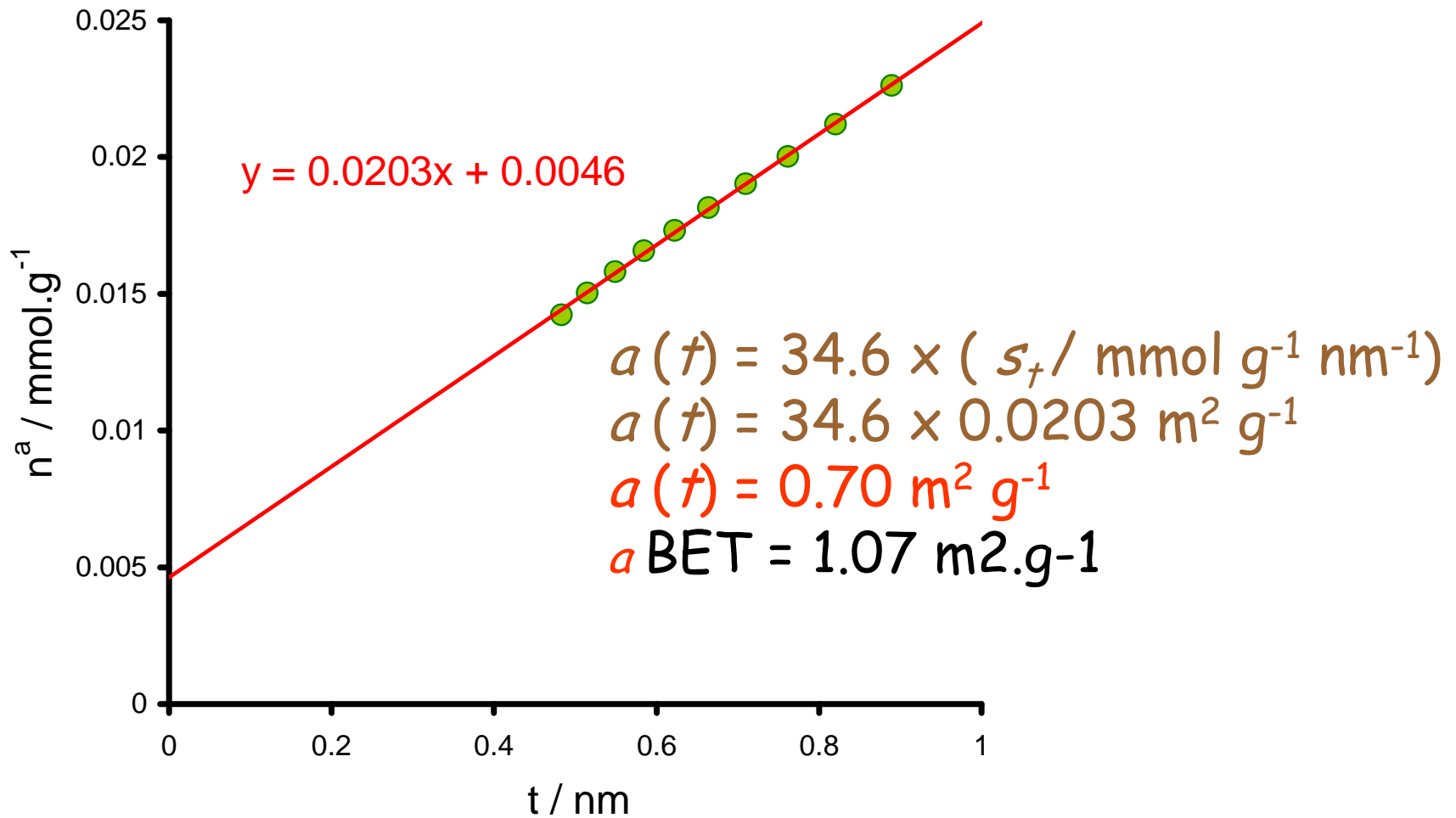


# Isotherms and corresponding 't' plots:

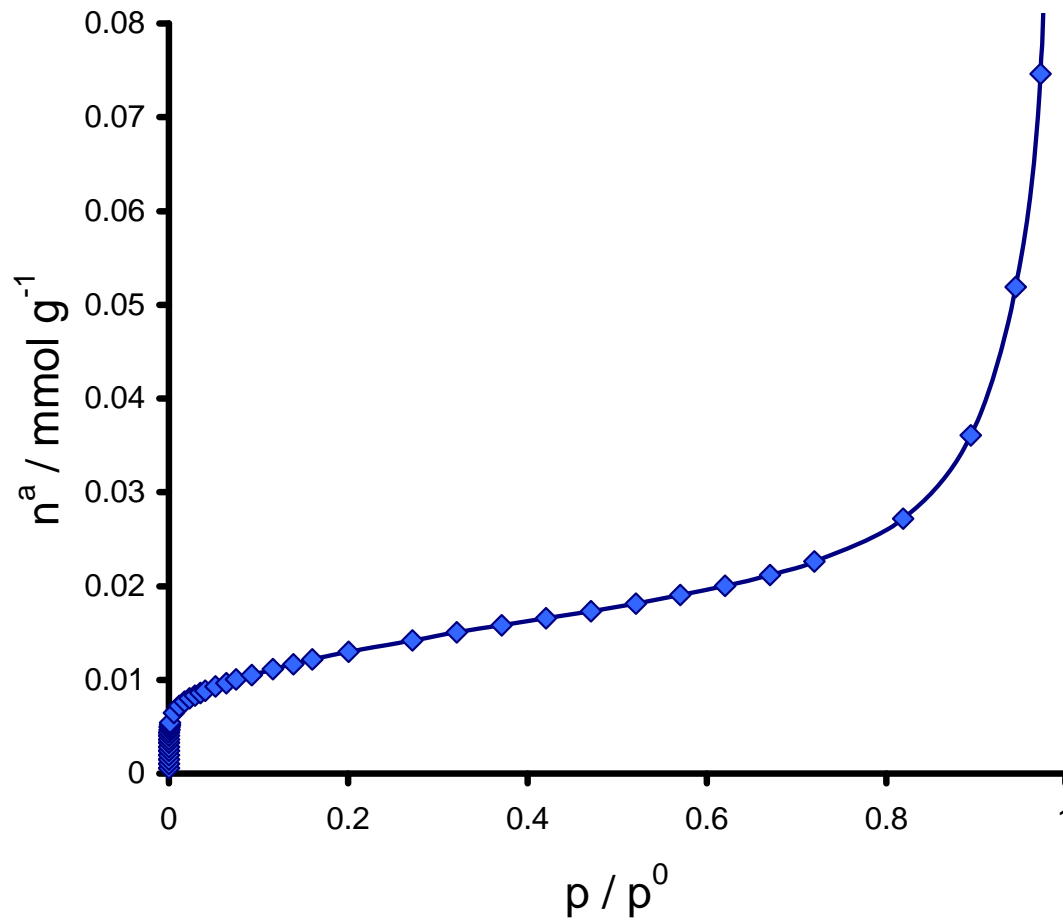
One easily detects any pore-filling mechanism and can assess the "external" surface after the filling



# Treatment of the isotherm using the 't' method example : alumina NPL / N<sub>2</sub> / 77 K



# Comparison of specific surface areas obtained : alumina NPL / N<sub>2</sub> / 77 K



$$a_{\text{BET}} = 1.07 \text{ m}^2 \cdot \text{g}^{-1}$$

$$a_{\text{t}} = 0.7 \text{ m}^2 \cdot \text{g}^{-1}$$

$\alpha_s$  method of Ken Sing  
K. S. W. Sing, Chem. & Ind., 1968, p.1520-1521.

## Criticisms of the 't' method

- The 't' method relies on the BET method and assumptions therein
  - ↳ Assumes that the adsorbate is liquid of hexagonal closed packed structure
  - ↳ Not really the case for the first adsorbed layer
- Low pressure adsorption depends strongly on the chemical nature of the surface, to expect a universal comparison curve is therefore unreasonable.





# $\alpha_S$ method (Sing)

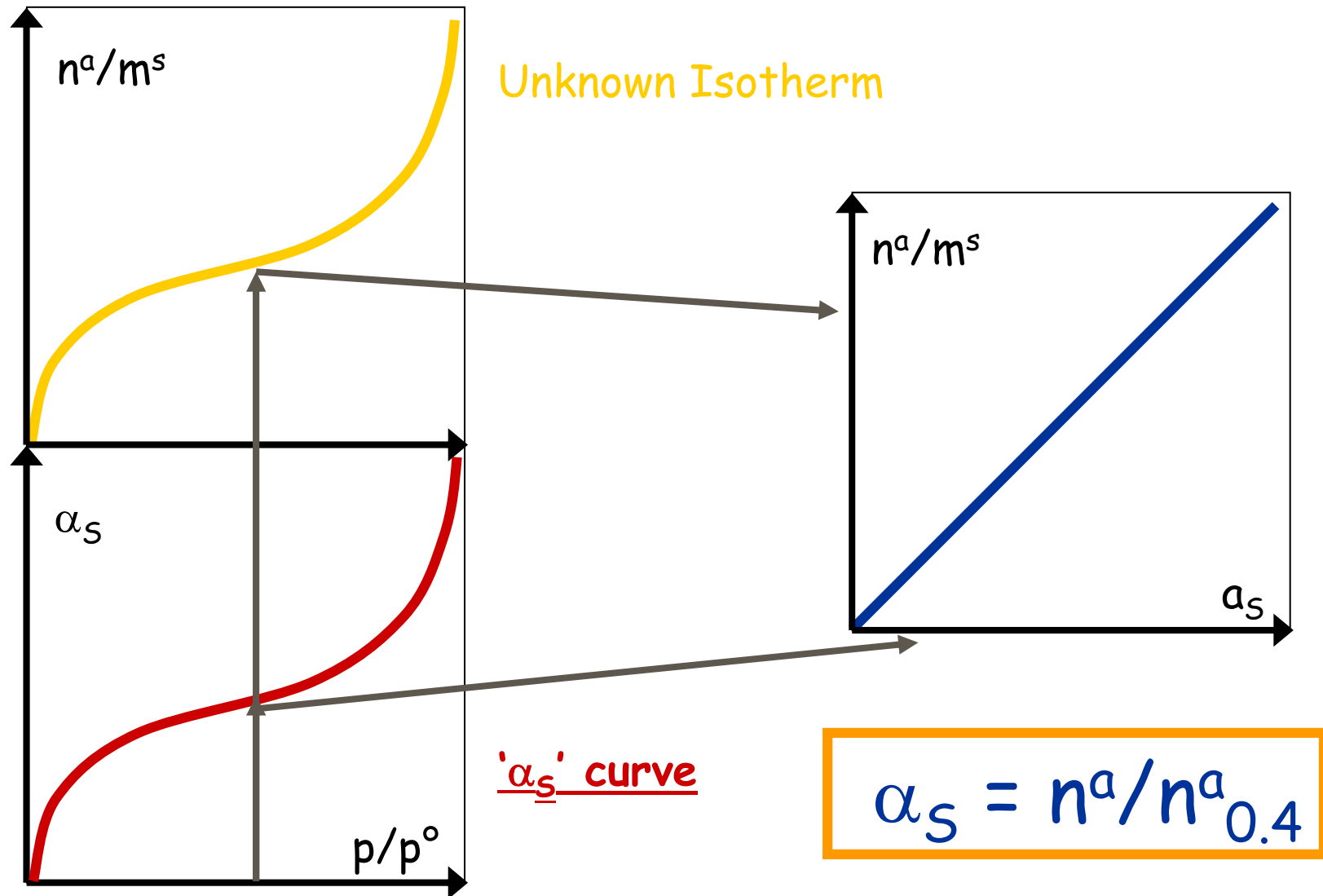
⌘ Replace  $t$  by  $\alpha_S = \frac{n^a}{n_{0,4}^a}$

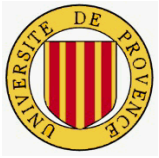
- ◆ non-porous reference  
(same chemical nature)  $\rightarrow \alpha_S$  curve
- ◆ unknown substance  
 $\rightarrow$  "transformed  $\alpha_S$  curve"

⌘ If linear region of slope  $s_S$

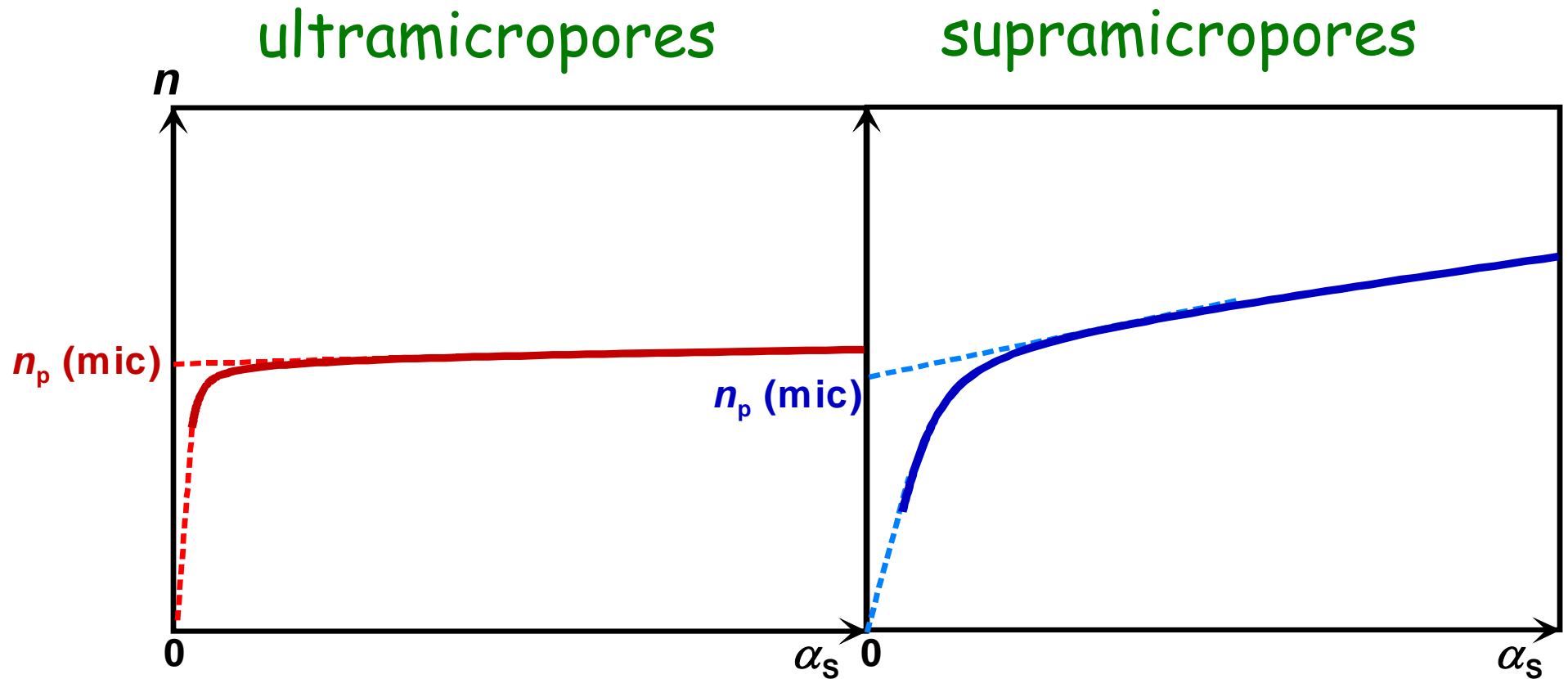
$$a_{\text{test}} = \frac{a_{\text{ref}}}{(n_{\text{ref}}^a)_{0,4}} \times s_S$$

# Construction of an $\alpha_s$ -plot



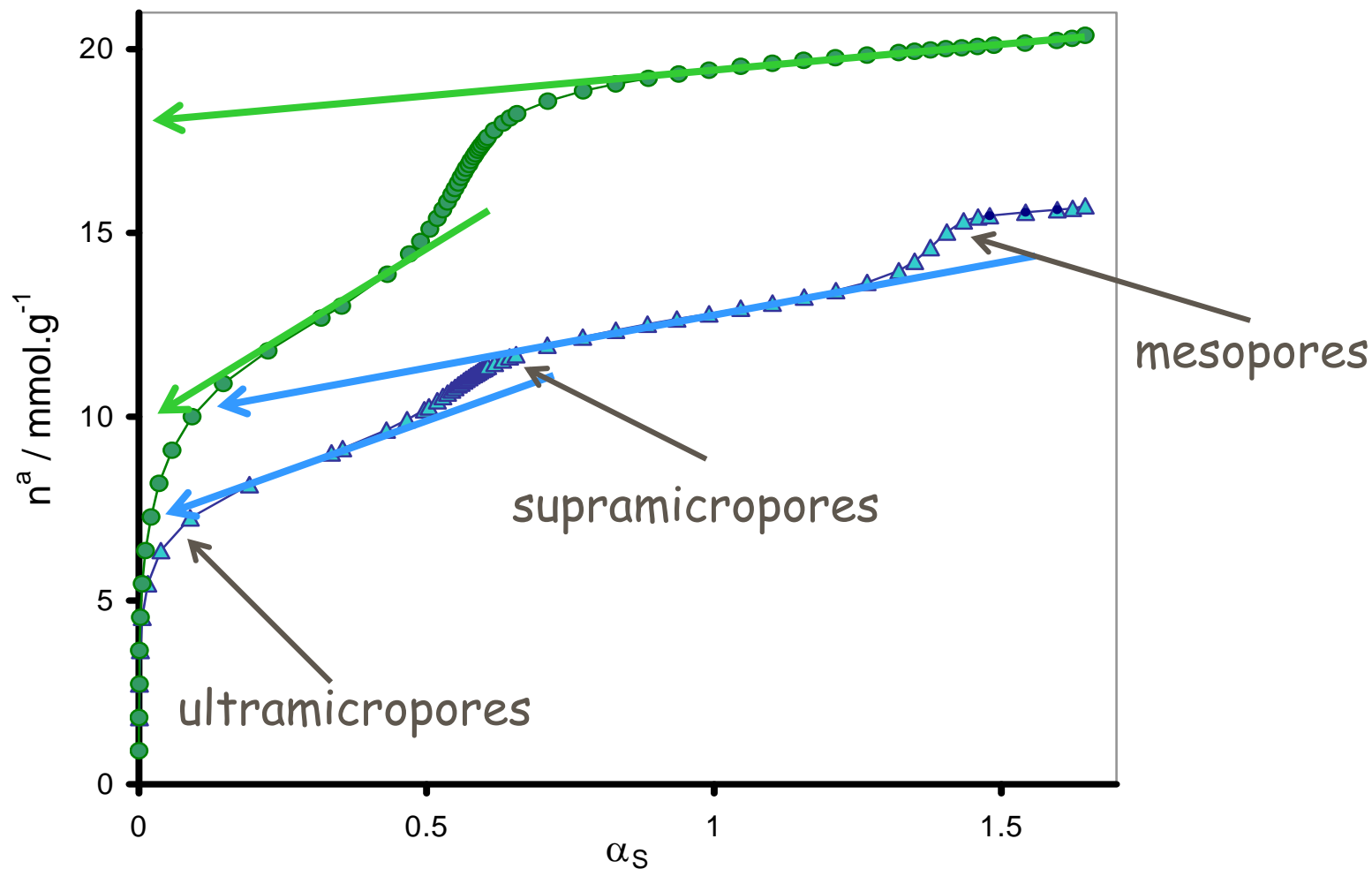


# Schematic $\alpha_s$ plots for microporous solids





# $\alpha_s$ plots obtained with carbon fibres Reference : non-graphitised carbon black



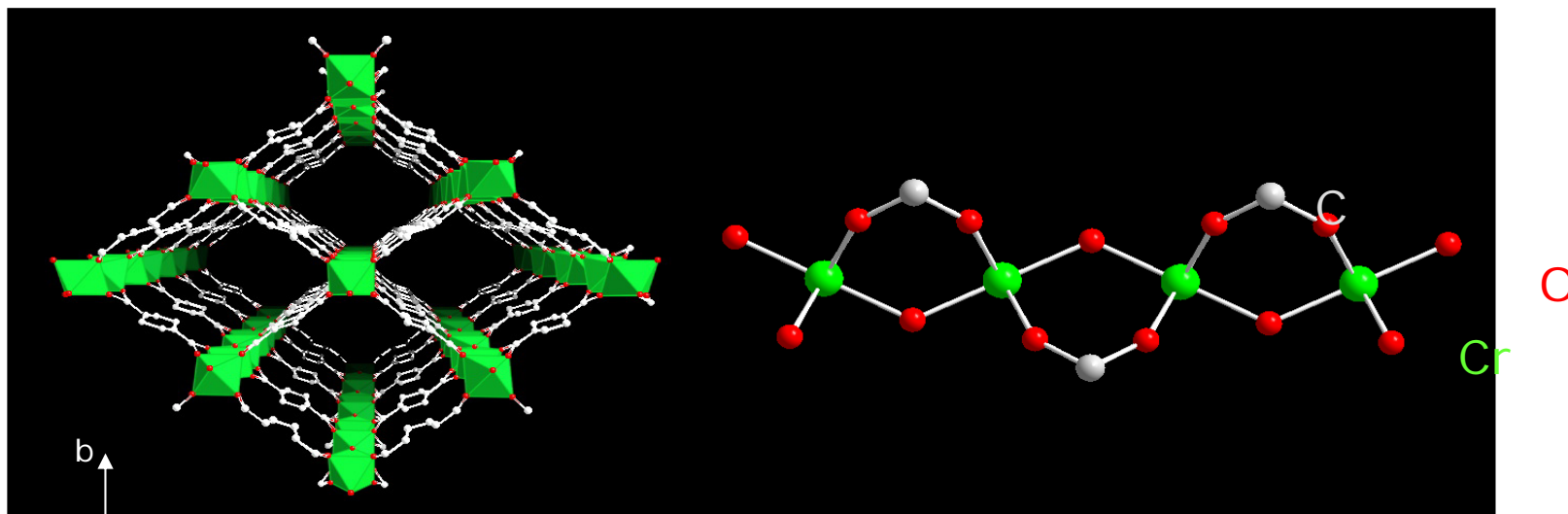


## Conclusions about the t and $\alpha_s$ methods for the characterization of microporous solids



- ⌘ The  $\alpha_s$  method is in principle sounder (avoids application of BET, takes into account specific adsorption before completion of 1st layer)
- ⌘ The t-method is much easier to apply, since the "universal" t-curve can easily enter any software
- ⌘ The  $\alpha_s$  method requires a specific reference isotherm for each chemical variety of adsorbent, which makes it more demanding

## Final story: how can calorimetry help understanding adsorption in a microporous MOF



MOF MIL-53 (Cr) : Chromium 1,4-benzenedicarboxylate

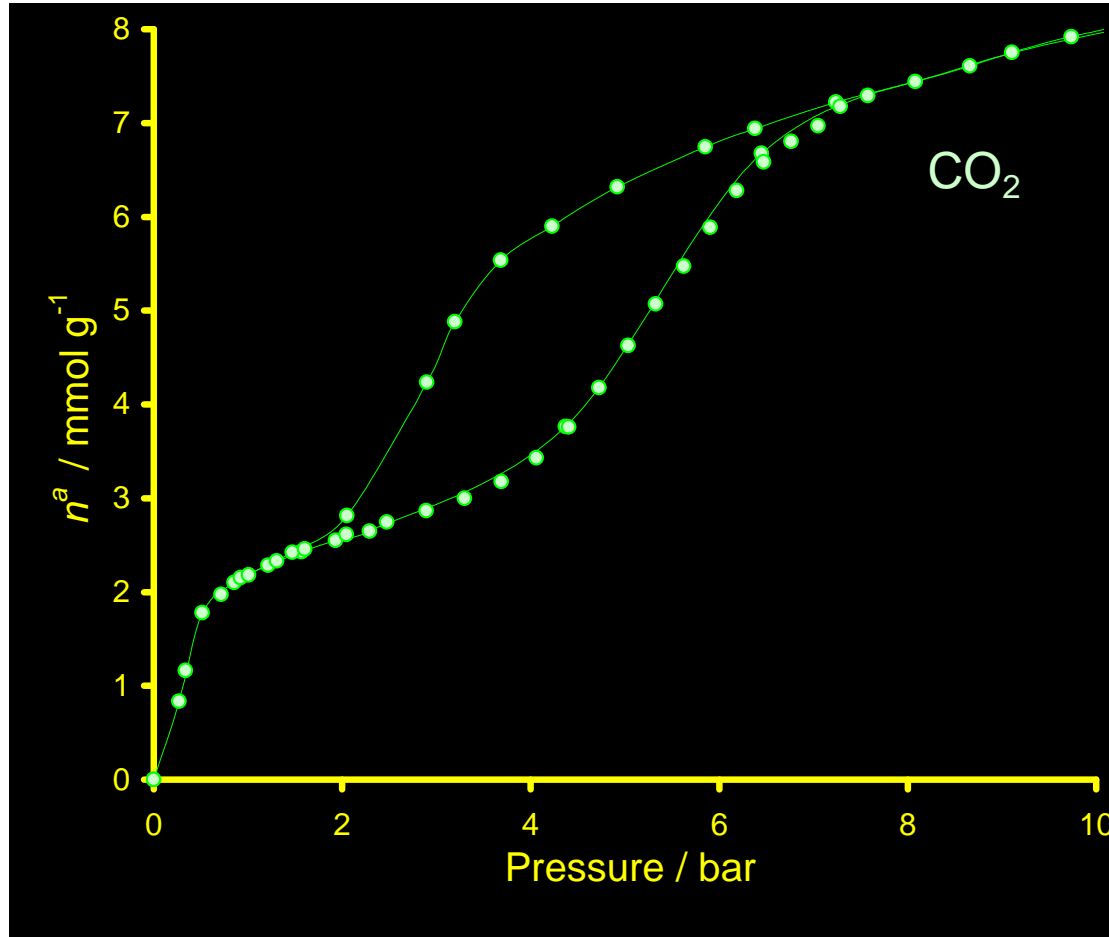


- ✓ Chains of corner-sharing  $\text{CrO}_4(\text{OH})_2$  octahedra interconnected by dicarboxylate groups
- ✓ Nanoporous open-framework with empty pores of width  $\sim 0.8$  nm

*G.Ferey et al., J.Amer.Chem.Soc.,2002*



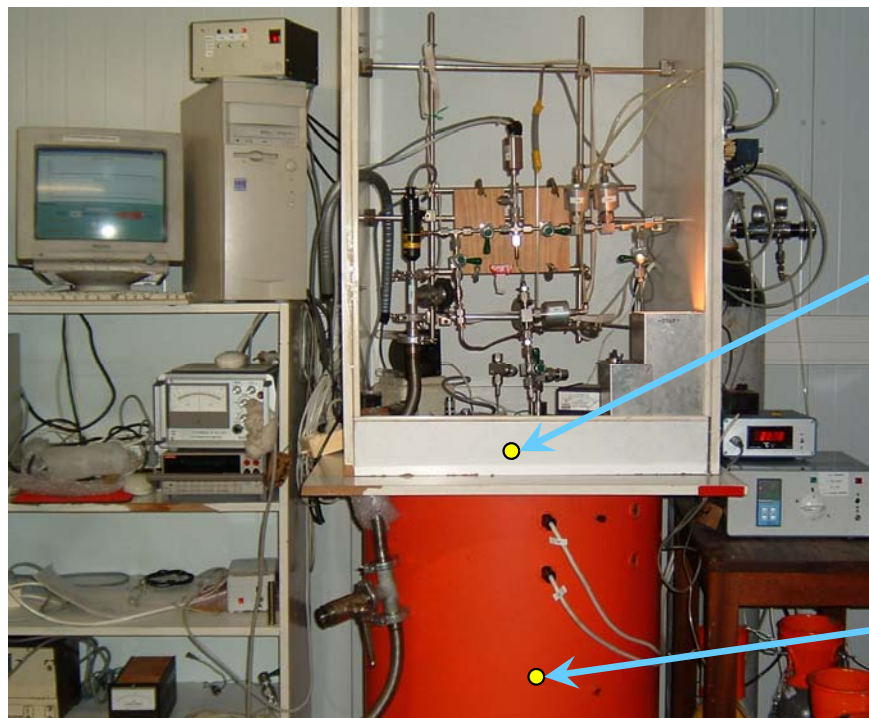
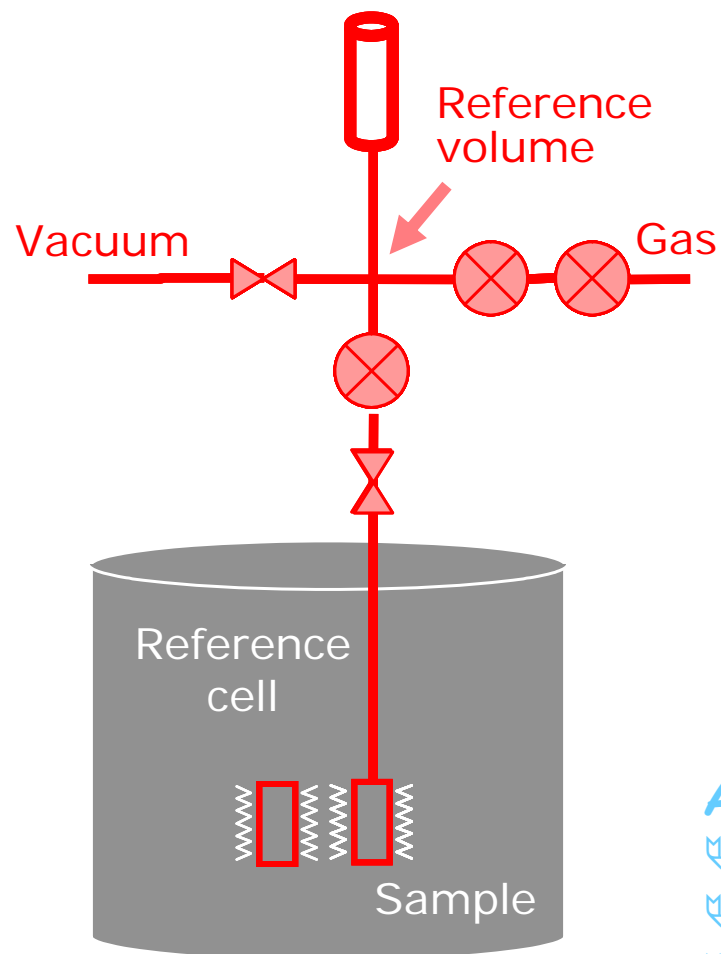
# MIL-53 : hysteresis with $\text{CO}_2$ at 304 K



Hypothesis 1  $\rightarrow$  two-step adsorption mechanism

Hypothesis 2  $\rightarrow$  structural flexibility

# Calorimetry → 50 bars



Top view



Thermopile block



Adapted to work for gas adsorption

- ↪ Up to 50 bars
- ↪ Temperature range : 20-150°C (nominal 30°C)
- ↪ ≈ 1000 thermocouples (sensitivity 5 mJ)

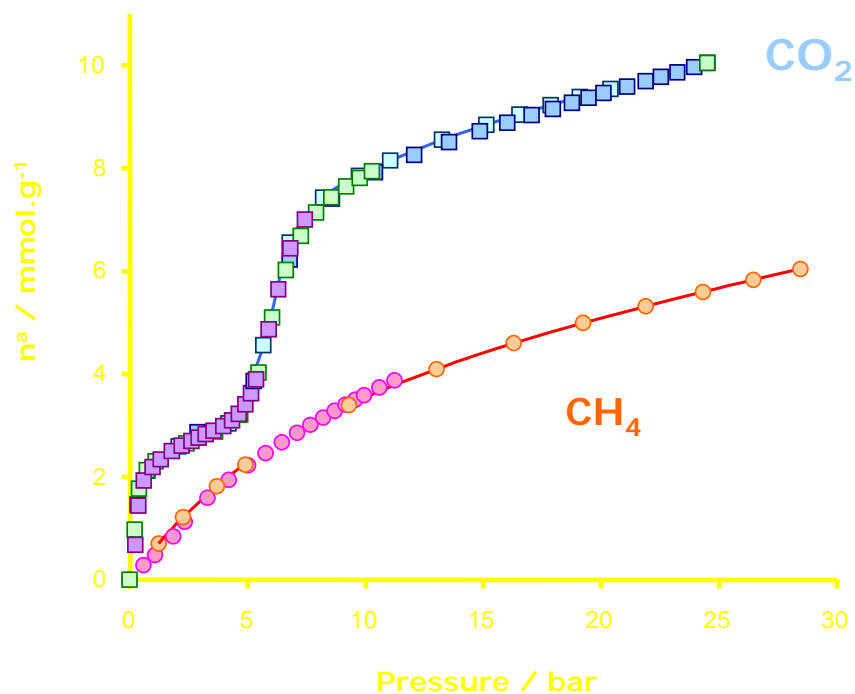




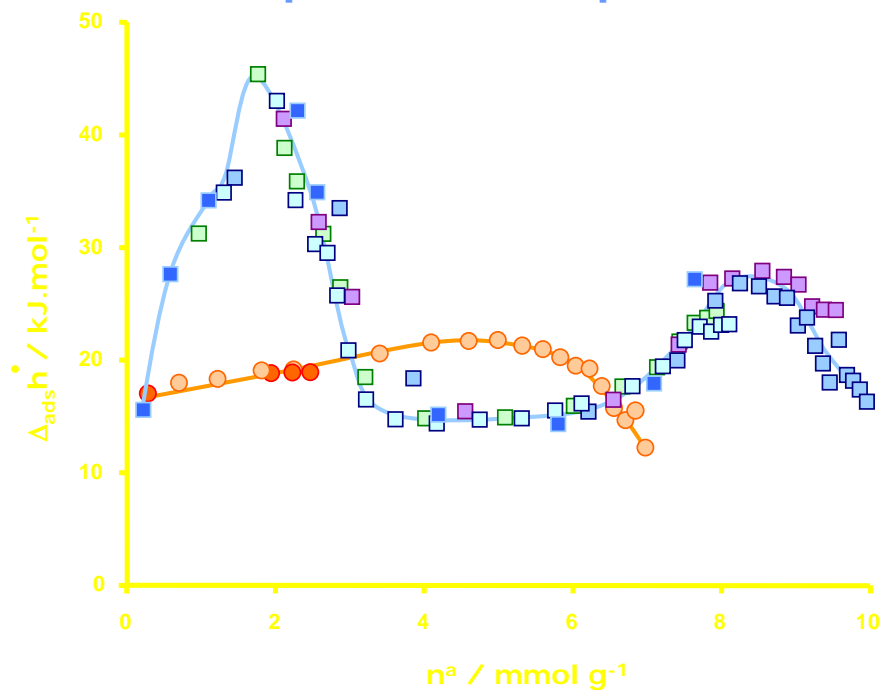
# vs. $\text{CH}_4$ on (Cr)MIL-53 @ 304K



### Isotherms



### Enthalpies of adsorption



Explanation: step (isotherm) and peak (enthalpies) correspond to enhanced interaction of  $\text{CO}_2$  with more compact porous framework.  
Why ?

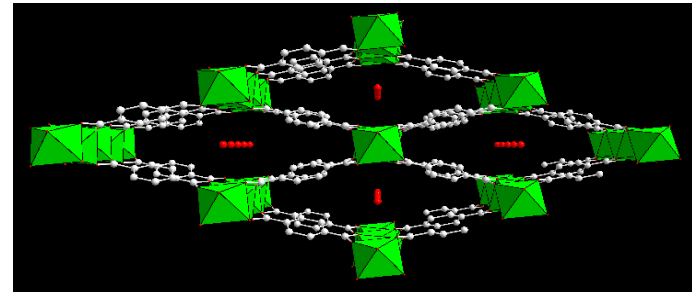
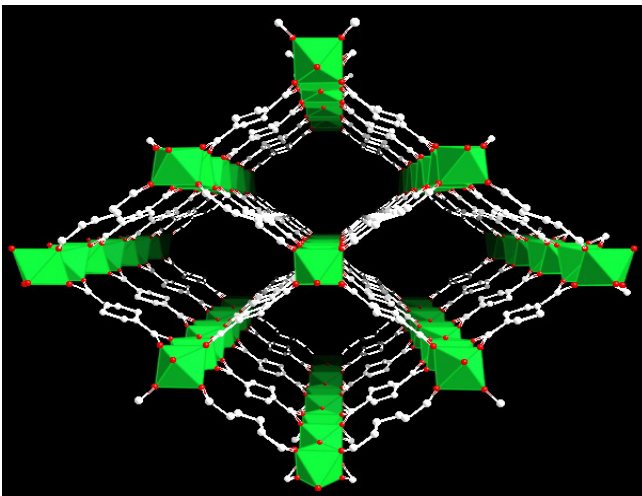


On MIL-53 (Cr),

a breathing phenomenon occurs with  $\text{CO}_2$ , like for  $\text{H}_2\text{O}$



Adsorption-desorption process is accompanied by a reversible breathing effect and shrinkage of the pores



Confirmed by synchrotron XRD (structure change) and FTIR (interaction change)

(C.Serre, S.Bourelly et al. *Adv.Mater.*2007, 19, 2246-2251)



# Finally...for the BET surface area:



- ⌘ Apply the BET equation with a few objective criteria, especially to select the appropriate pressure range
- ⌘ Do not give it an absolute meaning but, rather, that of a good and broadly employed procedure for comparison. Always state « BET( $N_2$ ) surface area »
- ⌘ For microporous adsorbents, either speak of « Equivalent BET ( $N_2$ ) specific surface area » or, even better, of « BET retention capacity »



# Finally...for the BET surface area (continued) :



- ⌘ For specific needs, other methods may be better: **immersion calorimetry** :
  - **into organic liquids, at 300K**, to assess surface area microporous carbons
  - **into liquid Ar or liquid N<sub>2</sub>** , to assess surface area of microporous oxides
- ⌘ The BET equation is a « **bright simplification** » with a kind of perfection and usefulness, for comparison purposes, **which does not need to be improved...**



# Pierre-Antoine Favre (1813-1880)



- ⌘ First Professor of Chemistry of the Faculty of Sciences of Marseilles ( 1854 )
- ⌘ Inventor, with Silbermann, of the **mercury calorimeter** or « thermometer for calories »; a huge mercury thermometer (several kg) with a finger hole to accommodate the sample
- ⌘ **First to measure and publish heats of adsorption of gases on solids (from 1854 to 1871)**

# Albert Tian (1880 - 1972)



- ⌘ Professor of Chemistry at the Faculty of Sciences of Marseille (1923-1950)
- ⌘ **Invents the heat-flux microcalorimeter**: isothermal, with a thermopile of 42 + 7 thermocouples and with Joule or Peltier power compensation
- ⌘ **Invents the multi-shielded thermostat** (stable within  $10^{-6}$  K)
- ⌘ Launches a school of calorimetry...





# Edouard Calvet (Marseille, 1895- Marseille, 1966)



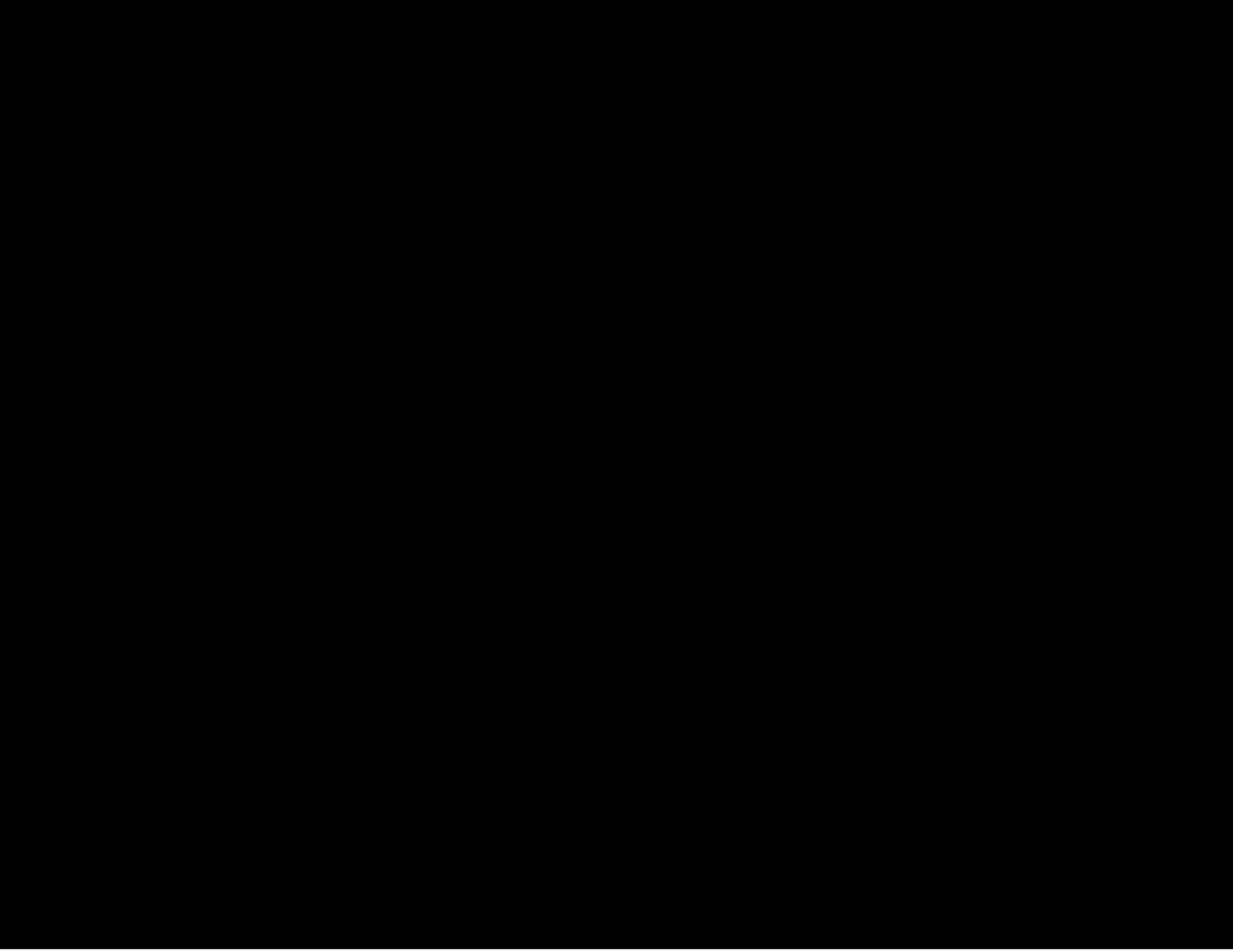
- ⌘ A. Tian's student, and then successor
- ⌘ Introduces, in 1947, the differential mounting
- ⌘ Makes the heat-flow microcalorimeter an extremely versatile piece of equipment
- ⌘ Has a special Institute built by the CNRS, in 1959, for the development of microcalorimetry

# Georgio Zgrablich



- ⌘ In San Luis, in 1985, starts a team on Physical Chemistry of Surfaces
- ⌘ In 1997, this becomes the Surface Science and Porous Media Laboratory
- ⌘ In 2007, the Institute of Applied Physics (INFAP-CONICET) is launched







# Langmuir Isotherm

$$n^{\sigma} = n_m^{\sigma} \frac{bp}{1+bp}$$

$\Rightarrow$  at low pressure  $bp \ll 1$ , therefore  $n^{\sigma} = n_m^{\sigma} bp$

Henry's Law

$\Rightarrow$  at high pressure,  $bp \gg 1$ , therefore  $n^{\sigma} = n_m^{\sigma}$

$$b = K \exp^{E/RT}$$



# Langmuir Equation



## ⊗ Thermodynamic Derivation by Volmer

⊗ M. Volmer, Z. Phys. Chem., 115 (1925) 253.

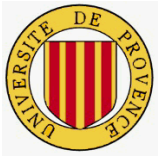
## ⊗ Statistical Derivation

⊗ R. H. Fowler, Proc. Cambridge Phil. Soc., 31 (1935) 260.

## ⊗ Derivation using the Theory Absolute Reaction Rates

⊗ K. J. Laidler, S. Glasstone, H. Eyring, J. Chem. Phys., 8 (1940) 659.

⊗ All arrive to : 
$$n^\sigma = n_m^\sigma \frac{bp}{1+bp}$$
 Linear : 
$$\frac{p}{n^\sigma} = \frac{1}{n_m^\sigma b} + \frac{p}{n_m^\sigma}$$



# Simple derivation of the BET equation(2)



$$k_{-i} s_i = k_i s_{i-1} p$$

Area of the adsorbent  $A = \sum_{i=0}^{\infty} s_i$

Total quantity of gas adsorbed

$$\frac{n}{An_0} = \frac{n}{n_m} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i}$$

If the properties of the layers are equal  $\frac{k_{-2}}{k_2} \dots \dots \frac{k_{-i}}{k_i} = g$

$$s_i = \left( \frac{k_i}{k_{-i}} \right) s_{i-1} \quad p = x s_{i-1} \quad \text{ou} \quad x = \frac{p}{g}$$

$$s_i = x s_{i-1} = C x^i s_0$$



# Simple derivation of the BET equation (3)



$$\frac{n}{n_m} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i} = \frac{C \sum_{i=1}^{\infty} i x_i}{1 + C \sum_{i=1}^{\infty} x_i}$$

$\xrightarrow{\hspace{10em}}$

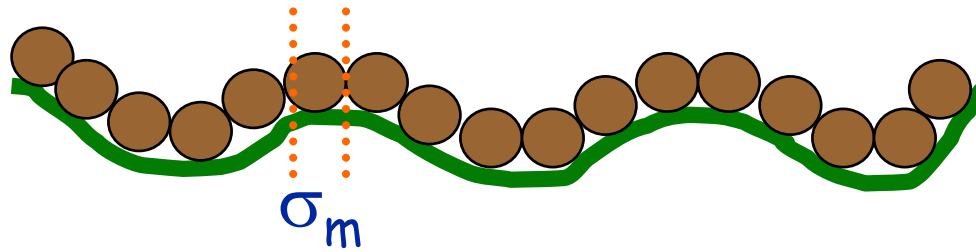
$$\sum_{i=1}^{\infty} i x_i = \frac{x}{(1-x)^2}$$
$$\sum_{i=1}^{\infty} x_i = \frac{1}{1-x}$$

$$\frac{n}{n_m} = \frac{Cx}{(1-x)(1-x+Cx)}$$

at  $p^0$  :  $\frac{Cx}{(1-x)(1-x+Cx)} = \infty$       **thus :**     $g = p^0$  ,     $x = \frac{p}{p^0}$

$$\frac{n}{n_m} = \frac{Cx}{(1-x)[1+x(C-1)]}$$

# Principle of the measurement of the specific surface area



$n_m^a$  = quantity of substance required to cover the surface with a monomolecular layer

$\sigma_m$  = area occupied by a single molecule on the surface in the monolayer

$$\frac{a}{\text{m}^2 \text{g}^{-1}} = \frac{n_m^a}{\text{mol g}^{-1}} \frac{N_A}{\text{mol}^{-1}} \frac{\sigma_m}{\text{m}^2}$$

For  $\text{N}_2$  at 77,35 K  $\sigma_m = 0,162 \text{ nm}^2$   $\frac{a}{\text{m}^2 \text{g}^{-1}} = \frac{0,097 n_m^a}{\text{mol g}^{-1}} = \frac{4,35 v_m^a}{\text{cm}^3 \text{g}^{-1}}$

where  $v_m^a$  Is the volume of adsorbed gas (STP) necessary to cover the surface of one gram of adsorbent with a single monolayer

# Cross sectional area of adsorbate molecules

## Assumptions

- \* adsorbed molecules treated as spheres of radius  $r$  occupying area  $\sigma_m$  in the completed monolayer
- \* monolayer supposed to be hexagonal compact and liquid (density  $\rho'$  at the temperature of adsorption)

## Calculations

$N_A$  Avogadro constant

$M$  Molar mass of substance adsorbed

$$\sigma_m = 1,091 \left( \frac{M}{N_A \rho'} \right)^{2/3}$$

Examples :  $N_2$  à 77,35 K  $\sigma_m = 0,162 \text{ nm}^2$      $H_2O$  à 300 K  $\sigma_m = 0,105 \text{ nm}^2$

## Issues

- The preferential orientation of the molecule can drastically change  $\sigma_m$ , as shown with help of gas adsorption calorimetry
- In micropores, area covered by molecule goes from 0 to 4 times the area above: BET does not give access to any reasonable surface area

# Suggested Practice for the Application of the BET Equation to Characterize Microporous Adsorbents

## Outline

A/Why BET for microporous adsorbents ?

B/Is the BET monolayer capacity a reproducible quantity ?

C/Is it reasonably supported by calorimetric evidence?

D/For micropores, is best suited than the Langmuir equation?

E/ For micropores, can it be meaningful and useful?

F/Conclusions

---



# Issues for the application of the BET method

## 2/ How does the BET method apply to microporous materials?

\* In theory, it should not be applied:

a/the equation assumes a **free, open**, adsorbing surface, with  $N=\infty$  (at least  $N=4$ )

b/the calculation of the surface area assumes that the molecules of the monolayer are lying **flat** on the adsorbing surface

\*

\*

•In micropores, area covered by molecule goes from 0 to 4 times the area above: BET does not give access to any reasonable surface area



# Langmuir Isotherm



$$n^{\sigma} = n_m^{\sigma} \frac{bp}{1+bp}$$

⇒ at low pressure  $bp \ll 1$ , therefore

$$n^{\sigma} = n_m^{\sigma} bp$$

Henry's Law

⇒ at high pressure,  $bp \gg 1$ , therefore

$$n^{\sigma} = n_m^{\sigma}$$

Linear

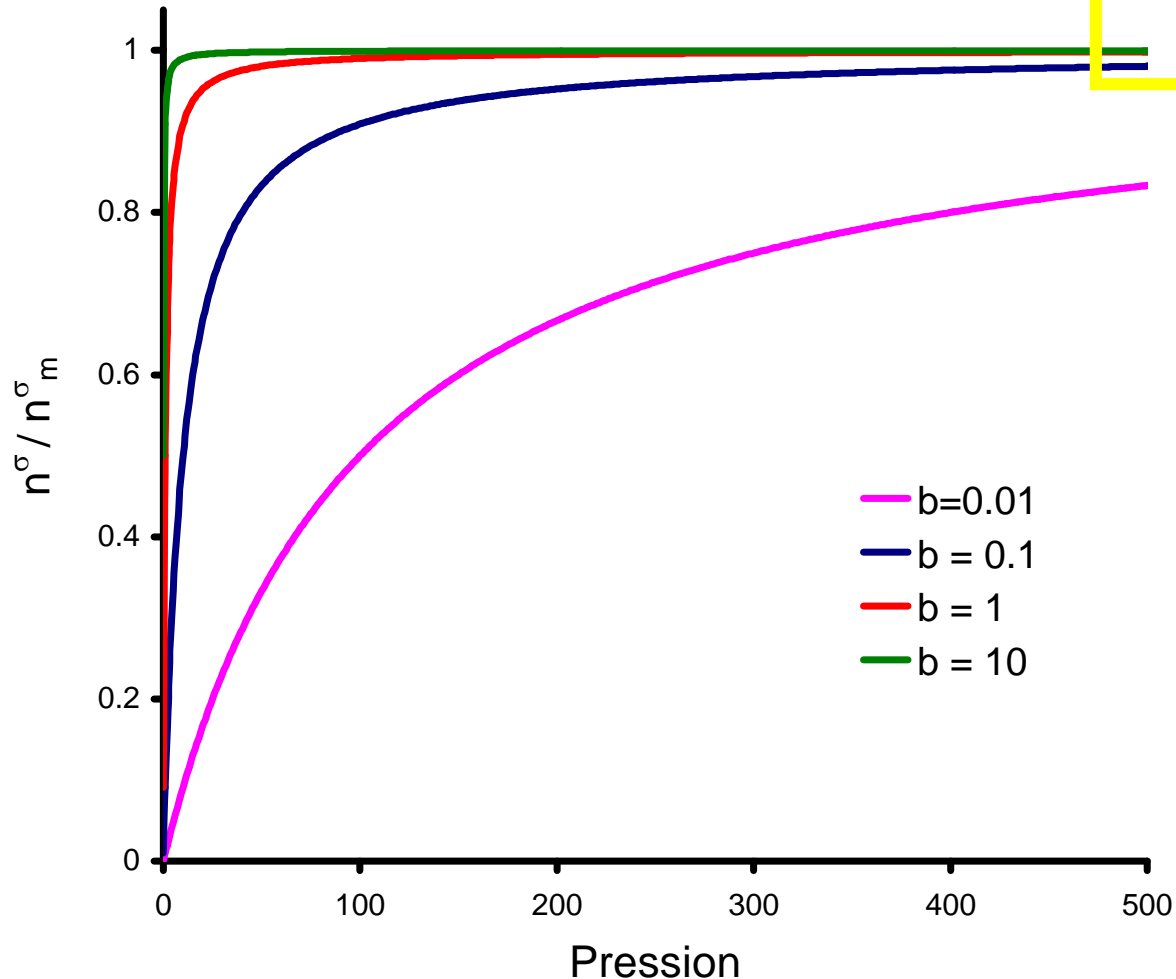
$$\frac{p}{n^{\sigma}} = \frac{1}{n_m^{\sigma} b} + \frac{p}{n_m^{\sigma}}$$

$$b = K \exp^{E/RT}$$



# Langmuir Isotherm :

$$n^{\sigma} = n_m^{\sigma} \frac{bp}{1 + bp}$$



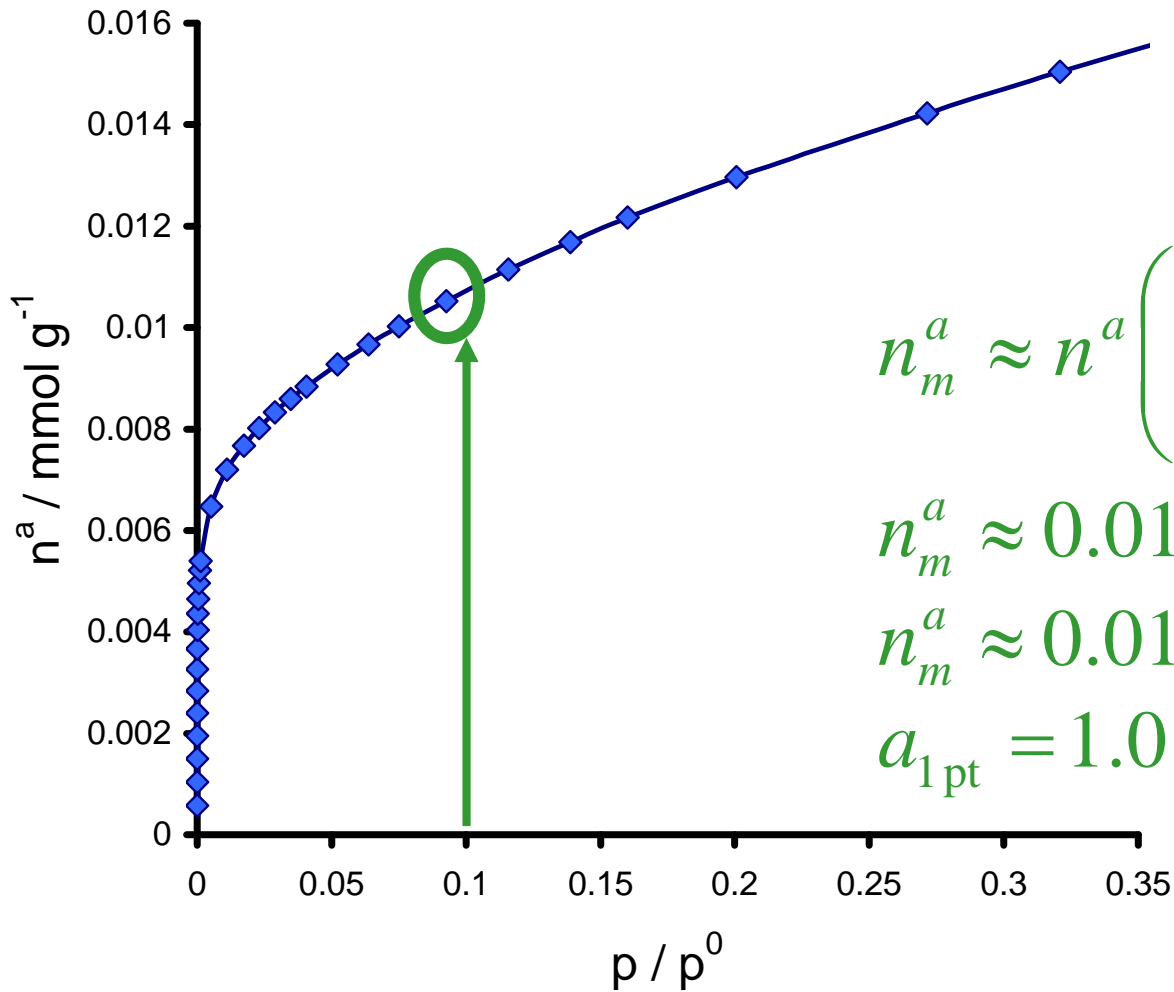
$$b = K \exp^{E/RT}$$

## Notes:

1/ A real Langmuir isotherm should show a plateau (otherwise incomplete, or not Langmuirian)

# Calculating the specific surface area using BET

example : alumina NPL / N<sub>2</sub> / 77 K



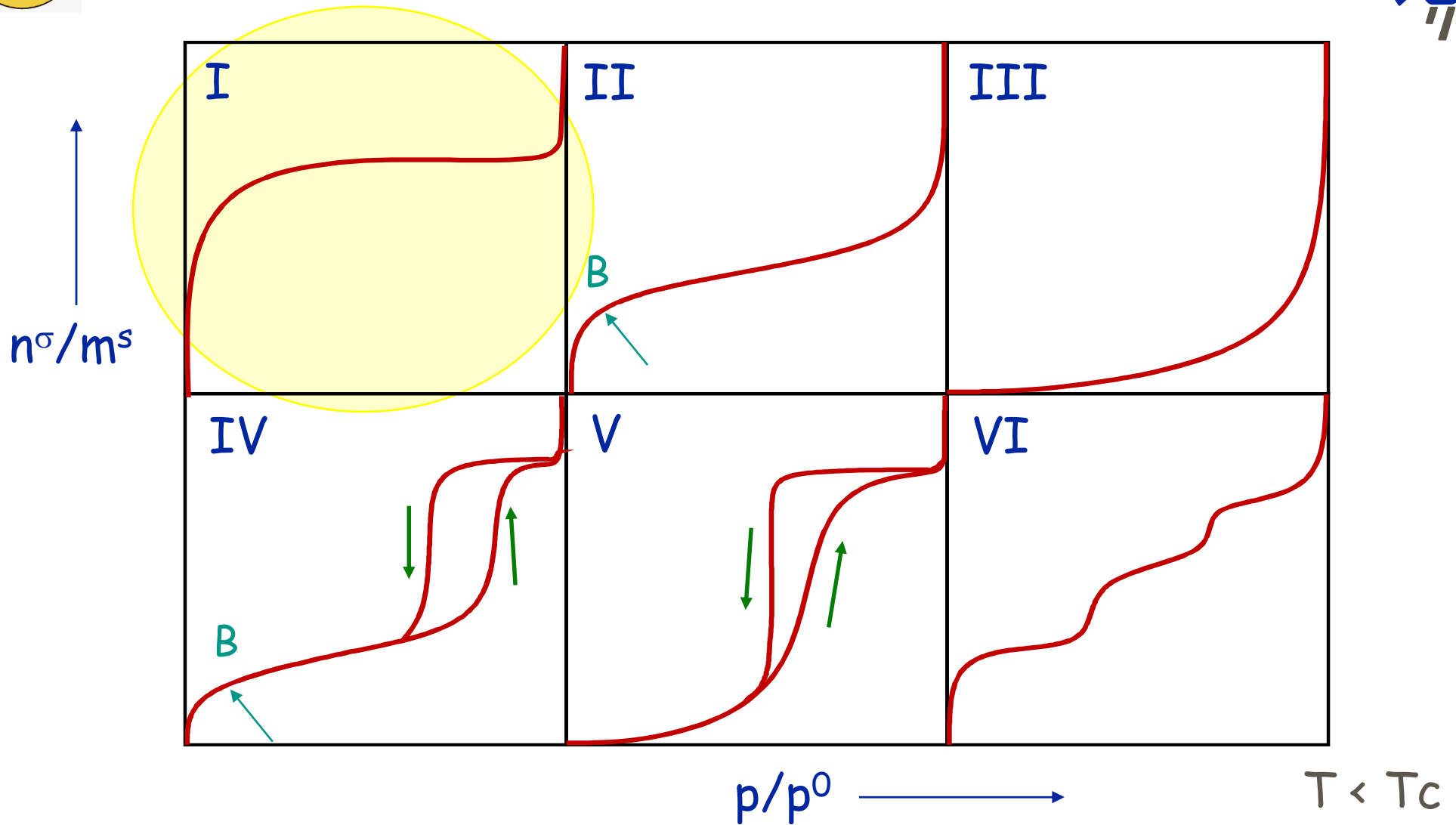
$$n_m^a \approx n^a \left( 1 - \frac{p}{p^0} \right)$$

$$n_m^a \approx 0.0105 \times (1 - 0.0926)$$

$$n_m^a \approx 0.0104$$

$$a_{1\text{pt}} = 1.01 \text{ m}^2 \text{ g}^{-1}$$

# IUPAC Classification of physisorption isotherms







Y gracias a todos os participantes da  
1ª Escola Sul Americana de Adsorção  
para sua atenção !





# Langmuir Theory (Chemisorption)



- 1 type of "adsorption site"
- no lateral interactions
- 1 adsorption site fixes 1 adsorptive molecule :  
the adsorption is limited to a single monomolecular layer

$N^s$  = number of adsorption sites

$N^a$  = number of molecules adsorbed

Degree of coverage

$$\theta = \frac{N^a}{N^s}$$



# Langmuir Theory (Chemisorption)



- 1 type of "adsorption site"
- no lateral interactions
- 1 adsorption site fixes 1 adsorptive molecule :  
the adsorption is limited to a single monomolecular layer

$N^s$  = number of adsorption sites

$N^a$  = number of molecules adsorbed

Degree of coverage

$$\theta = \frac{N^a}{N^s}$$





# The spirit of this talk : positive criticism of some gas adsorption methods



- ★ Survey a number of methods used to examine the surface area, the mesopore size-distribution or the micropores
- ★ Because they all enter the software of excellent commercial equipment, the results provided by these methods are often considered « as granted »
- ★ We shall focus attention on assumptions, limitations, meaning of the results, way to improve their usefulness
- ★ The above interpretations will often take benefit from gas adsorption calorimetry results



# Methods to analyse type I isotherms *(continued)*

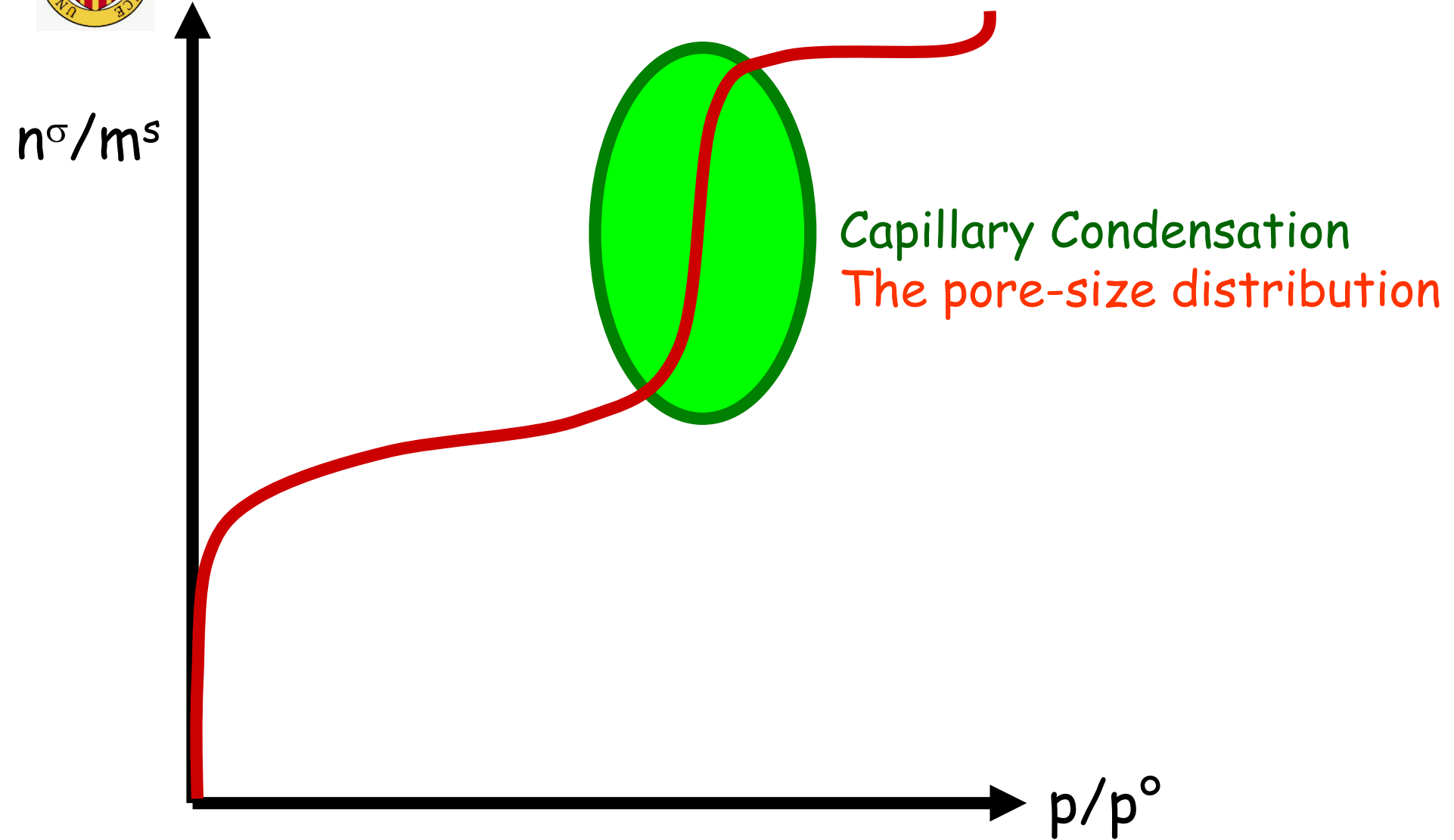


- "DFT"

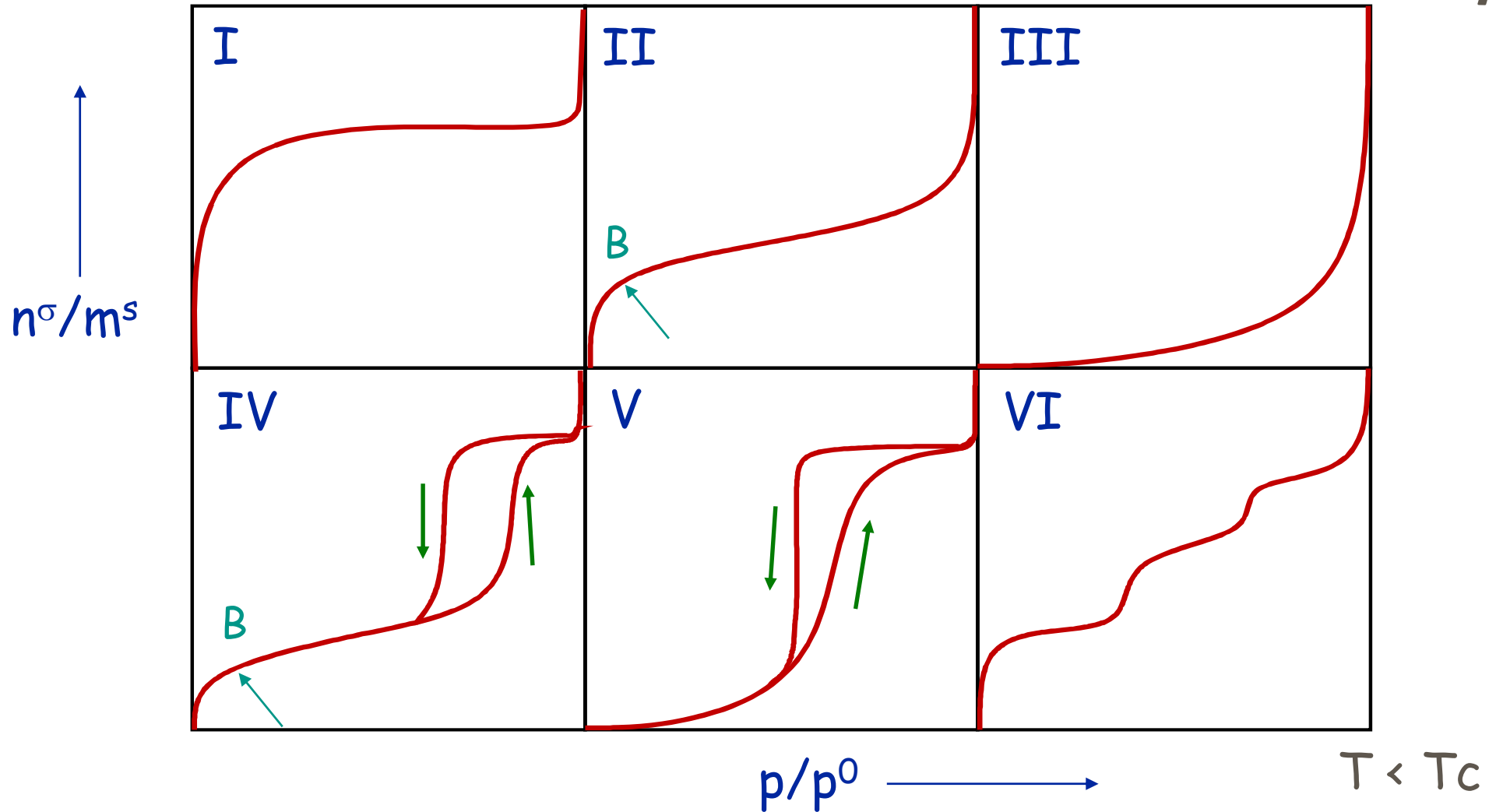




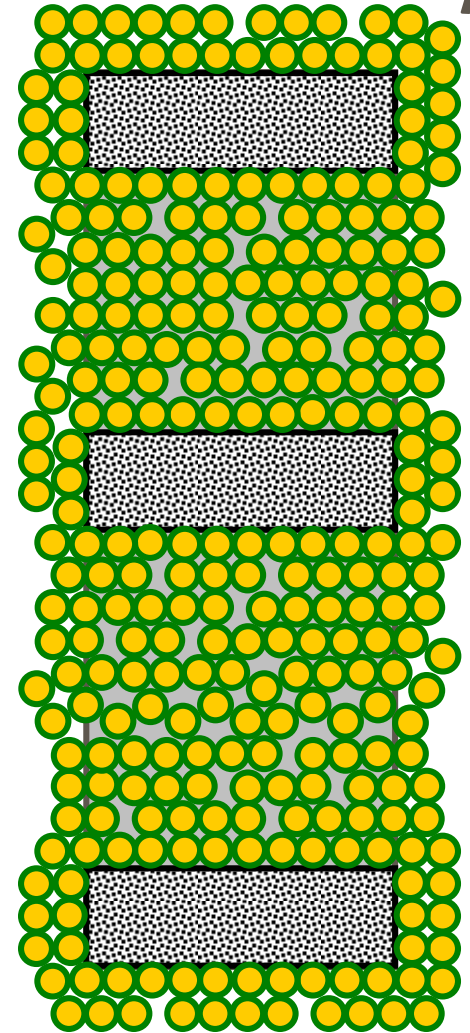
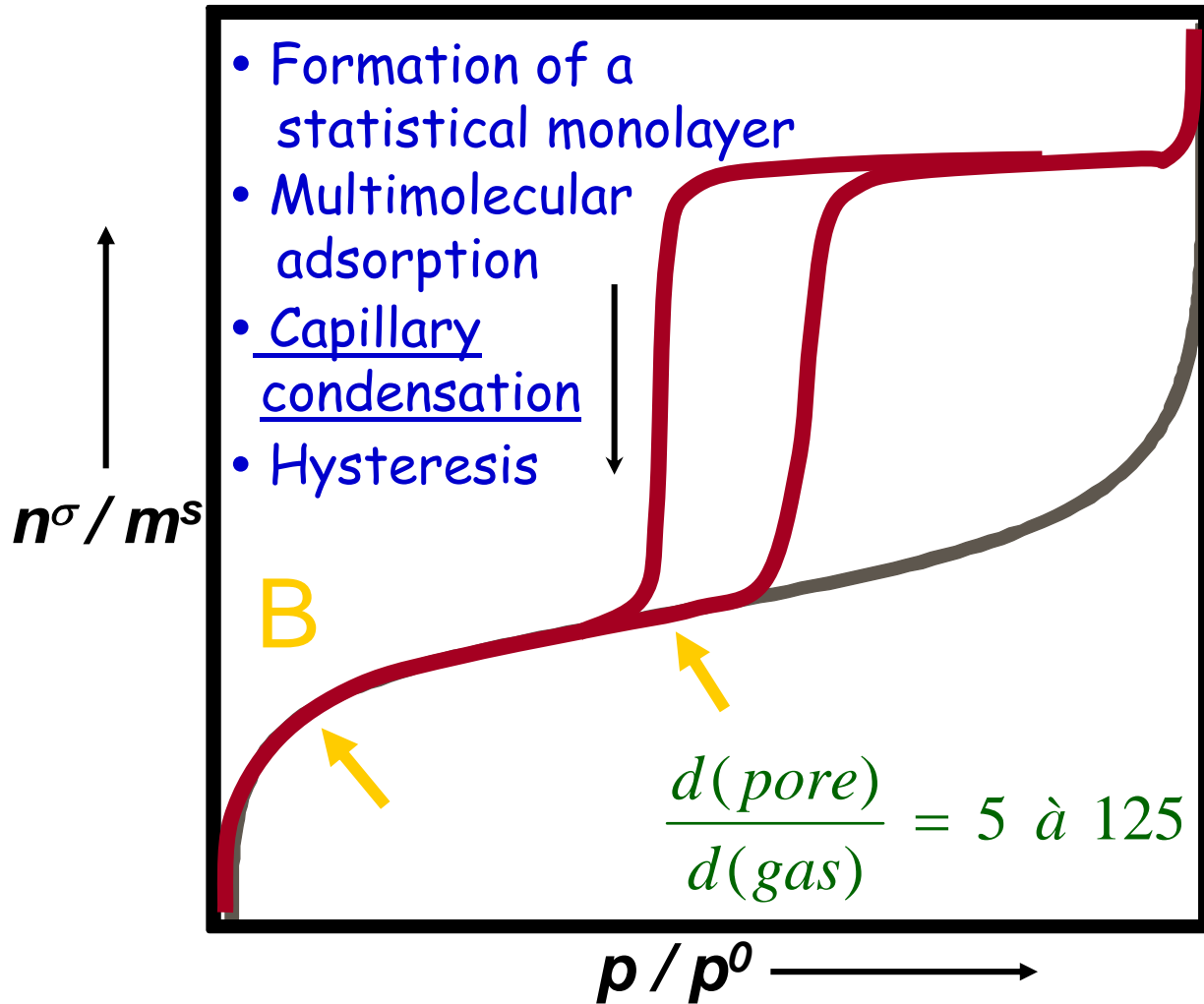
# The adsorption *isotherm* of a vapour

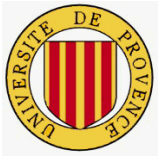


# IUPAC Classification of physisorption isotherms



# Adsorption on a purely mesoporous sample : $d \approx 2$ to $50$ nm





# The Barrett, Joyner and Halenda (BJH) analysis of the N<sub>2</sub> adsorption-desorption isotherm



## Assumptions made :

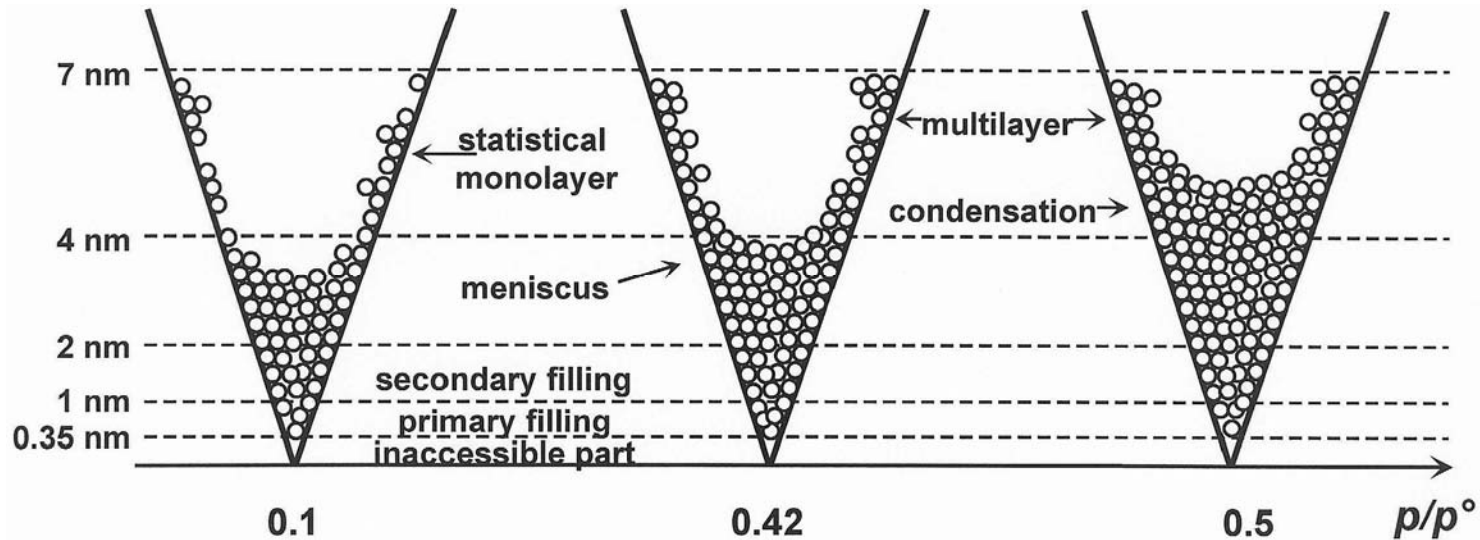
- ☒ The hysteresis loop indicates the presence of mesopores (2-50 nm wide)
- ☒ In the mesopores, the N<sub>2</sub> vapour condenses more easily than on a flat surface, i.e. at a lower pressure
- ☒ This pressure depends on the meniscus radius « r » through the Kelvin equation, which, for a cylindrical pore, writes:

$$r_K = \frac{-2\gamma \cdot v_m}{RT \ln\left(\frac{P}{P^\circ}\right)}$$

Laboratoire Chimie Provence, Site MADIREL, CNRS-Université de Provence, Marseille

- ☒ Same equation already used to derive mesopore size distribution (2-50 nm) from N<sub>2</sub> adsorption-desorption

# The Barrett, Joyner and Halenda (BJH) analysis of the N<sub>2</sub> adsorption-desorption isotherm



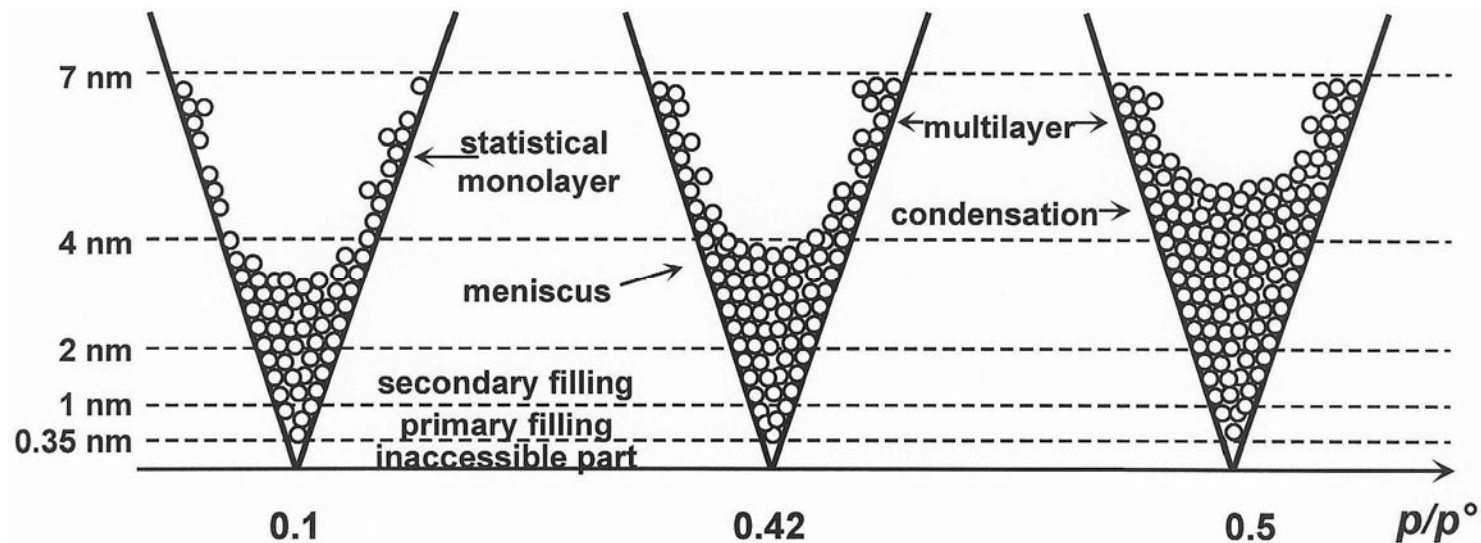
## Assumptions made (continued):

- ⊞ Pores are rigid and all with the same shape (cf cylindrical, slit-shaped etc...)
- ⊞ The condensation occurs in the same way as that visible at a larger scale, i.e. with similar meniscus and surface tension
- ⊞ Liquid N<sub>2</sub> perfectly wets the adsorbent (wetting angle=0)
- ⊞ Condensation occurs in pore already lined with multilayer

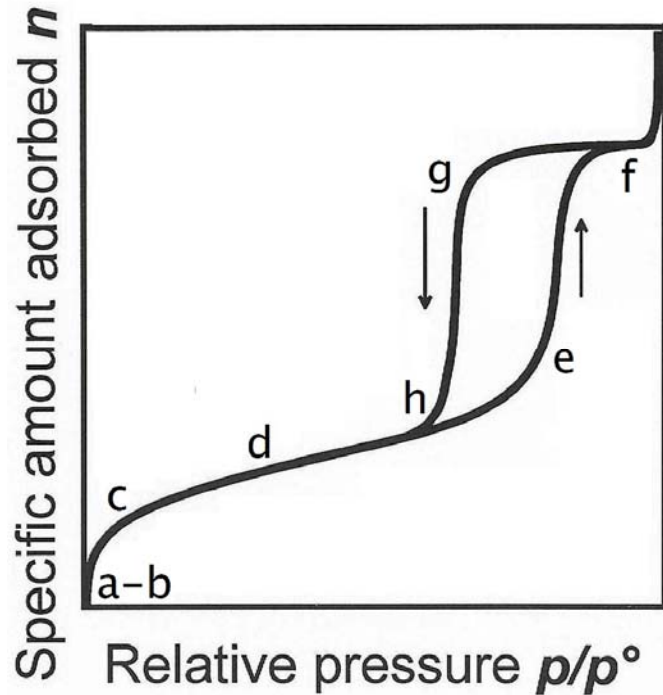


## Assumptions made (continued):

- Thickness of multilayer vs  $p/p^{\circ}$  is known (de Boer, Halsey...)
- Thickness of this multilayer must be added to Kelvin radius (that of the meniscus) to assess pore radius
- A plateau in upper part of isotherm indicates saturation of mesopores







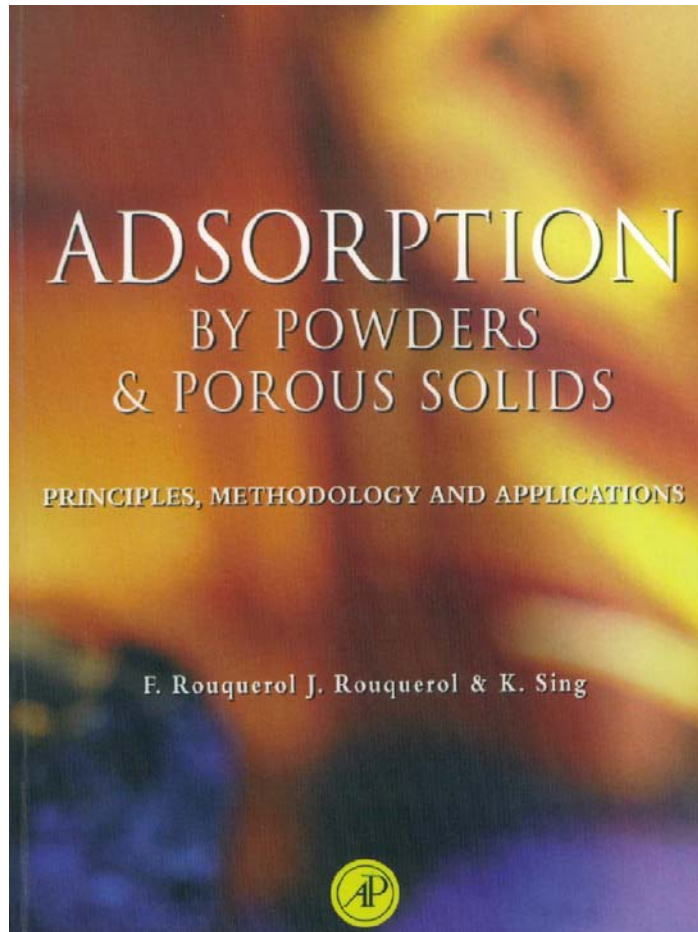
## Derivation of the pore-size distribution :

- ☒ Select branch of hysteresis corresponding to thermodynamic equilibrium (most often the desorption branch)
- ☒ Start from saturation plateau, with small steps of desorption

- ☐ Each step provides a pore diameter (from the mean pressure)  
and a pore volume (from amount desorbed, converted into liquid state)

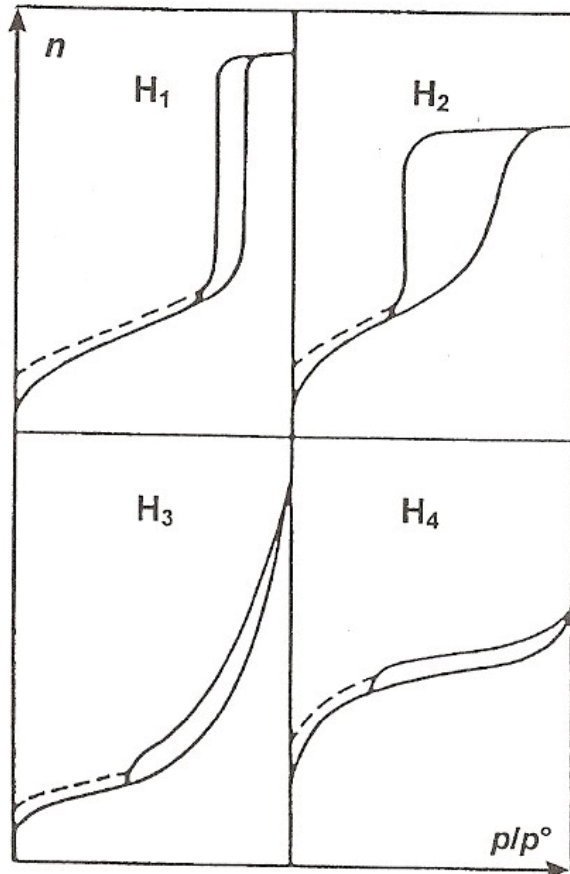


# The Barrett, Joyner and Halenda (BJH) analysis of the N<sub>2</sub> adsorption-desorption isotherm



## Derivation of the pore-size distribution (continued):

- ☒ Simplified equation for N<sub>2</sub> at 77 K :  
$$r_k / \text{nm} = 0.415 / \log_{10} (p/p^\circ)$$
- ☒ End with mesopore size-distribution (either in volume or in surface-area)
- ☒ Compare « cumulative surface area » with BET surface area
- ☒ For more detailed procedure, see a text book !



H<sub>1</sub>: Narrow distribution of uniform pores (MCM-41)

H<sub>2</sub>: Complex, interconnected pore networks (oxides) structure,

H<sub>3</sub>, H<sub>4</sub>: Non-rigid slit-shaped pores (swelling clays)

Note 1: for N<sub>2</sub>, lower closure point never lower than 0.42

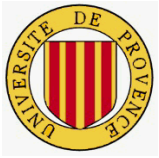
Note 2: these are limiting cases; reality often in-between



# Part of gas adsorption calorimetry in the study of mesopores



- ✘ Not expected to be high, since  $\Delta_{\text{ads}}H$  is practically equal to  $\Delta_{\text{liq}}H$ ).
- ✘ For this reason, a calorimetric attempt to see a difference in  $\Delta_{\text{ads}}H$  between the adsorption and desorption branches, to see which one corresponded to equilibrium, did not work (*Kington and Smith, 1964*)
- ✘ Conversely, by assuming that  $\Delta_{\text{ads}}H$  was practically equal to  $\Delta_{\text{liq}}H$ , it was possible to determine a full « calorimetric adsorption-desorption isotherm » (water/alumina) by only using calorimetric data



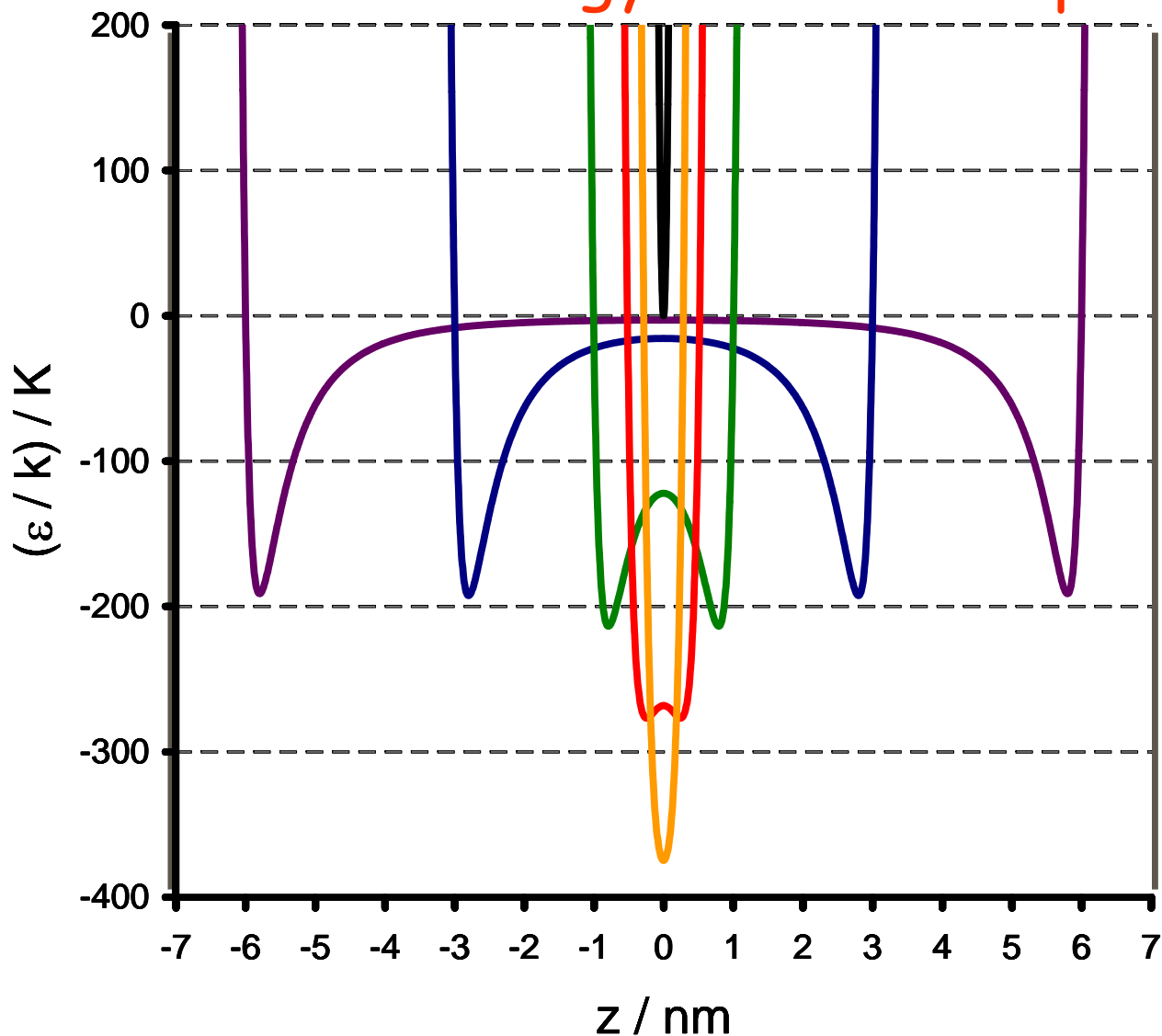
# Methods to study micropores



- ⌘  $^{129}\text{Xe}$  NMR
- ⌘ Small angle XRD
- ⌘ Immersion Microcalorimetry
- ⌘ Gas Adsorption



# Potential energy in a slit-shaped pore



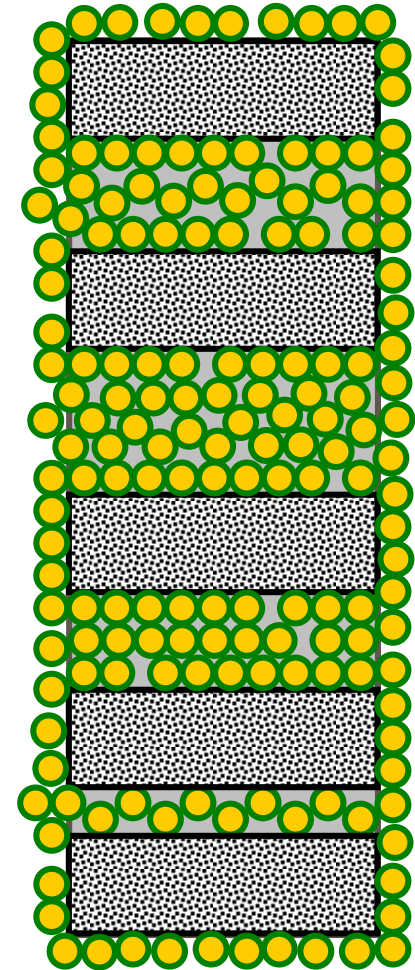
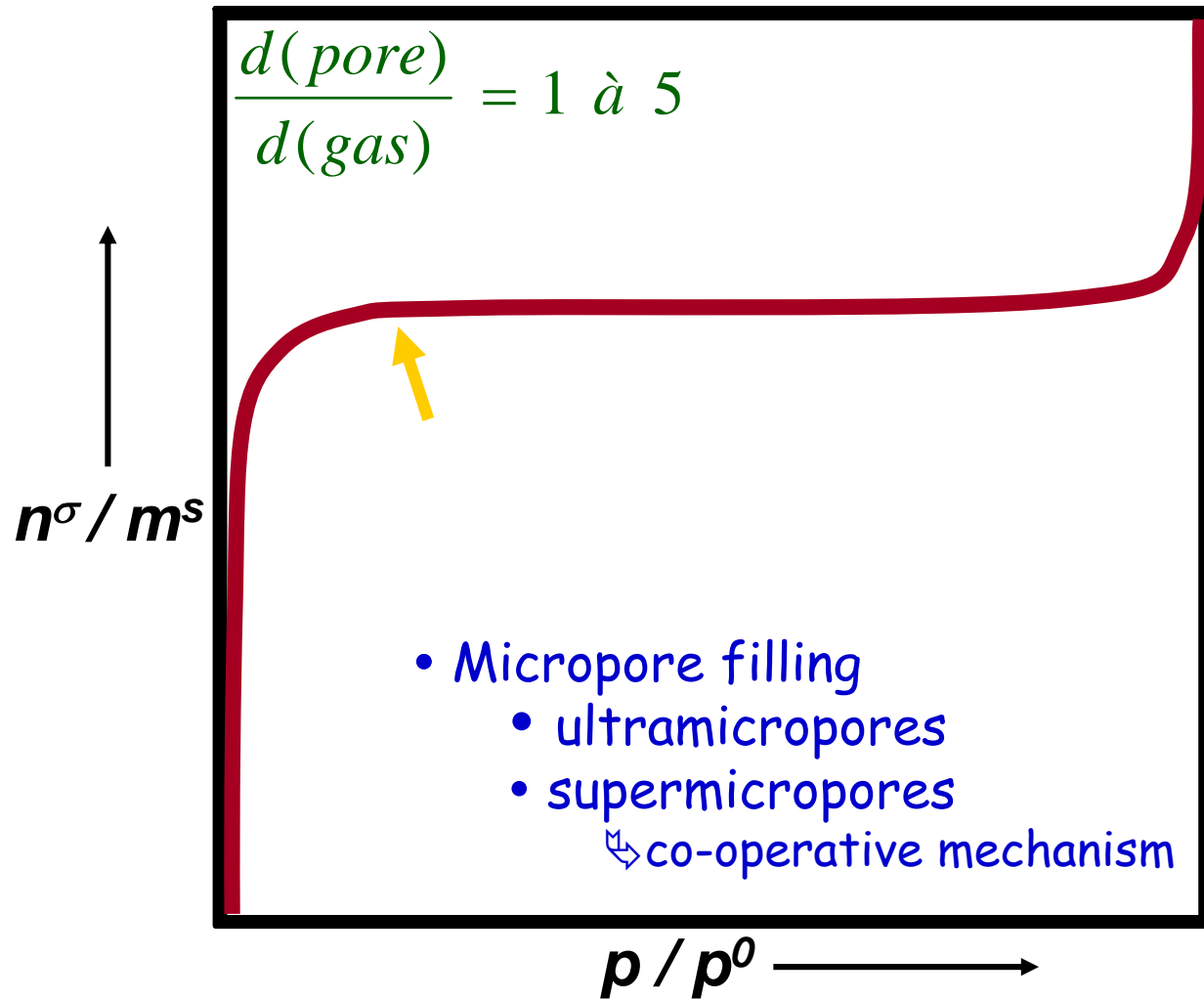
- $w = 14 \sigma$
- $w = 8 \sigma$
- $w = 4 \sigma$
- $w = 3 \sigma$
- $w = 2.5 \sigma$
- $w = 2 \sigma$

$\sigma \approx r_{\text{gas}}$

$$\varepsilon(z) = 4\varepsilon_{g-s} \left[ \left( \frac{\sigma}{z} \right)^9 - \left( \frac{\sigma}{z} \right)^3 \right]$$

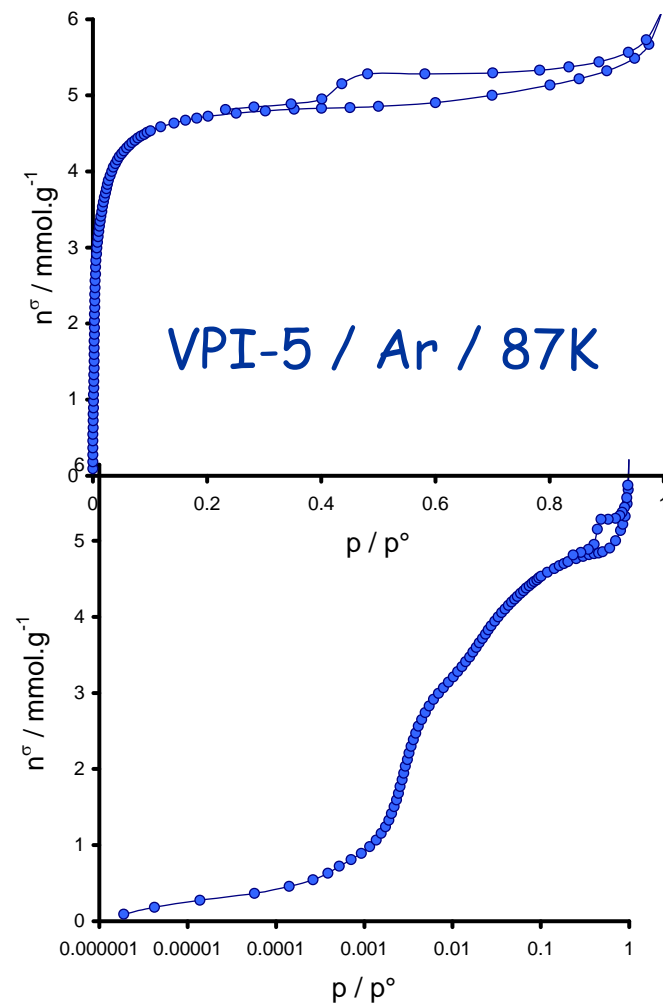
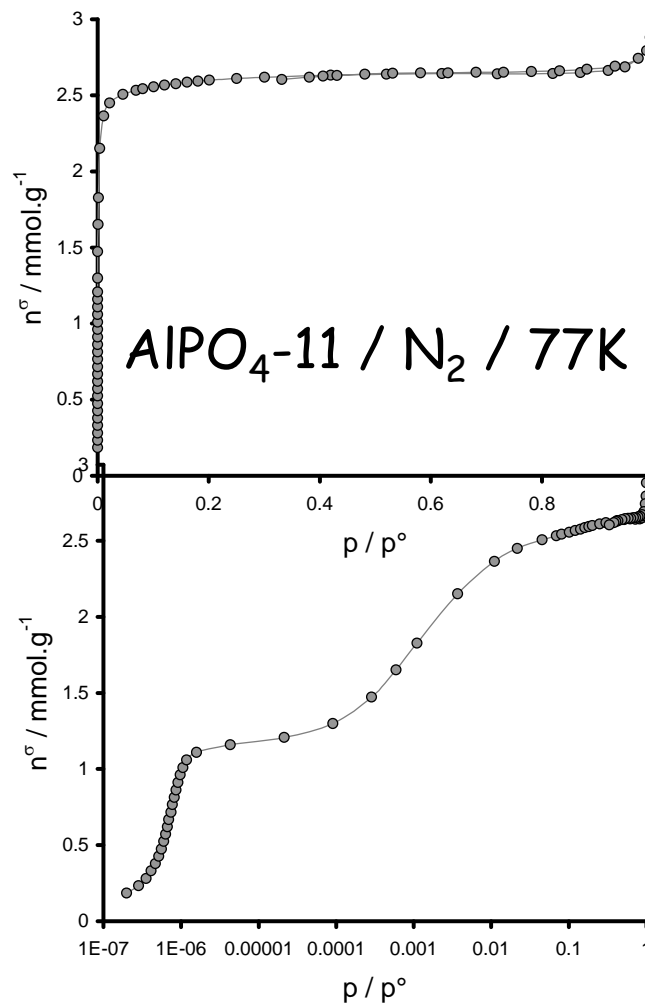
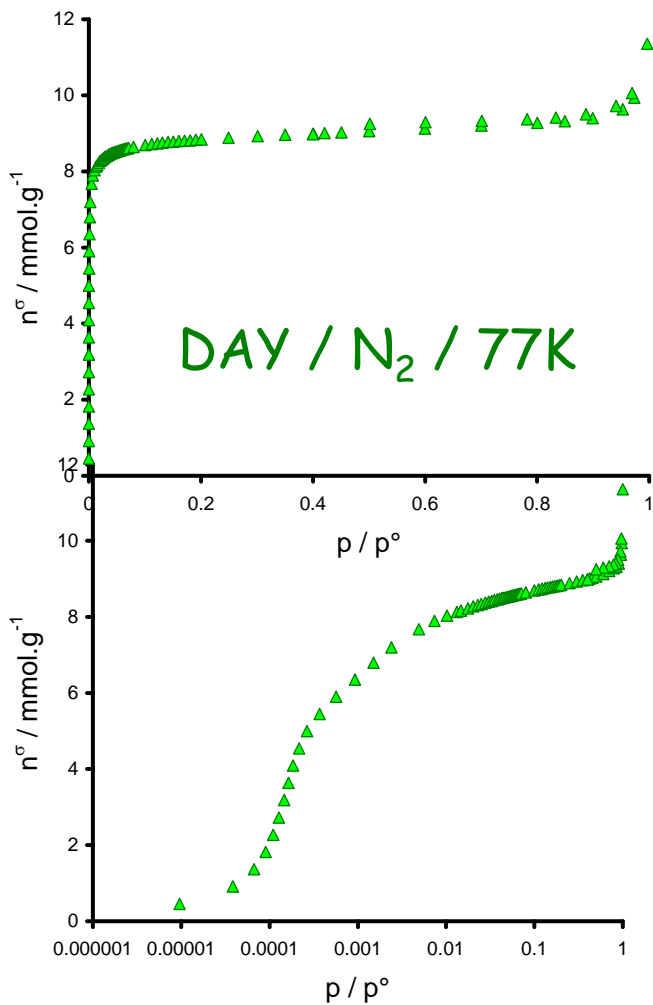
$\sigma = 1 \text{ nm}$   
 $\varepsilon / k = 124 \text{ K}$

# Adsorption on a purely microporous sample : $d \approx 0.4$ to $2$ nm





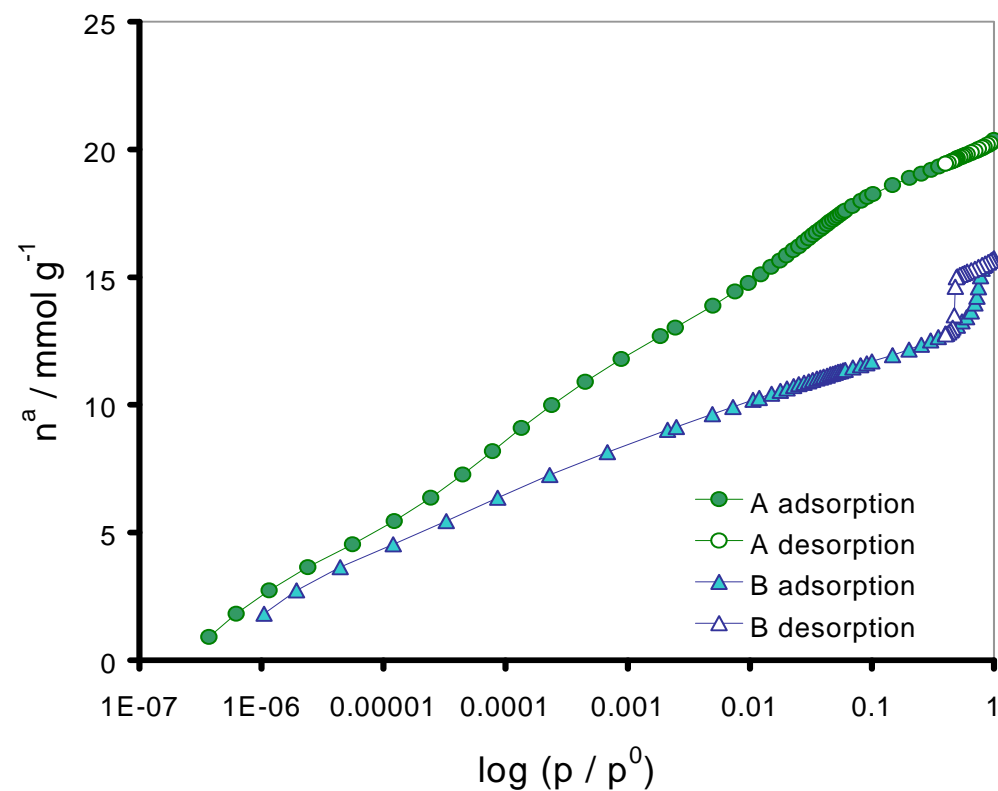
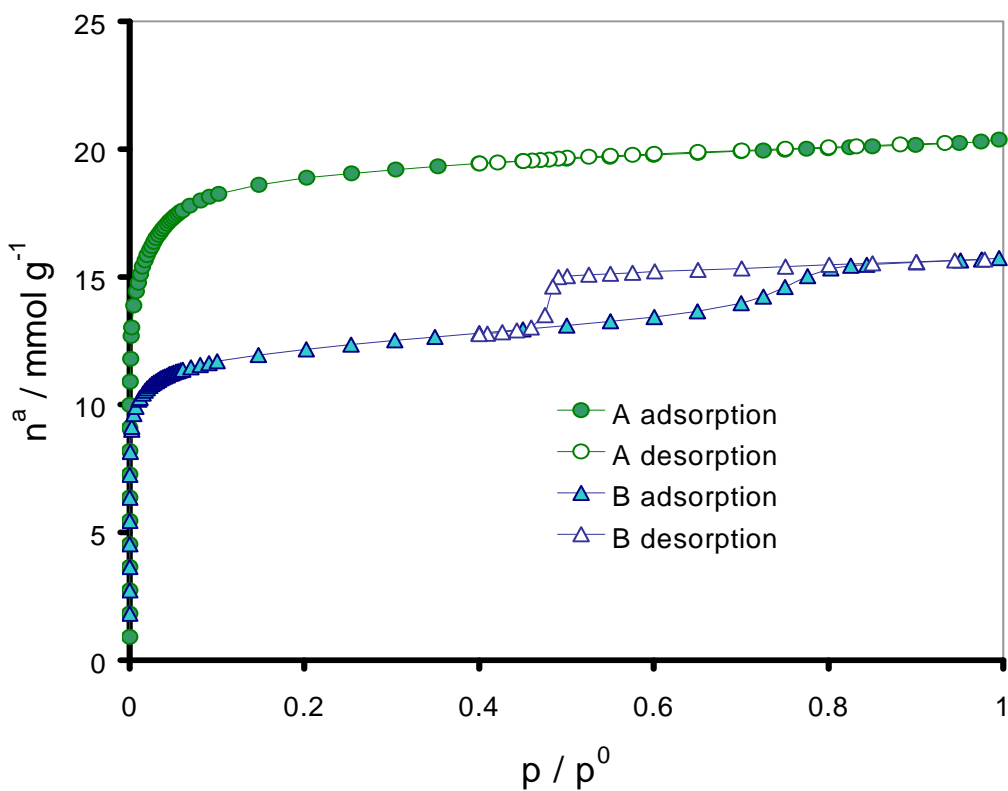
# Adsorption isotherms with microporous samples : use of semi-log plots







# Adsorption isotherms of $N_2$ at 77 K obtained with samples of carbon fibres





# Empirical methods to analyse type I isotherms

- isotherm comparison
- "t" method
- $\alpha_s$  method



# For the study of micropores :



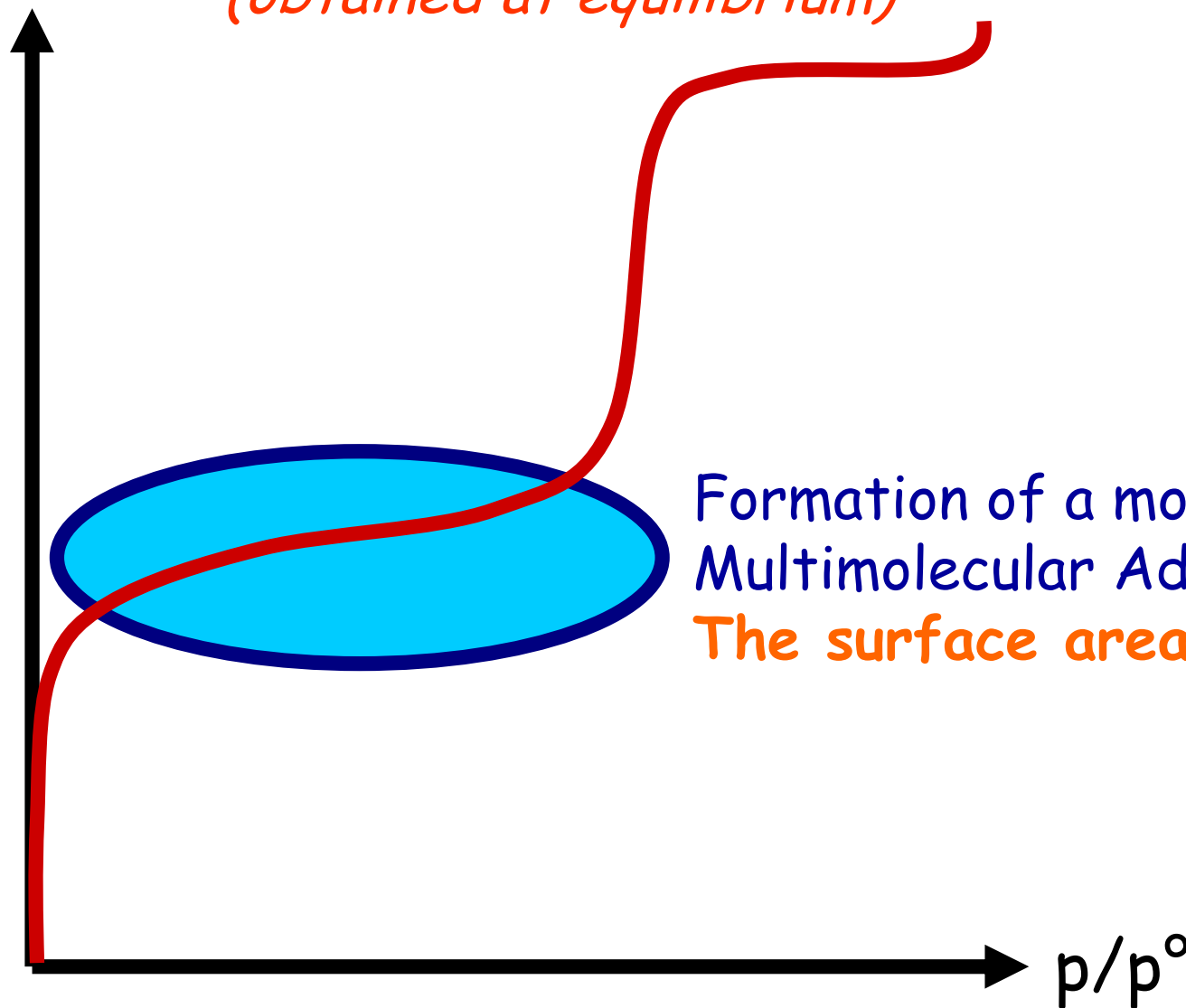
- ⌘ First of all, determine the adsorption isotherm in the low pressure range (0.005 - 0.3)
- ⌘ Apply either the  $t$ -method (no need of reference) or the  $a_s$  method (need of reference material and isotherm)
- ⌘ Derive micropore volumes (ultra, super)
- ⌘ Derive « external » (non-microporous) surface area



# The adsorption *isotherm* of a vapour (obtained at equilibrium)



$n^{\sigma}/m^{\sigma}$



Formation of a monolayer  
Multimolecular Adsorption  
The surface area determination



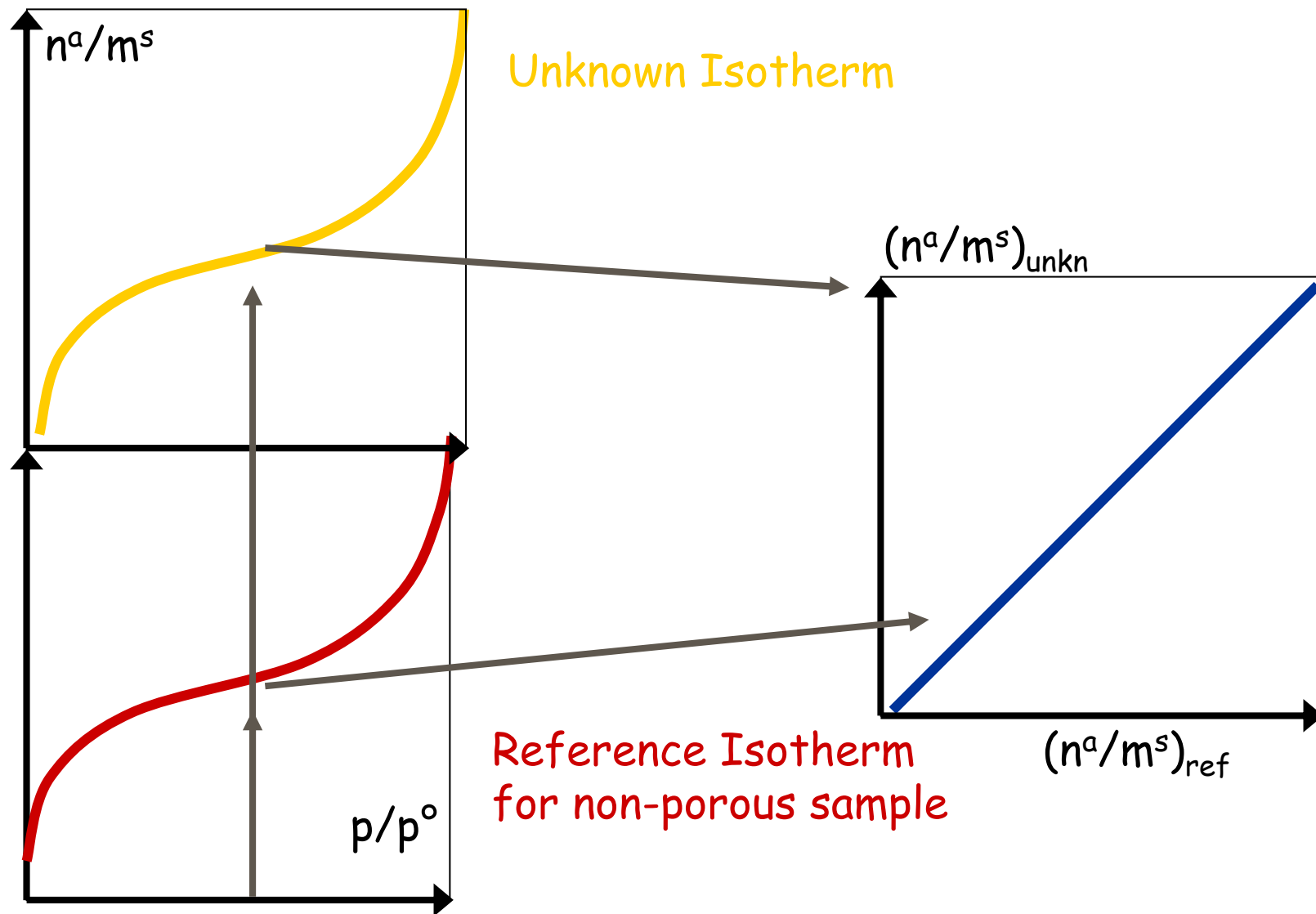
# For the study of mesopores :



- ⌘ Always have a look at the shape of the isotherm, the « identity picture » of the adsorbent
- ⌘ Consider that, most often, the mesopore size-distribution is necessarily an approximation
- ⌘ Remember it always assume the same, single shape, for all pores in the material studied
- ⌘ Any more sophisticated procedure of calculations should be justified by extra, independent, information about pore shapes and connectivity
- ⌘ Combining the adsorption isotherms with image analysis and adsorption modeling, is at present the main way to improve our knowledge about any specific adsorbent



# Isotherm Comparison





# t or $\alpha_s$ method: background



## ⌘ Kiselev 1957

⊞ search for the **standard isotherm** - non-porous

⊞  $\Gamma = n/A_{\text{BET}} \Rightarrow n/n_m$

## ⌘ Lippens-de Boer 1965

⊞ **thickness of the layer, t**

⊞  $t = (n/n_m)d' \Rightarrow d' = M / (s L r_{\text{liq}}) = 0.354$

⊞  $t = 0.354 n/n_m$

## ⌘ Sing 1968

⊞  $n_m$  implies  $A_{\text{BET}}$

⊞ chemical effects of the surface, at low coverage, are not taken into account

⊞ **reference** sample of **same chemical nature**

⊞ replace  $n_m$  by  $n_{0.4}$  ( $n$  at  $p/p^0 = 0.4$ )



$$\alpha_s = \frac{n}{n_{0.4}}$$



## $\alpha_s$ method: reference data



### ⌘ Nitrogen at 77 K on Lichrosphere 1000 (silica gel)

☒ M. Kruk, M. Jaroniec, J. P. Olivier, Langmuir 15 (1999) 5410-5413.

### ⌘ Argon at 87 K on Lichrosphere (silica gel)

☒ M. Kruk, M. Jaroniec, Chem. Mater 12 (2000) 222-230.

### ⌘ Nitrogen at 77 K on Vulcan (non-porous carbon )

☒ J. Fernandez-Colinas, R. Denoyel, Y. Grillet, F. Rouquerol, J. Rouquerol, Langmuir, 5 (1989) 1205-1210.





# Specific methods to analyse Type I isotherms (*continued*)



- Dubinin's method

Laboratoire Chimie Provence, Site MADIREL, CNRS-Université de Provence, Marseille



# Dubinin Method : Background



## ⌘ Polyani - 1915

☒ characteristic curve which does not vary with temperature

$$\Rightarrow A = -RT \ln (p/p^0)$$

A, adsorption potential

## ⌘ Dubinin-Radushkevich - 1947

$$\text{☒ } W/W_0 = \exp[-(A/E)^2]$$

W, n(mic)

$W_0$ ,  $n_p$ (mic) total

E, characteristic energy

## ⌘ Dubinin-Astakhov - 1970

$$\text{☒ } W/W_0 = \exp [-(A/E)^N]$$

N, empirical constant

## ⌘ Stoekli - 1977

☒ DR ok for narrow pore size distributions

☒ sum of several DR equations for several distributions !

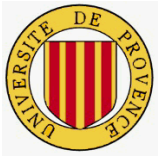
☒ simplification - Gaussian distribution



# Dubinin "Methods": summary



- ⌘ Assume a **single** pore size distribution
- ⌘ **Gaussian** Distribution
- ⌘ D-A : 'N' value varies according to the pressure region used
- ⌘ Method especially suited for a sample containing a single distribution of ultramicropores and **essentially used for carbons**



# Methods to analyse type I isotherms

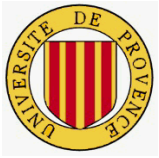
Dubinin's method

De Boer's  $t$ -method

Sing's  $a_s$  method

Horwath and Kawazoe method (HK)

Density Functional Theory (DFT)



# Horwath-Kawazoe Method : background



## ⌘ Horwath-Kawazoe - 1983

- ☒ expression for slit shaped pores (carbons)
- ☒ N<sub>2</sub> interactions at 77 K

## ⌘ Saito-Foley - 1991

- ☒ expression for cylindrical pores
- ☒ Ar-O<sub>2</sub> (87 K)

## ⌘ Cheng-Yang - 1994

- ☒ expression for spherical pores
- ☒ correction for isotherm non-linearity



## Horwath-Kawazoe method : summary

⌘ Require good points at very low pressure

☒  $< 10^{-5} p/p^0$

☒ equilibrium pressure gauge stability

⌘ HK proper

☒ aimed for carbons and nitrogen at 77K

⌘ Saito-Foley

☒ aimed at zeolite cylinders and argon at 87K

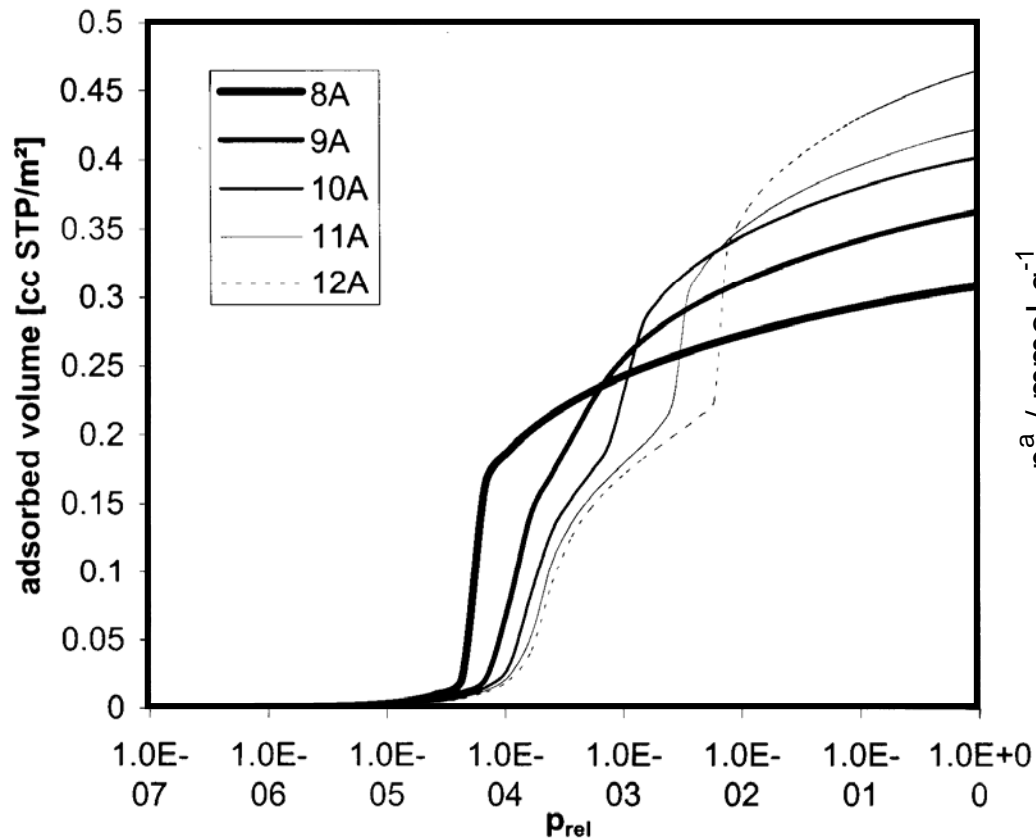
⌘ Attention first peak : artefact in calculation



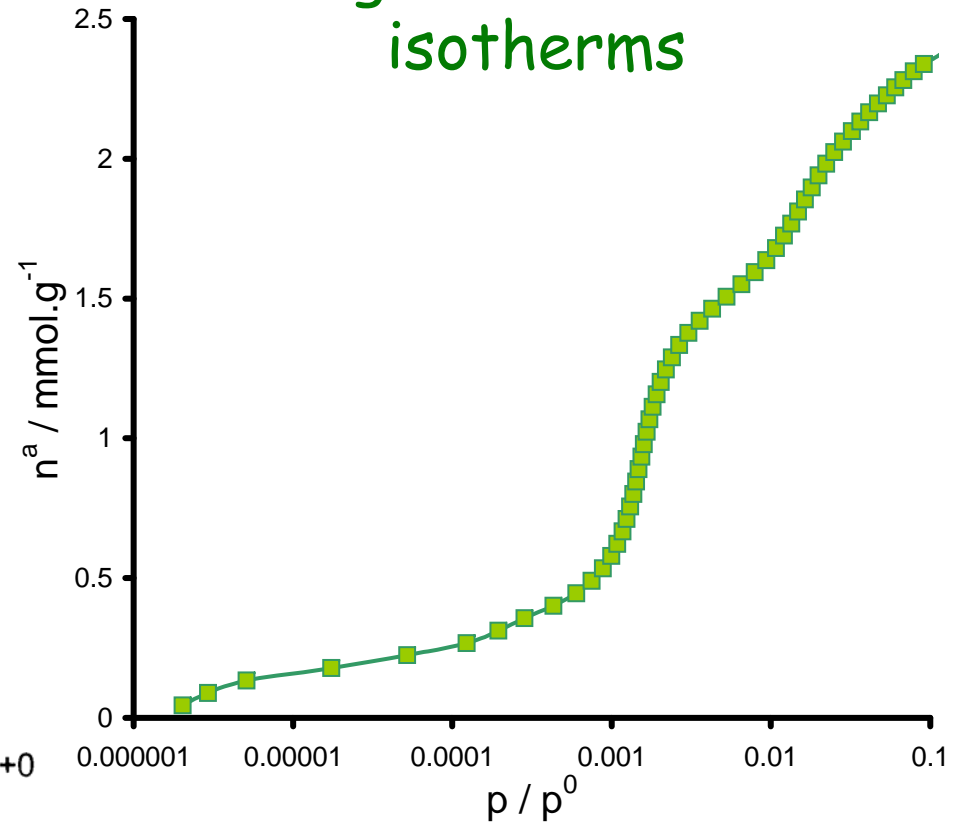
# DFT



## 1. Construction of reference isotherms



## 2. Reconstruction of the experimental isotherm using the reference isotherms





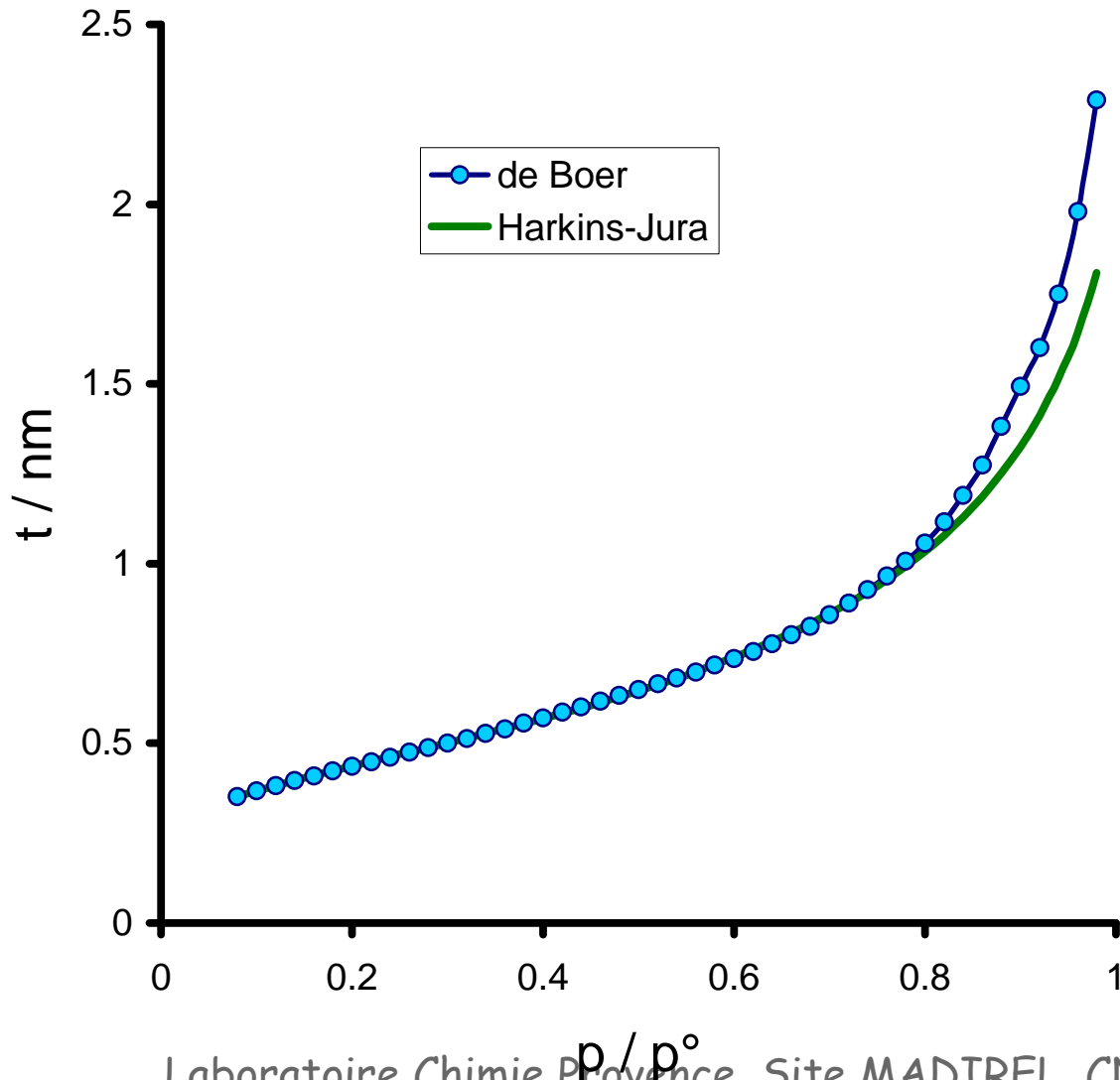
# Fitting the 't' curve



## Data from «de Boer»

'Physical and Chemical Aspects of Adsorbents and Catalysts'

Ed B. G. Linsen, Acad. Press, London (1970) p.33.



## Harkins and Jura

$$t = \left( \frac{0.1399}{0.034 - \log(p / p^\circ)} \right)^{1/2}$$