UNIVERSITÉ SAVOIE MONT BLANC

Introduction to gas adsorption onto solid and the related characterization methods

Prof. Laurent Duclaux

email : laurent.duclaux@univ-smb.fr

laboratoire edytem

environnements dynamiques territoires montagnes

Part I. Introduction to gas adsorption onto solid

I.1 Description of the adsorption process : physisorption

Determination of the number of collision of a gas molecule on a solid surface

$$v_{average} = \sqrt{\frac{8kT}{\pi.m}}$$

$V_{average}$: mean speed of an ideal gas for a Maxwell-Boltzman distribution

T : temperature

m : mass of the molecule

K : Boltzman constant

$$Z = \frac{1}{4}.\frac{N}{V}.v_{average} = \frac{P}{\sqrt{2\pi.m.kT}}$$

Z : number of collision on a plane surface

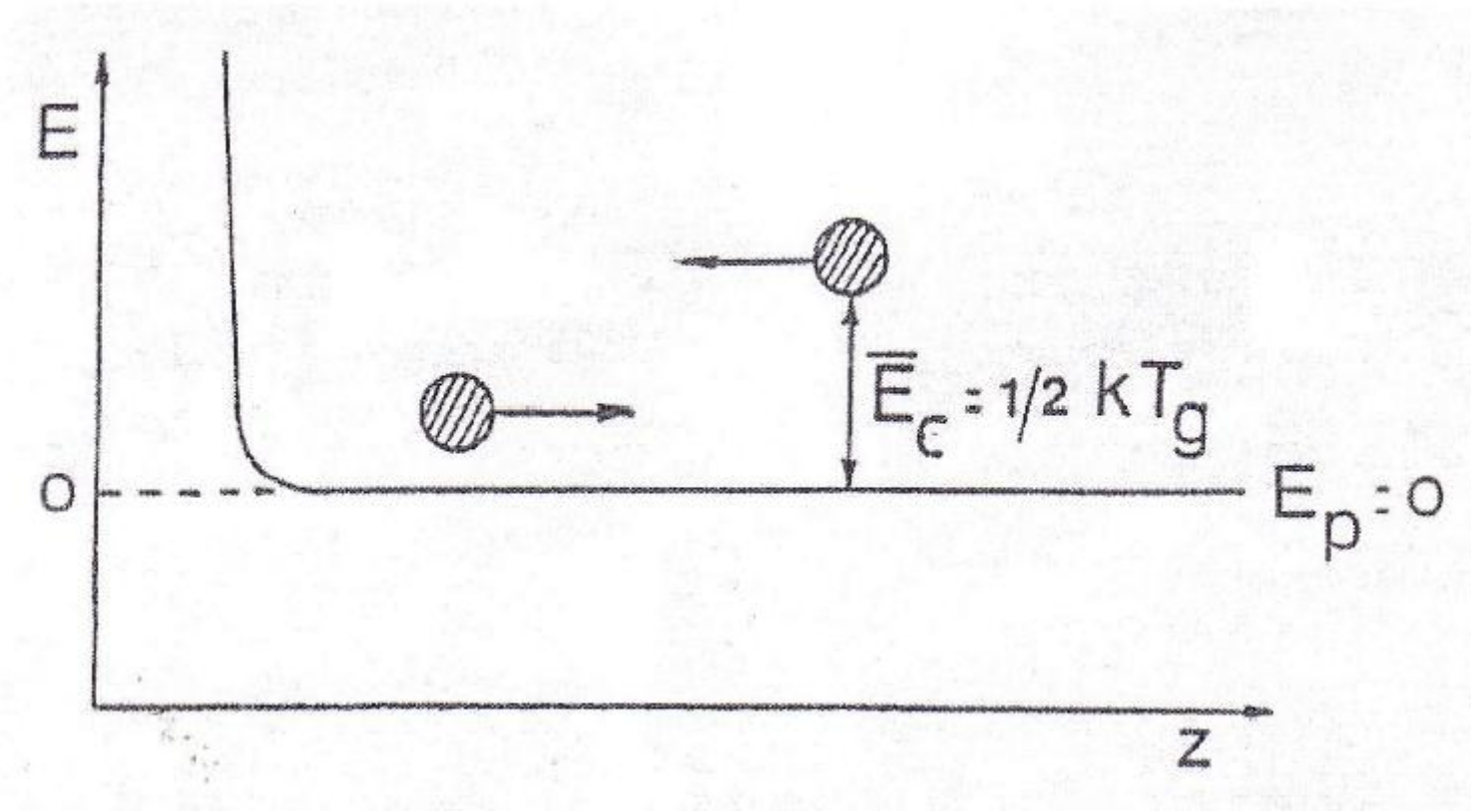
Number N of molecule in a V volume

Example : O_2 at $P=10^{-2}$ torr= $10^{-2}/760 \times 10^5$ Pa = 1.316 Pa , and T=298 K; m= MO_2/N_a ; MO_2=32 g.mol^{-1} ; k= R/N_a ; R=8.314 J. K^{-1}.mol^{-1} ; N_a = $6.022.10^{23}$

$Z=1.316 \times 6.022.10^{23} / (2\pi \times 32 \times 10^{-3} \times 8.314 \times 298)^{1/2} = 3.55\ 10^{22}$ collisions.m^{-2}.s^{-1}

Z= $3.55\ 10^{18}$ collisions.cm^{-2}.s^{-1}

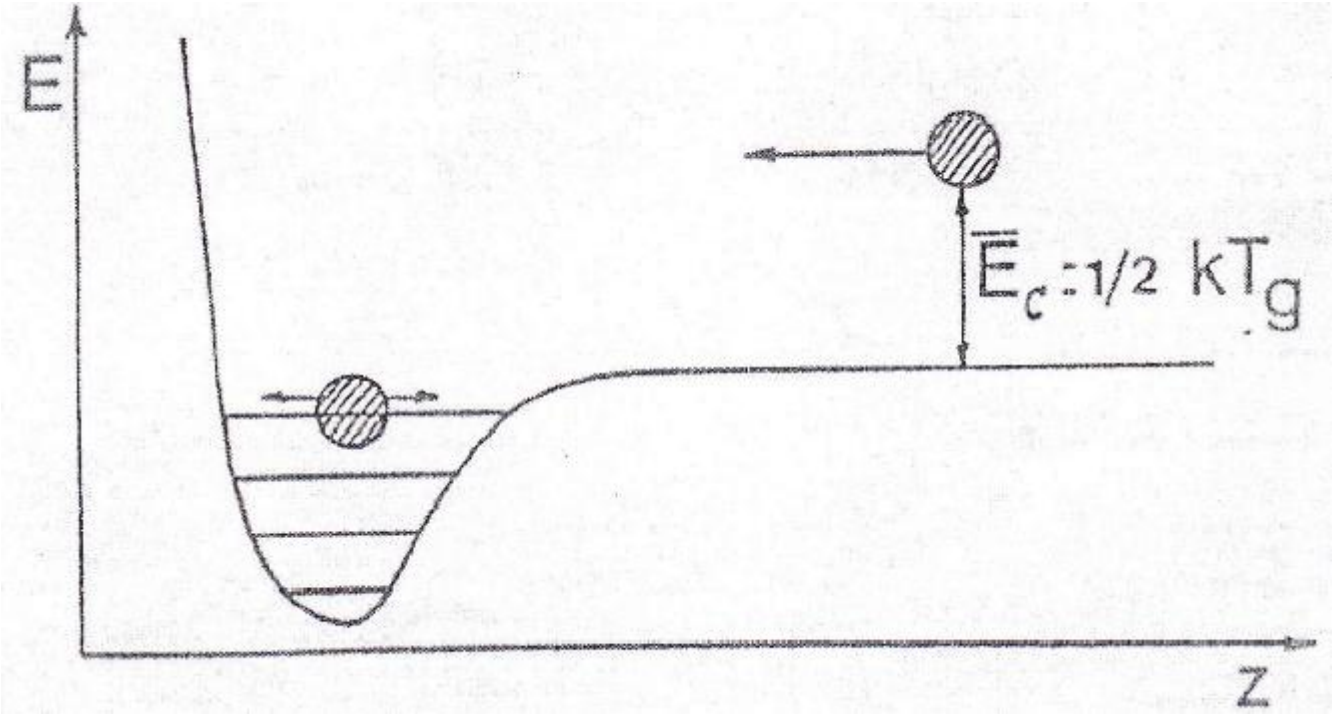
Interaction without attraction forces (only repulsion)



Energy diagram of the interaction of a molecule with the surface : quasi-elastic shock (diffusion) of the molecule on the surface

Part of the energy of the molecule is transmitted in the form of lattice vibration wave (phonons)

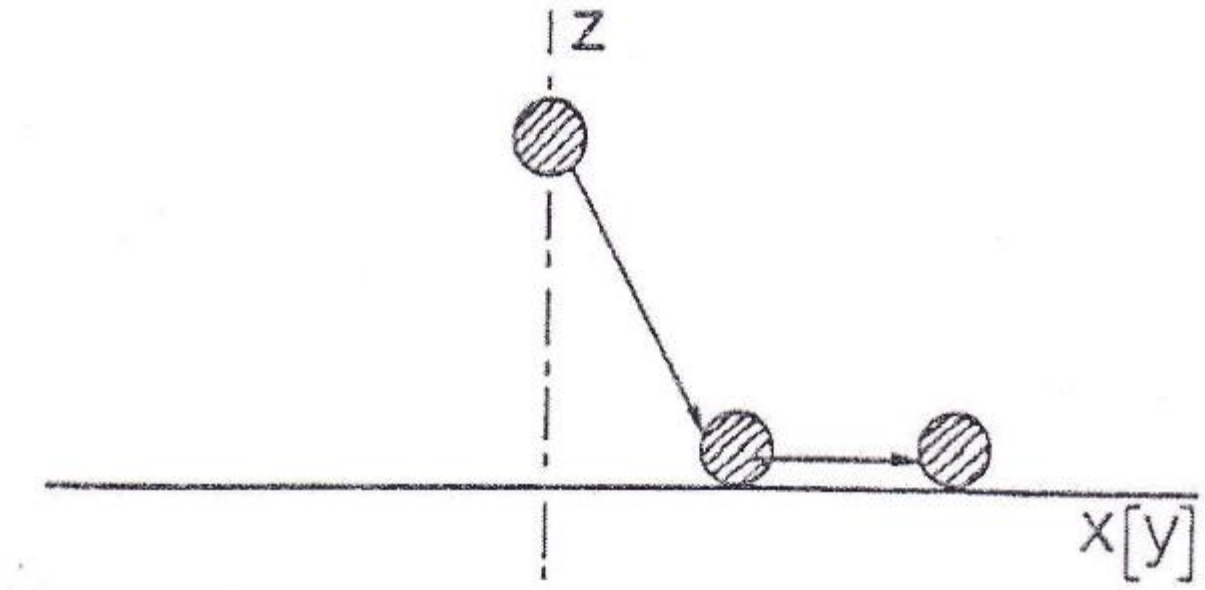
Interaction with attraction forces



Energy diagram of the interaction of a molecule with the surface : the potential hole is resulting from the combination of attraction and repulsion forces.

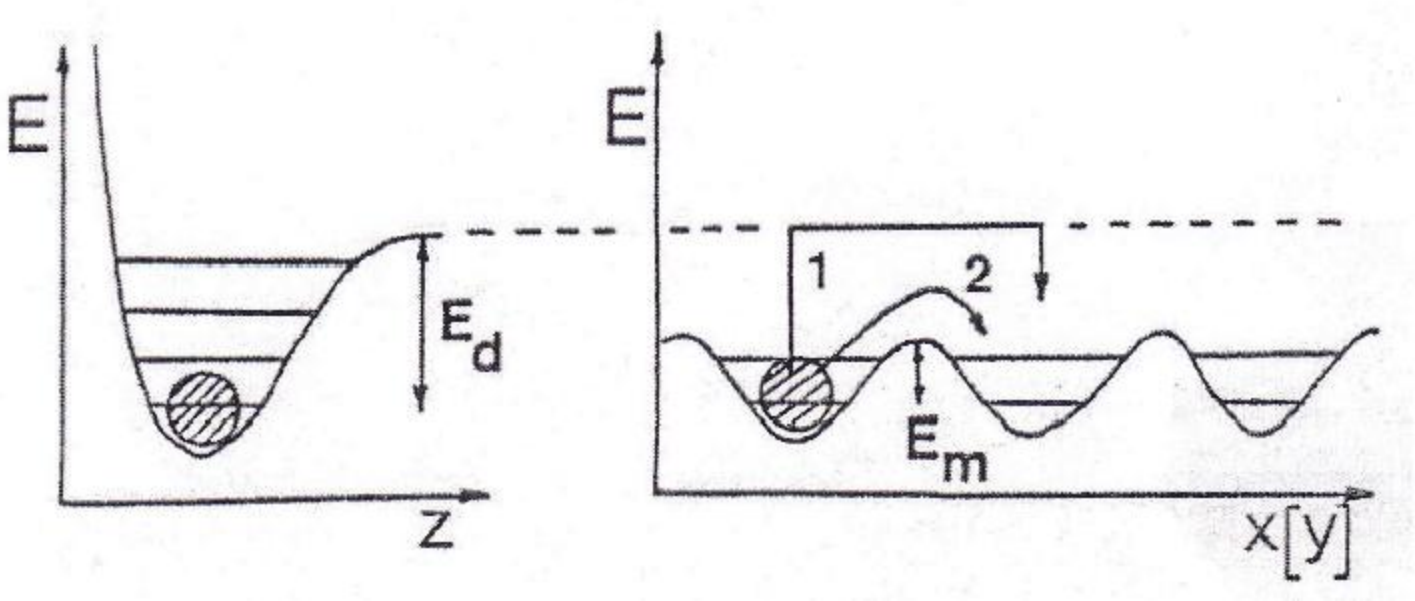
The molecule is trapped on some energy levels of vibrations in the potential holes. The molecule has lost one degree of translation but has gained several degree of vibrations ($\Delta S<0$ if adsorption is spontaneous then $\Delta H<0$). The molecule can change of energy levels depending on the thermal fluctuations.

Mobility of the adsorbed molecule



The adsorbed molecules is at constant distance from the surface along the z axis but can be moving in the in-plane direction (x or y)

Periodic potential holes distribution along x (or y)

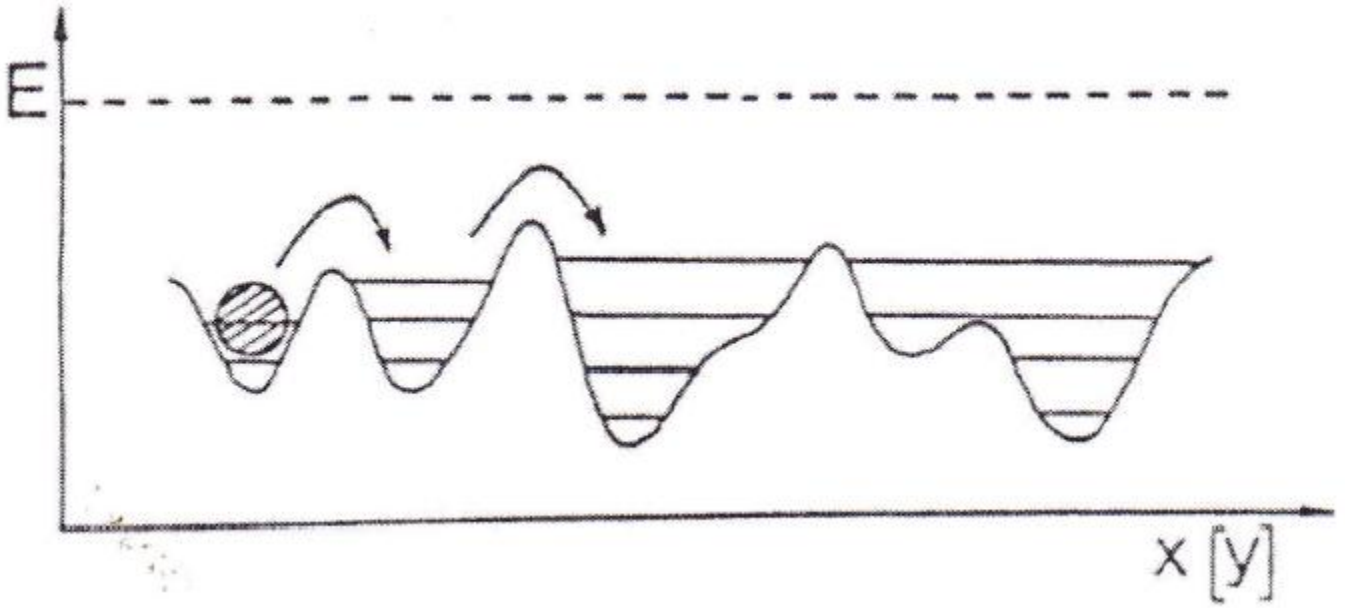


Energy diagram of an adsorbed molecule : along the z direction and along x (or y) direction

The potential holes are periodically arranged along x (or y) direction due to the periodic arrangement of the atoms of the surface plane.

The molecule can be trapped in potential along z direction, but still moving along x (or y) direction due to thermal fluctuations

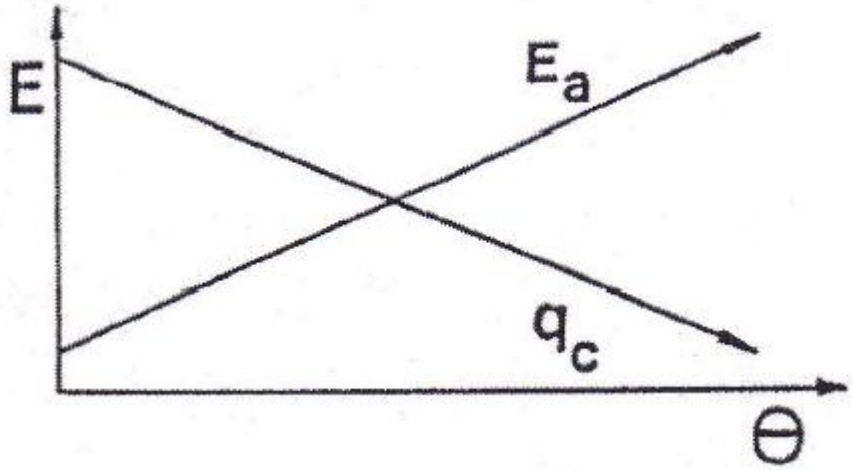
Distribution of the potential holes in the in-plane direction for a real surface (heterogeneous)



Energy diagram of an adsorbed molecule on an heterogeneous surface

The adsorption sites are potential holes of various depth (various adsorption energy).

The molecule can be trapped at first in a not much deep potential holes, but it can move deeper potential holes when equilibrium is reached.

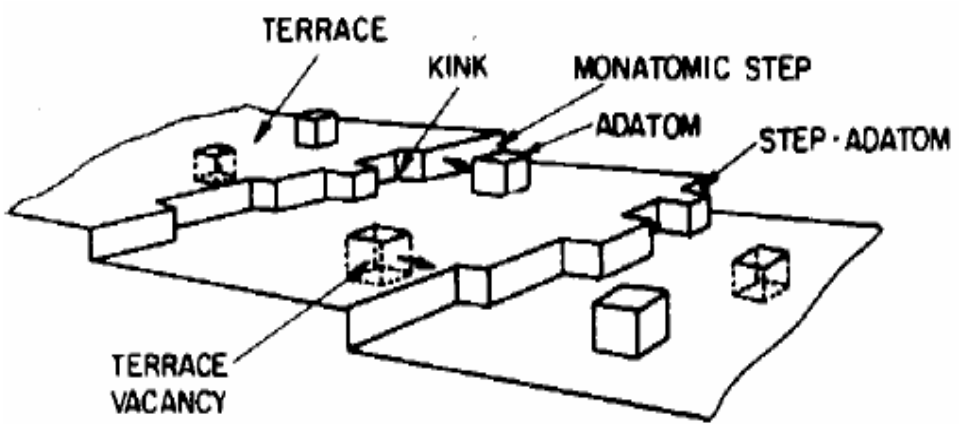


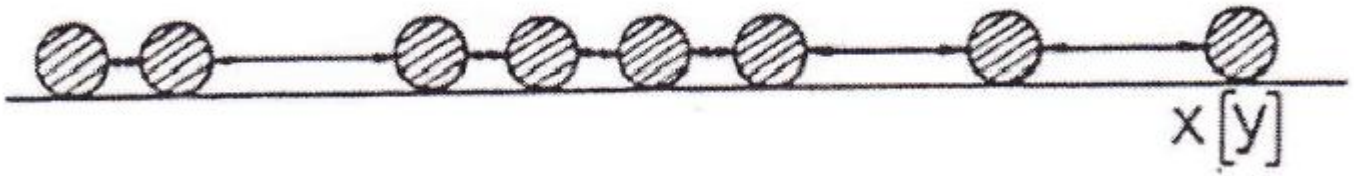
Evolution of the adsorption heat (q_c) and of the energy of activation (E_a) as a function of the cover ratio for a chemisorption

The adsorption heat decreases together with the coverage to due to the surface heterogeneity

Example of inhomogeneous surface

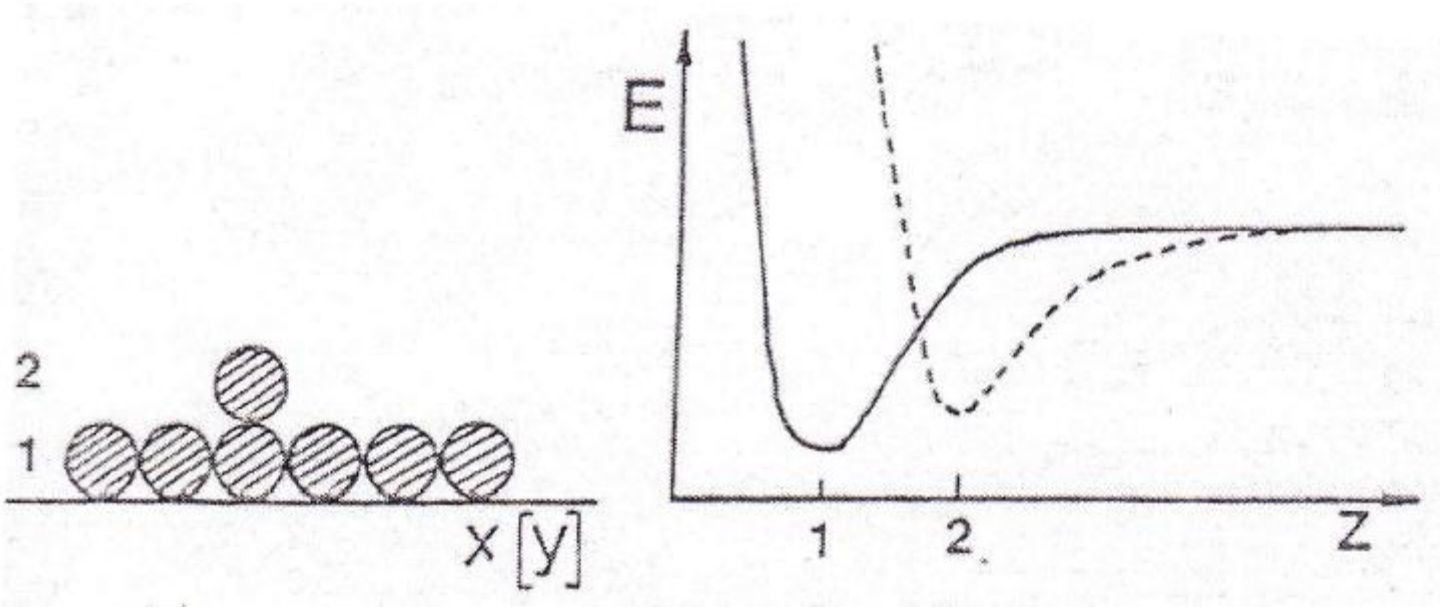
Extrinsic inhomogeneity from defects
(steps, domain boundaries, kinks, adatoms, vacancies, contaminants…)





The molecules undergo lateral interactions : adsorbate/adsorbate interactions

Multilayer adsorption



The molecules are adsorbed on the solid surface forming a first monolayer then they can be adsorbed on the adsorbed layer in a second layer, …etc

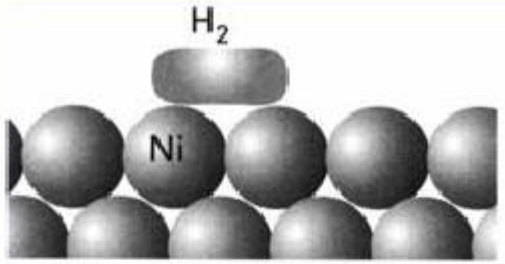
The adsorption on the second layer is less energetic

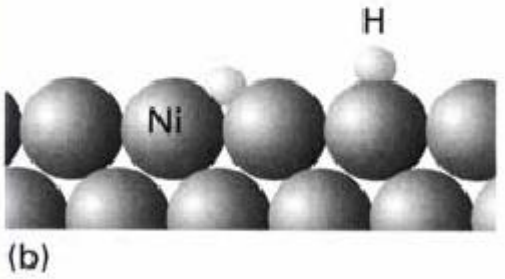
I.2 Physisorption and chemisorption

Physisorption and Chemisorption

1- **Physisorption**
Van der Walls forces
ΔH_{ads}= 2-10 kJ/mol
Long distances interactions (a few Å)
No chemical bond, reversible
Time of the molecule stay ~ 10 ns at room temperature
Multilayer adsorption possible

2- **Chemisorption with low activation energy**
New chemical bond are formed mainly irreversible
ΔH_{ads}= -200 kJ/mol
Various adsorption sites
Time of the molecule stay ~ 1h at room temperature
a monolayer is formed at the most





17.7 Schematic representation of (a) physisorption and (b) chemisorption of hydrogen on a nickel metal surface.

Physisorption and Chemisorption

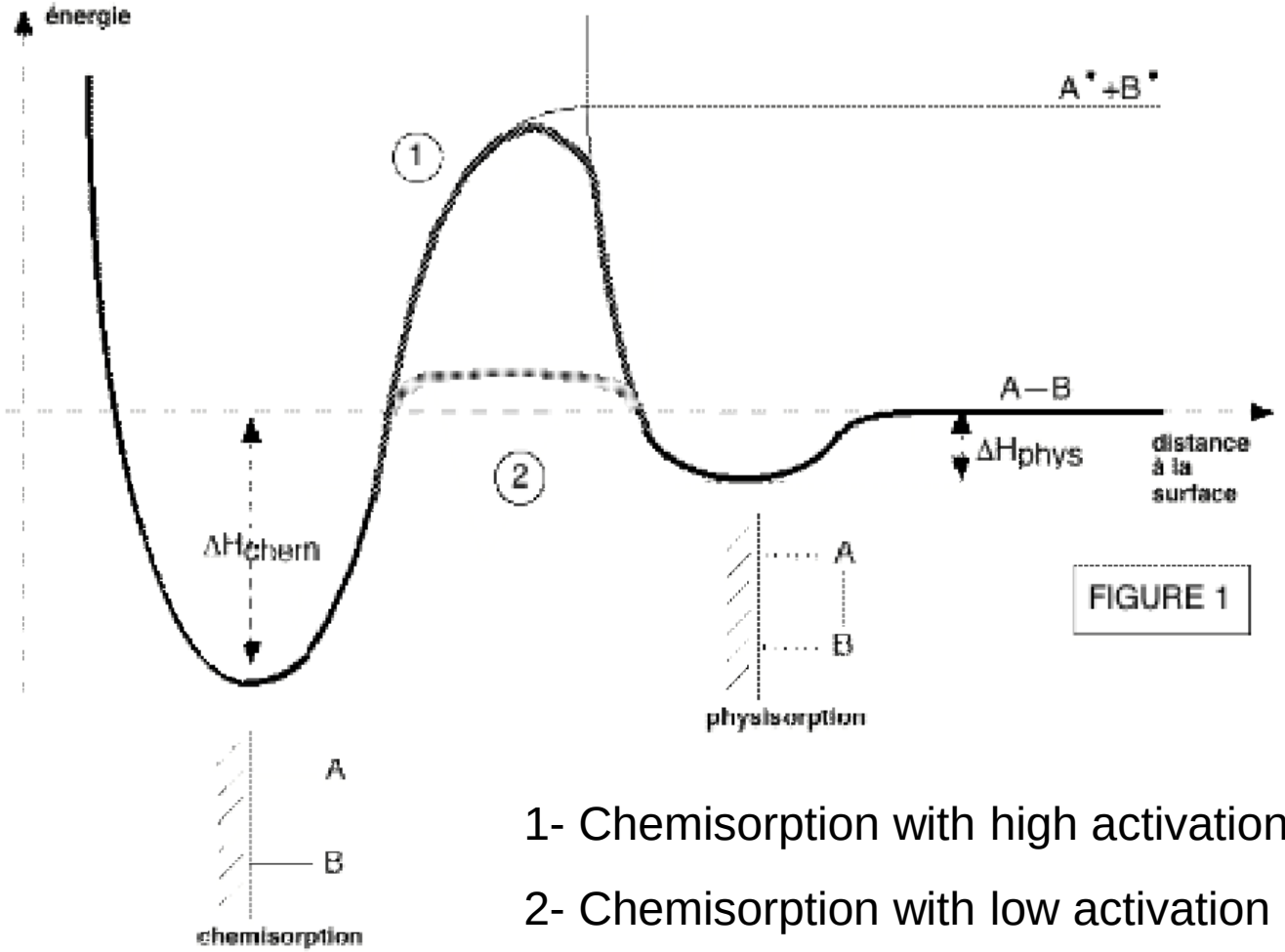
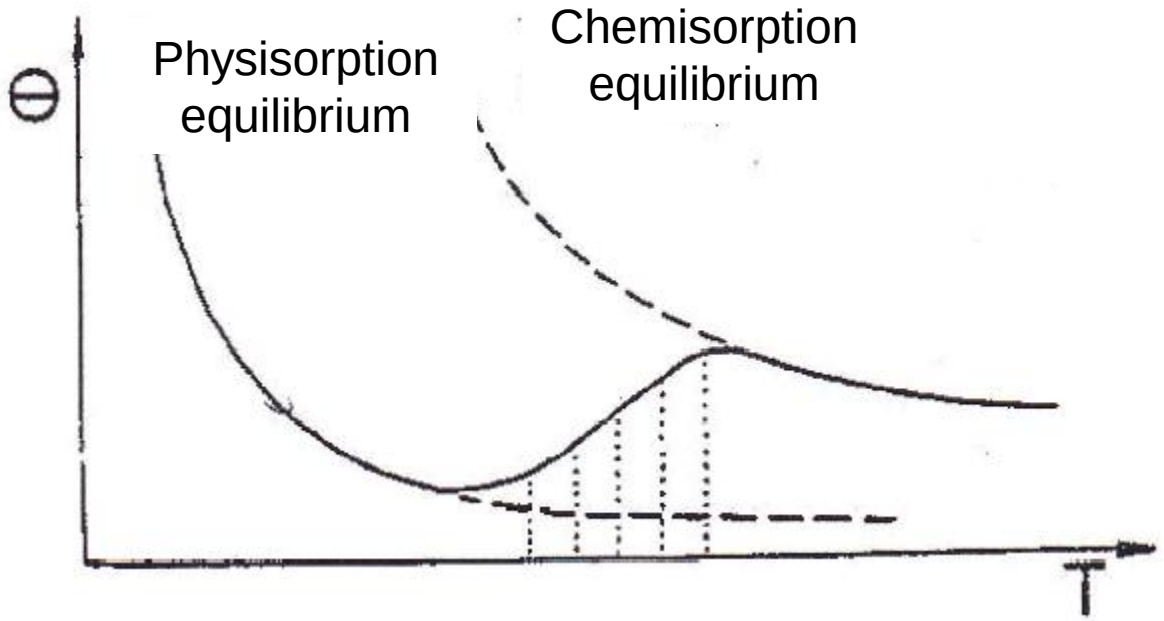


FIGURE 1

1- Chemisorption with high activation energy

2- Chemisorption with low activation energy



Evolution of the **adsorption isobars** (constant pressure) as a function of temperature for the physisorption and the chemisorption

Example of chemisorption : formation of hydride

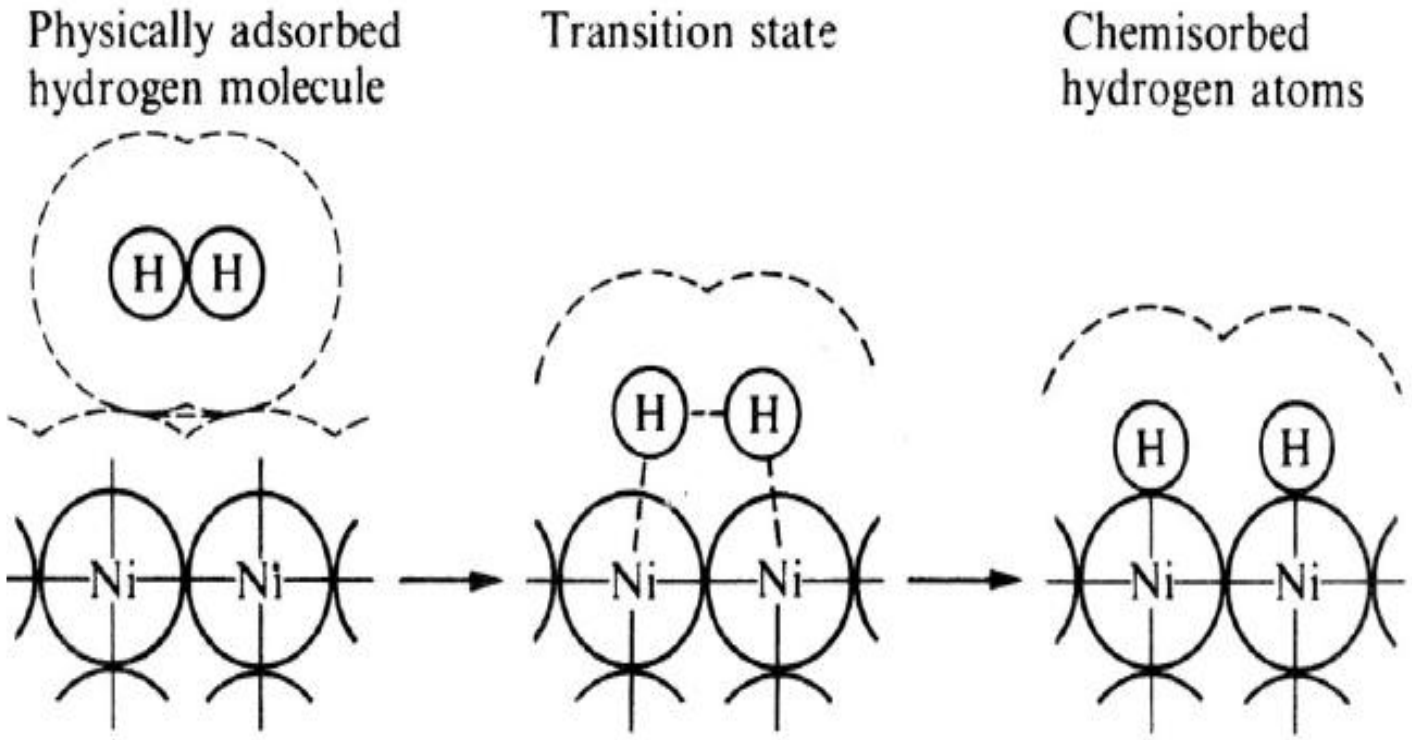


FIG. 3.3. Chemisorption of a hydrogen molecule on a nickel surface.

I.3 The interaction energy for physisorption

Table of Force Energies

Type of Force	Energy (kJ/mol)
Ionic Bond	300-600
Covalent	200-400
Hydrogen Bonding	20-40
Ion-Dipole	10-20
Dipole-Dipole	1-5
Instantaneous Dipole/ Induced Dipole	0.05-2

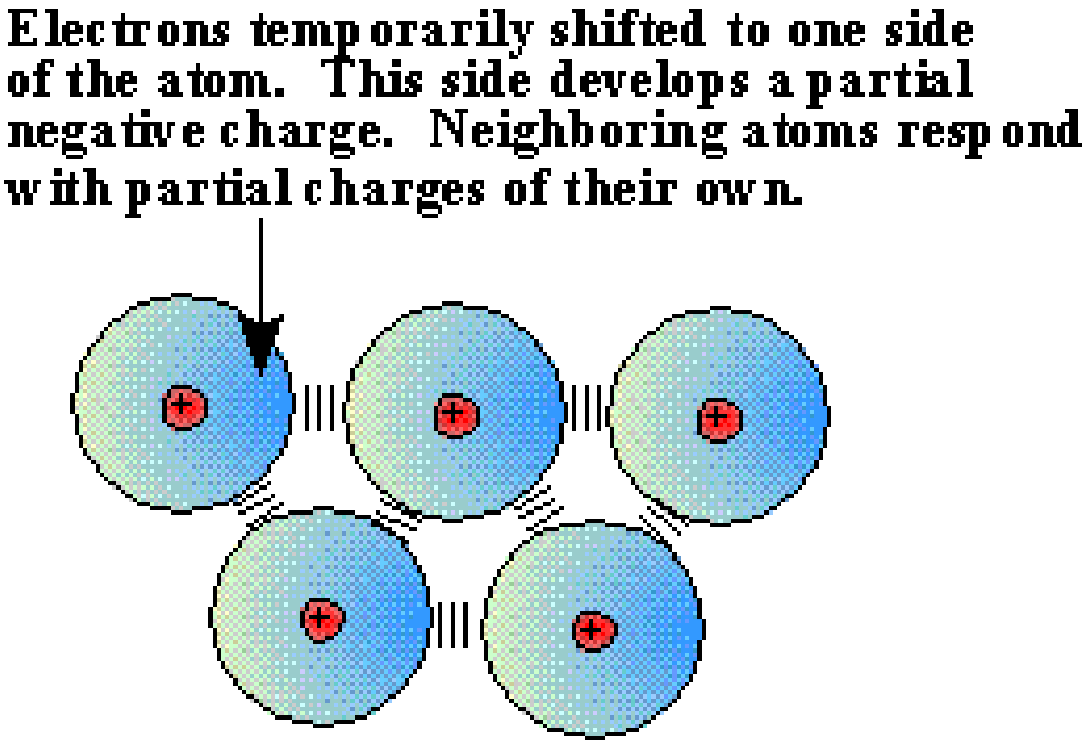
London Dispersion Forces

- One instantaneous dipole can induce another instantaneous dipole in an adjacent molecule (or atom).
- The forces between instantaneous dipoles are called London dispersion forces.
- Polarizability is the ease with which an electron cloud can be deformed.
- The larger the molecule (the greater the number of electrons) the more polarizable.

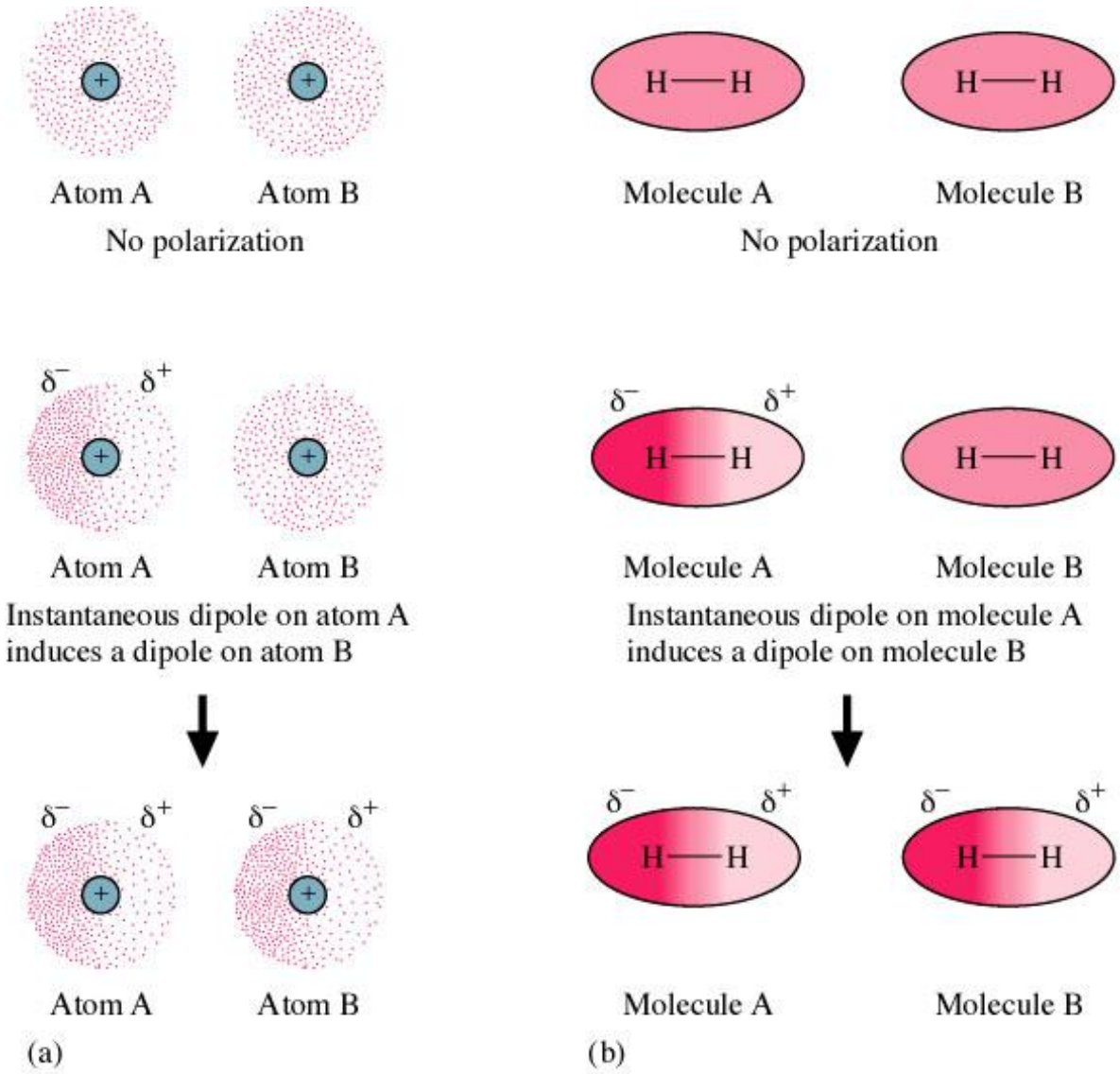
London Dispersion Forces

Temporary Induced Dipole-Dipole interactions

Very Weak always present in the condensed phase



London Dispersion Forces



Attractive London Dispersion Forces (1930)

Expression of the energy of the dispersion forces

$$E_{dispersion} = \frac{-C_d}{r^6}$$

C_d (α_1, α_2, I_1, I_2, …)

r is the distance

α is the polarisability and I the dipolar momentum

Repulsive Forces

Repulsive forces are due to the interpenetration of the electronic clouds

Expression of the energy of repulsion:

$$E_{repulsion} = \frac{B}{r^m}$$

B is a constant for which no theoretical expression is derived

$9 \leq m \leq 14$

6-12 Lennard-Jones potential : $$E = \frac{B}{r^{12}} - \frac{C_d}{r^6}$$

This potential allows to calculate the total energy of an adsorbate for physisorption by London forces.

Comparison of calculated and experimental dispersive energies for adsorption of rare gases on graphite

site c site b site h

Adsorbate	c	b	h	Average	Experimental results	E_L
Ne	0.77	0.84	1.11	0.91	0.89	0.42
Ar	1.95	2.07	2.64	2.22	2.7	1.60
Kr	2.69	2.78	3.47	2.95	3.9	2.14

(énergies en Kcal $mole^{-1}$)

The adsorption energies calculated by Avgul and Kiselev for various adsorption sites (sites a, b and c), compared to experimental values of adsorption energies on graphitized carbon black, and to the E_L liquefaction heat.

Polarisation Forces

- Due to superficial electric field F

  Graphite : 3.6 ×10^6 V. cm^{-1}; Zeolite (X and Y) : 2-5 ×10^7 V. cm^{-1}

- (I) In case of permanent dipole of adsorbate μ $E_{polarisation} = -\mu.F$

- (II) In case of induced dipole of adsorbate μ_{ind} $E_{polarisation} = -\mu_{ind}.F + W$

where $\mu_{ind} = \alpha F$ α is the adsorbate polarisability

and W is the work to form the induced dipole $W = \frac{1}{2}\alpha.F^2$

then $E_{polarisation} = -\frac{1}{2}\alpha.F^2$

Adsorbate	$\alpha(cm^3)$	$-E_{pol}(Kcal\ mole^{-1})$	Energy of adsorption (kcal. mol^{-1})
Ne	0,398	0,043	0,89
Ar	1,63	0,180	2,7
Kr	2,48	0,256	3,9

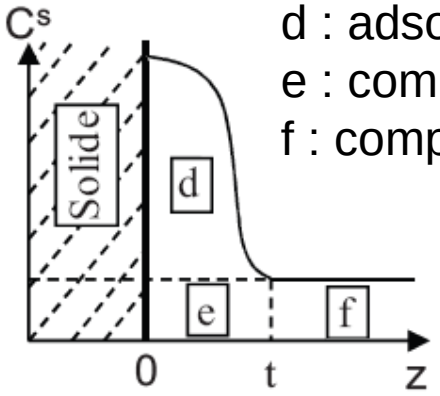
Contribution of the polarization energy to adsorption of rare gas on graphite (interaction of the superficial electric fields with induced dipole of the adsorbate molecule)

$E_{polarisation} = -1/2\ \alpha\ F^2$ (F electric field)

I.4 The adsorption isotherms

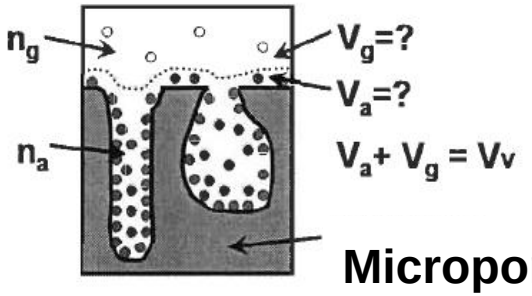
I.4.1 The isotherm's models

Excess adsorption and absolute adsorption



d : adsorbed in pores
e : compressed in pores
f : compressed out of pores

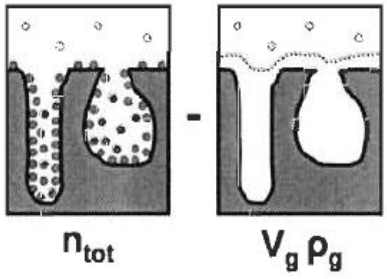
C^g gas concentration



Microporous adsorbent

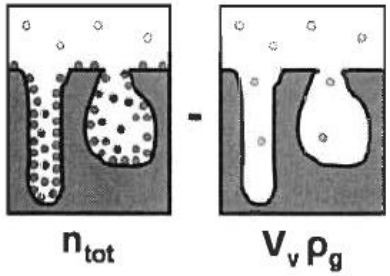
Absolute

$n_a =$



Excess

$n_{ex} =$



Reference volume :

$$V = V^{S,0} + V^{g,0} = V^S + V^a + V^g$$

Total gas volume :

$$V^{g,0} = V^a + V^g$$

in pores (adsorbed) + gaseous form

Excess adsorbed amount n^σ:

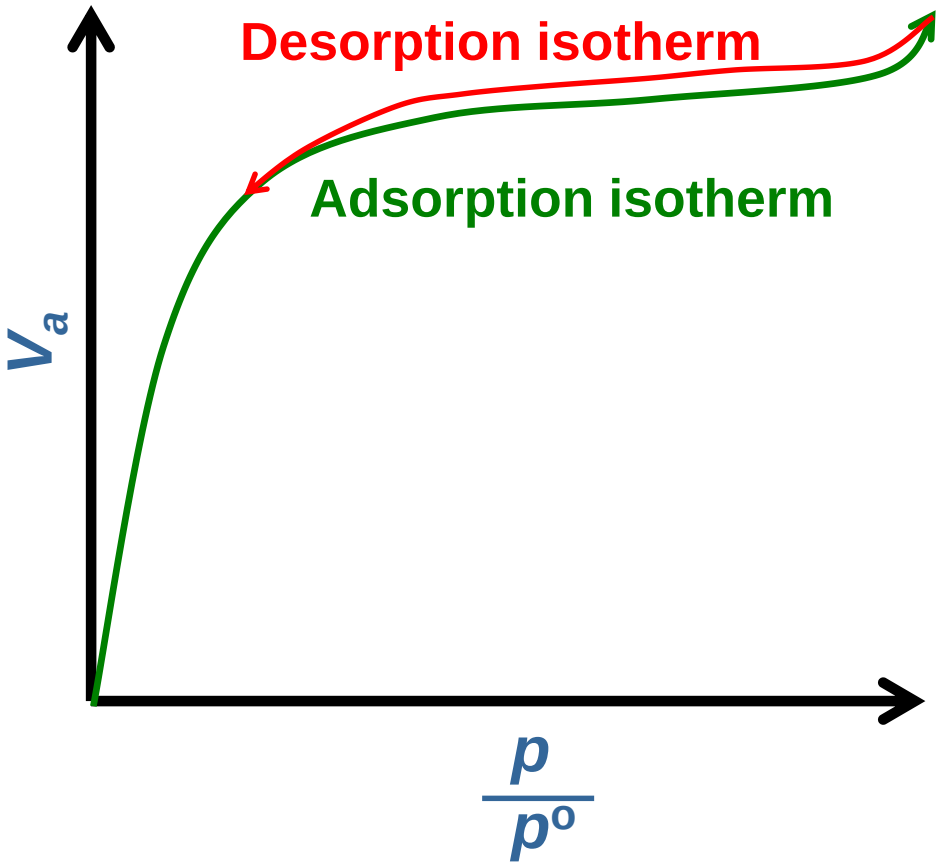
$$n^\sigma = n - C^g V^{g,0}$$

$$n^\sigma = n - C^g V^g - C^g V^a$$

<u>Absolute adsorption</u> : adsorbed amount at the surface + compressed gas in pores

<u>Excess adsorption</u> : only the adsorption amount at the surface

Gas adsorption: Isotherm



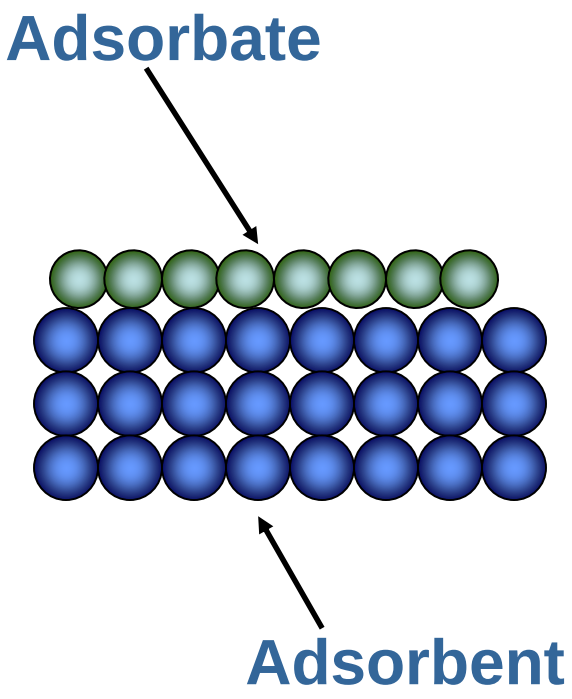
$$V_a = f\left(\frac{p}{p^o}\right)$$

where

$$\frac{p}{p^o} = \frac{\text{pressure of adsorbate}}{\text{saturated pressure of adsorptive}}$$

- Isotherm is a measure of the volume of gas adsorbed at a constant temperature as a function of gas pressure.
- Isotherms can be grouped into six classes.

Adsorption Theories: Langmuir



Assumptions:

- **homogeneous surface (all adsorption sites energetically identical)**
- **monolayer adsorption (no multilayer adsorption)**
- **no interaction between adsorbed molecules**

I. Langmuir The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids. *J. Am. Chem. Soc.*, 1916, 38 (11), 2221-2295

Langmuir Isotherm

Langmuir adsorption isotherm

$$A + M \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} A\text{-}M$$

p n(1-θ) n θ

pressure Vacant sites

A: the adsorbed molecule -- adsorbate

M: an adsorption site -- adsorbent

N : adsorbed amount (mole) on n sites (total number of sites)

N_m : monolayer amount (mole) ;

P is the Pressure (**in atm** because the activity is P/P_0 where P_0=1 atm)

θ : **fractional surface coverage**, θ= N/Nm= Vads/ Vm = number of sites occupied/ n

K_1 and K_{-1} : are Kinetic constant of the adsorption reaction

At equilibrium the reaction speed is both directions (1) and (-1) $v_1 = v_{-1}$

thus K_1 P. n (1-θ)= K_{-1} n θ and K_1 P. (1-θ)= K_{-1} θ

$$\theta = K_1/K_{-1}\ P/\ (1+ K_1/K_{-1}\ P)$$

If b= K_1/K_{-1} **θ=b P/ (1+ b P)**

If the system is thermodynamically activated $b = b_0 \exp(-\Delta H_{ads}/RT)$

were ΔH_{ads} is the enthalpy of reaction (kJ/ mol) and $\Delta H_{ads} = Ea_1 - Ea_{-1}$

Ea_1 and Ea_{-1} are the activation energy in the right-side and reverse direction

Langmuir Isotherm

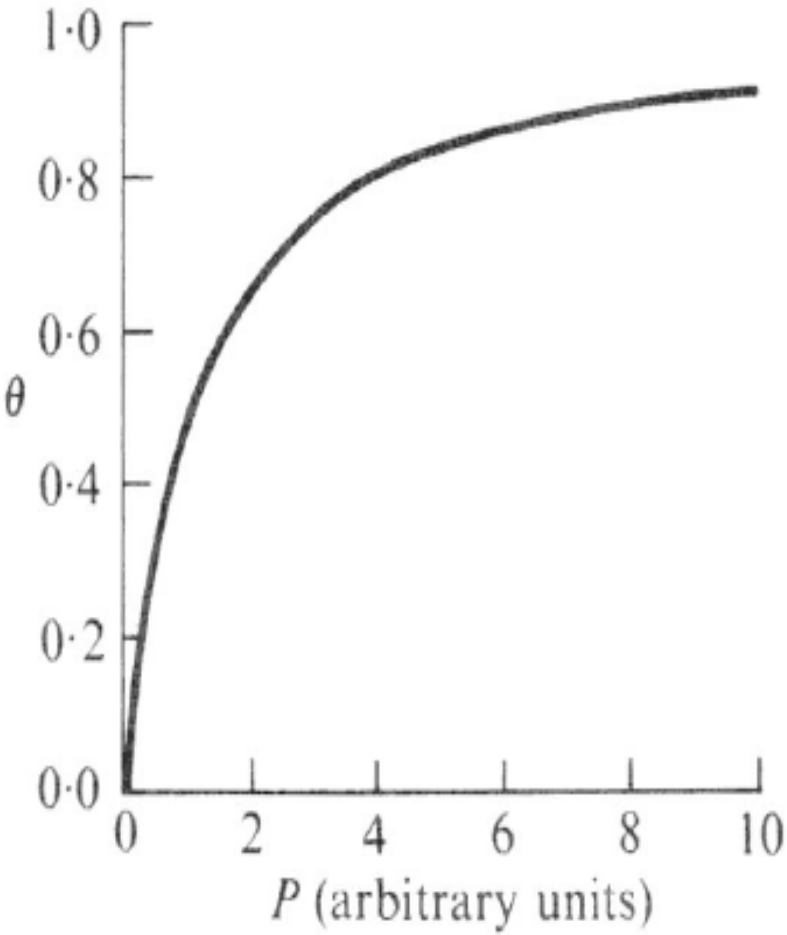
$$\theta = \frac{bp}{1 + bp}$$

Taking the most widely encountered form of the Langmuir equation (equation (30)) and bearing in mind that we may write $\theta = v/v_m$, we have:

$$v = \frac{v_m\, bp}{1 + bp} \qquad (42)$$

an equation which, at very low pressures ($bp \ll 1$) predicts, as does Henry's isotherm (equation (25)), a linear relationship ($v = v_m bp$) between amount adsorbed and equilibrium pressure. As the pressure approaches infinity, equation (42) predicts that v approaches v_m asymptotically.

Langmuir Isotherm



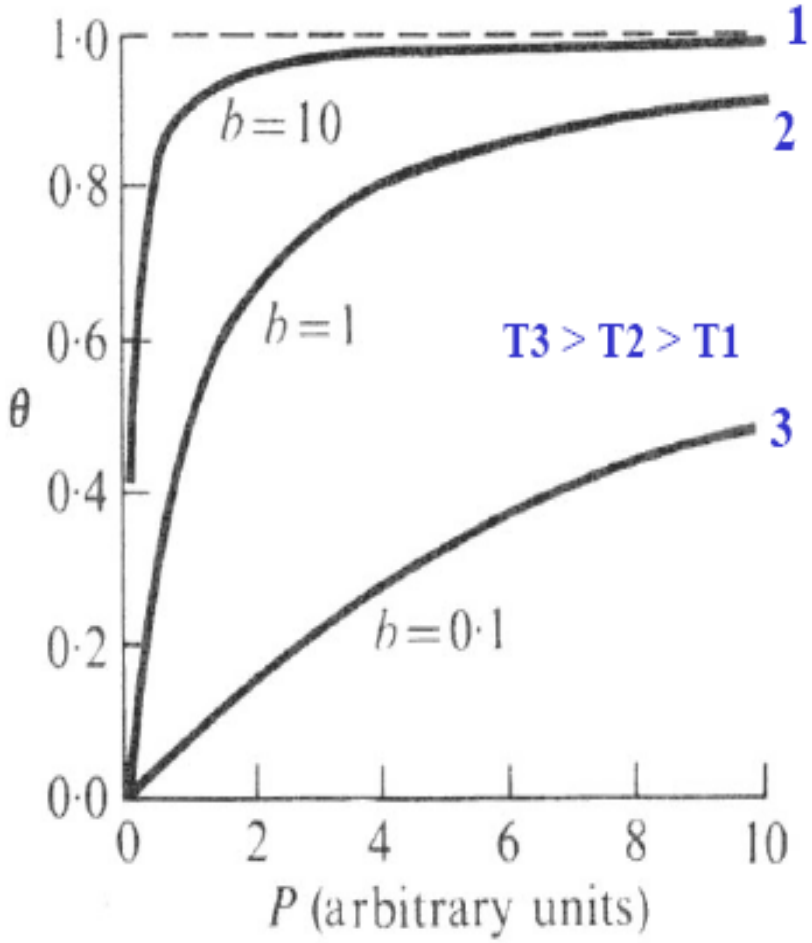


FIG. 2.3. The Langmuir adsorption isotherm.

FIG. 2.4. Langmuir adsorption isotherms with various values of b.

✣ **Adsorption is almost always exothermic, b must decrease with increase of temperature.**

Linearisation of Langmuir Isotherm

$$\frac{p}{v} = \frac{1}{bv_m} + \frac{p}{v_m}$$

V/P vs -V

$$\frac{v}{v_m p} + \frac{bv}{v_m} = b$$

1/V vs 1/p

$$\frac{v_m}{v} = \frac{1}{bp} + 1$$

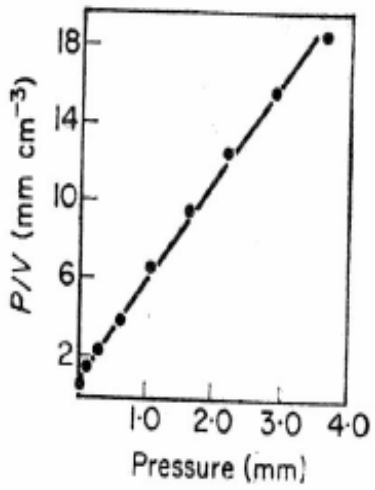


FIG. 10. The Langmuir plot obtained from the data of Fig. 9.

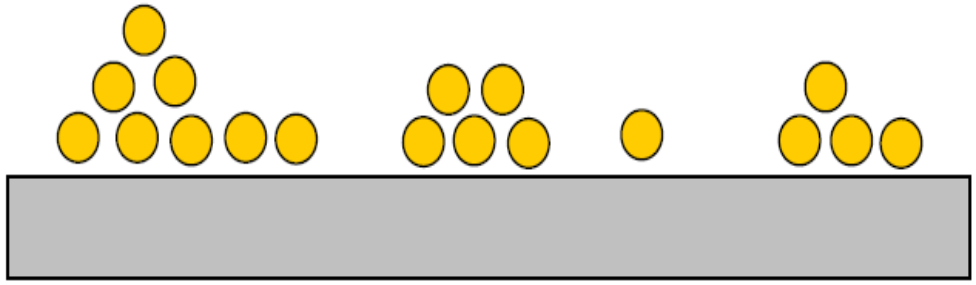
Slop = 1/Vm

$$\frac{V}{Vm} = \theta = \frac{bp}{1 + bp}$$

Vm: the monolayer capacity

$$b = \frac{\theta}{P(1 - \theta)}$$

BET Model
(Brunauer, Emmet et Teller, 1939)



Multilayer adsorption

- **Modification of Langmuir isotherm**
- **Both monolayer and multilayer adsorption**

- **Assumptions:**

(a) **gas molecules physically adsorb on a solid in layers infinitely;**

(b) **there is no interaction between each adsorption layer;**

(c) **the Langmuir theory can be applied to each layer.**

[S.Brunauer, P. Emmett, E.Teller , J. Am. Chem. Soc., 60 (2), 1938, Adsorption of Gases in Multimolecular Layers]

$$\frac{P}{N_a(P_o - P)} = \frac{1}{N_{am} \cdot c} + \frac{c-1}{N_{am} \cdot c} \frac{P}{P_o}$$

Applicable in the range
$0.05 < P/P_0 < 0.35$

P_0 : vapor saturating pressure ; N_a : number of adsorbed moles at the pressure P;

N_{am} : number of adsorbed moles in the monolayer

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

C : BET constant indicating the molecule affinity on the solid (C<< 1 low affinity with the solid)

E_1 : adsorption heat of the 1st layer; E_L : liquefaction heat

S_{BET}: Specific surface area determined by the BET method $S_{BET} = N_{am} \times A_m \times N_{AV}$

A_m : Surface area of the adsorbed molecule (pour N_2; A_m=16.2 $Å^2$/molecule)

N_{AV} : Avogadro number

$$\frac{P}{N_a(P_o - P)} = \frac{1}{N_{am} \cdot c} + \frac{c-1}{N_{am} \cdot c} \frac{P}{P_o}$$

Applicable in the range
$0.05 < P/P_0 < 0.35$

P_0 : vapor saturating pressure ; N_a : number of adsorbed moles at the pressure P;

N_{am} : number of adsorbed moles in the monolayer

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

C : BET constant indicating the molecule affinity on the solid (C<< 1 low affinity with the solid)

E_1 : adsorption heat of the 1st layer; E_L : liquefaction heat

S_{BET}: Specific surface area determined by the BET method $S_{BET} = N_{am} \times A_m \times N_{AV}$

A_m : Surface area of the adsorbed molecule (pour N_2; A_m=16,2 $Å^2$/molécule)

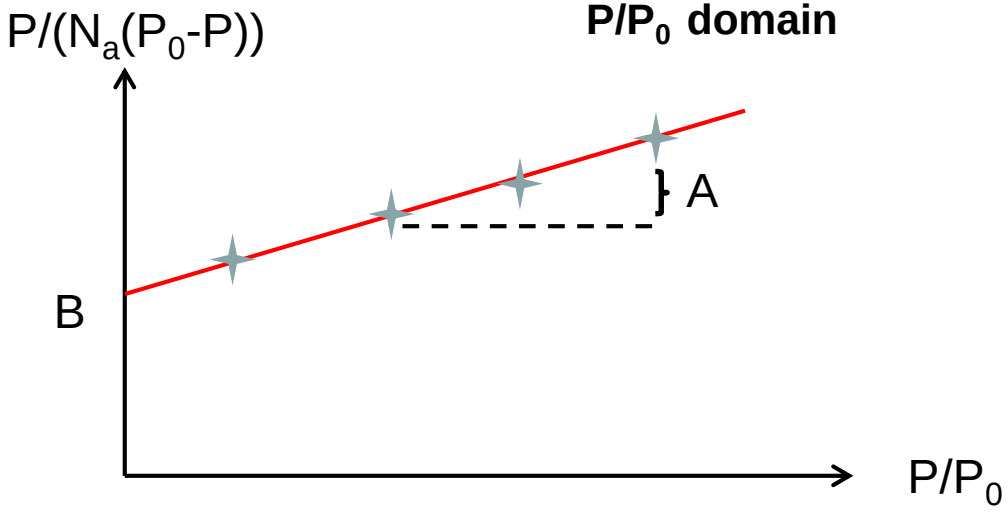
N_{AV} : Avogadro number

$$\frac{P}{N_a(P_o - P)} = \frac{1}{N_{am} \cdot c} + \frac{c-1}{N_{am} \cdot c}\frac{P}{P_o}$$

Applicable in the range
$0.05 < P/P_0 < 0.35$

c : BET constant indicating the molecule affinity on the solid

Linearisation in a certain P/P_0 domain



$A = (c-1)/(N_{am}.c)$

$B = 1/(N_{am}.c)$

$1/Nam = A+B$; $c = A/B+1$

- **c should be positive**
- **S_{BET} can be calculated from N_{am}**

S_{BET}: Specific surface area determined by the BET method $S_{BET} = N_{am} \times A_m \times N_{AV}$

A_m : Surface area of the adsorbed molecule (pour N_2; A_m=16,2 Å^2/molécule)

N_{AV} : Avogadro number

Applicability of the BET Model

- The model is applicable for a multilayer domain (**not possible in micropores (<2 nm**)
- The **c parameter should be positive** $c = \exp\left(\frac{E_1 - E_L}{RT}\right) > 0$

c : BET constant indicating the molecule affinity on the solid
(c<< 1 low affinity with the solid)

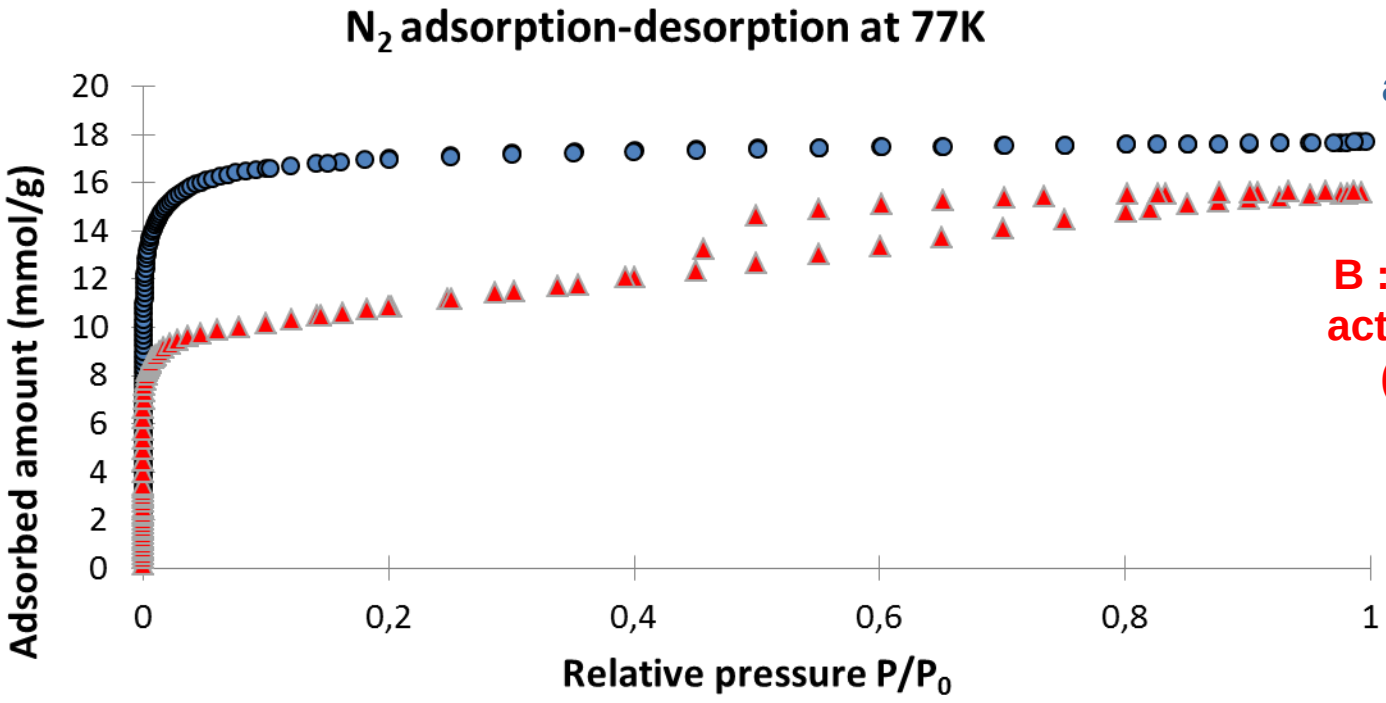
E_1 : adsorption heat of the 1st layer; E_L : liquefaction heat

P/P_0 applicability range of BET Model

• In mesoporous and macroporous materials, in the range $0.05 < P/P_0 < 0.35$

• In microporous materials, necessity to define a range where the c parameter is positive,
- Usual range $0.01 < P/P_0 < 0.05$ where c>0
- The S_{BET} has no physical sense, and is more an a comparison index proportional to an adsorption capacity

Example of Applicability of the BET Model



A : microporous activated carbon fabric (type I isotherm)

B : micro-mesoporous activated carbon fabric (type IV isotherm)

P/P_0 applicability range of BET Model

- in the range $0.1 < P/P_0 < 0.3$; C= -31; $S_{BET} = 1111\ m^2/g$
- in the range $0.1 < P/P_0 < 0.3$; C= -45; $S_{BET} = 756\ m^2/g$

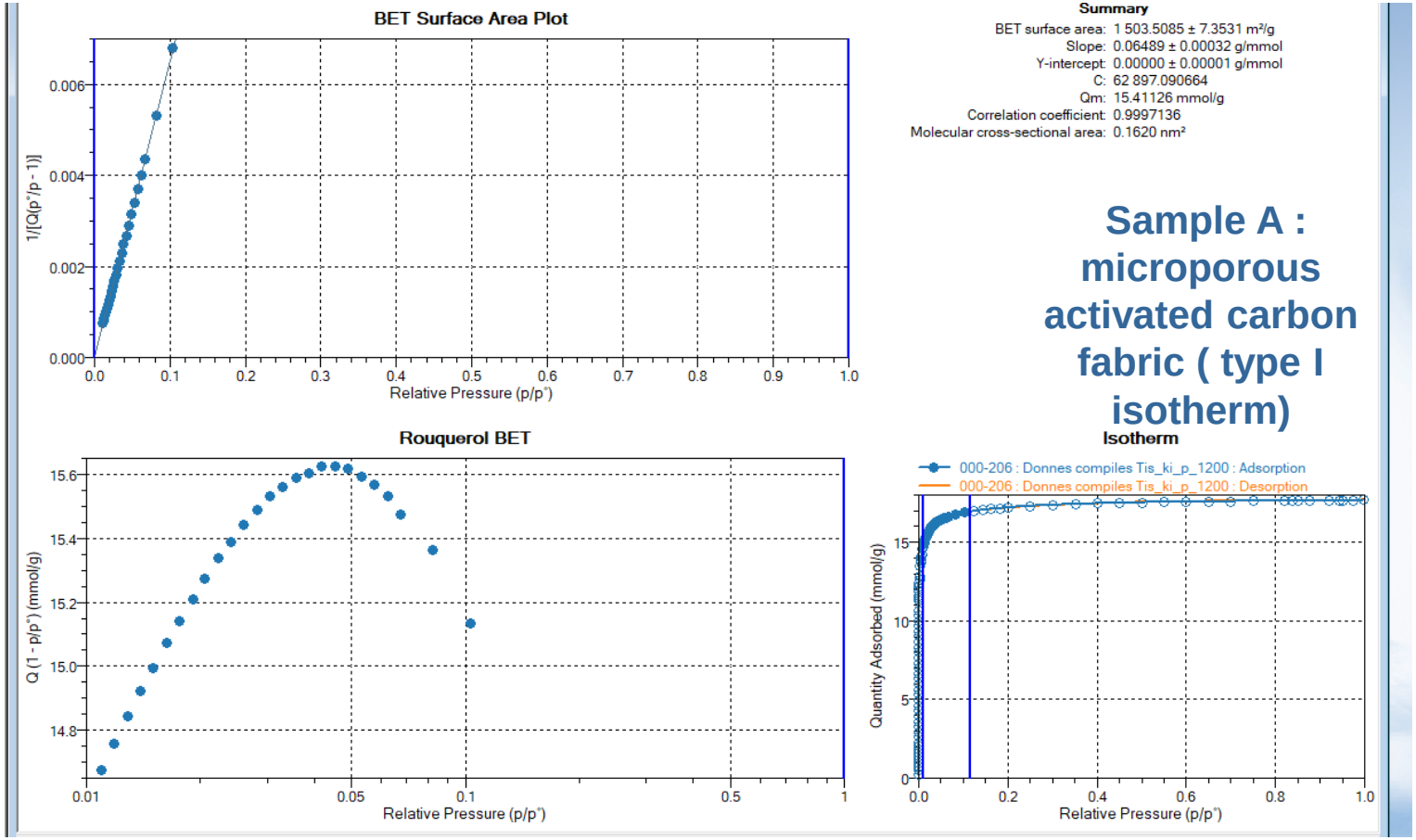
} The BET model is not appropriate as C<0

- in the range $0.01 < P/P_0 < 0.05$; C=+972; $S_{BET} = 1523\ m^2/g$
- in the range $0.01 < P/P_0 < 0.05$; C= +1183; $S_{BET} = 922\ m^2/g$

} In this range a S_{BET} can be calculated though it has not the sense of the real surface area of the solid

Choice of P/P_0 domain for application of the BET Model (Rouquerol criterion)

- In the chosen P/P_0 domain the **c parameter should be positive**
- In the chosen P/P_0 domain, **$N_a.(1- P/P_0)$ is increasing continuously with P/P_0**
- The value of P/P_0 at which the monomolecular layer is formed (adsorption reach N_{am}) should be included in the P/P_0 chosen domain



Summary of adsorption isotherms

Name	Isotherm equation	Application	Note
Langmuir	$\theta = \frac{C_s}{C_\infty} = \frac{B_0 P}{1 + B_0 P}$	Chemisorption and physisorption	Useful in analysis of reaction mechanism
Temkin	$\theta = c_1 \ln(c_2 P)$	Chemisorption	Chemisorption
Freundlich	$\theta = c_1 p^{1/C_2}$	Chemisorption and physisorption	Easy to fit adsorption data
BET	$\frac{P/P_0}{V(1-P/P_0)} = \frac{1}{cV_m} + \frac{c-1}{cV_m}(P/P_0)$	Multilayer physisorption	Useful in surface area determination

Table 2.1 A selection of adsorption isotherms.[a]

Name	Isotherm equation	Applicability	Equation no.
Langmuir[b]	$\frac{V}{V_m} = \theta = \frac{bp}{1+bp}$	Chemisorption and physical adsorption	(41)
Henry[c]	$V = k'p$	Chemisorption and physical adsorption at low coverages	
Freundlich	$V = kp^{1/n} (n > 1)$	Chemisorption and physical adsorption at low coverages	(49)
Temkin	$\frac{V}{V_m} = \theta = A \ln Bp$	Chemisorption	(50)
Brunauer–Emmett–Teller (BET)	$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} \cdot \frac{p}{p_0}$	Multilayer, physical adsorption	(51)
Polanyi[d]	$\varepsilon = RT \ln(p_0/p)$	Physical adsorption	(53)
Dubinin–Radushkevich[e]	$\ln x = \ln(W_0 \rho) - D[\ln(p_0/p)]^2$	Multilayer formation in microporous solids	(58)
Dubinin–Kaganer–Radushkevich (DKR)	$x = x_m \exp(-B\varepsilon^2)$	Physical adsorption up to a monolayer	(62)
Virial	$\frac{p}{RT} = x(1 + a_1 x + a_2 x^2 + \ldots)$	Multilayer formation in micropores	(63)

[a] Amounts adsorbed at pressure p are represented either by volume V or mass x. Unless otherwise specified, all other symbols in these equations are constants.

[b] V_m (and x_m) correspond to monolayer coverage.

[c] This equation is the limiting form of the Langmuir equation.

[d] The adsorption potential ε is defined by this equation.

[e] W_0 stands for the total volume of all the micropores in a solid.

I.5.2 Capillary condensation

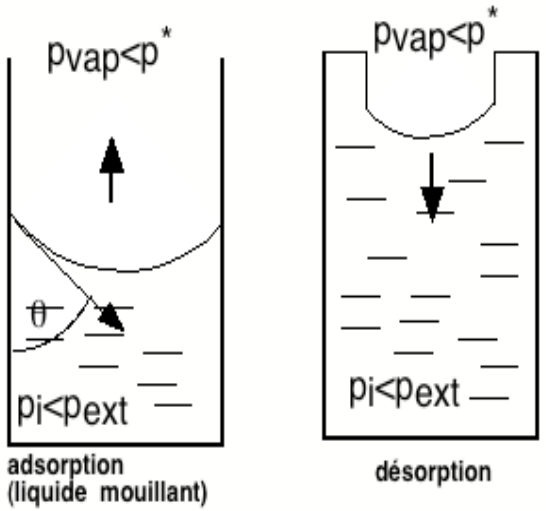
Capillary condensation in the mesopores (2-50 nm)

A pore of effective radius r_k filled of a liquid is in equilibrium with its P pressure vapor as the **Kelvin equation** (for water Kelvin radius is : 2-3 nm) is established :

$$r_k = \frac{-2\gamma V\cos(\theta)}{RT\ln(P/P_0)} = \frac{-k}{\log(P/P_0)}$$

P_0 : saturation vapor pressure
R : Constant of perfect gas
T : temperature of the system
V: molar volume of condensed state
γ : surface tension of condensed state
θ : wetting angle

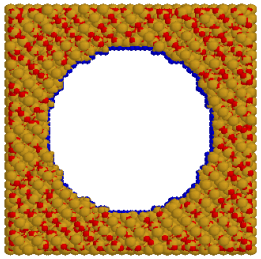
Effective Radius $1/r_k = [1/r_{k,1}] + [1/r_{k,2}]$

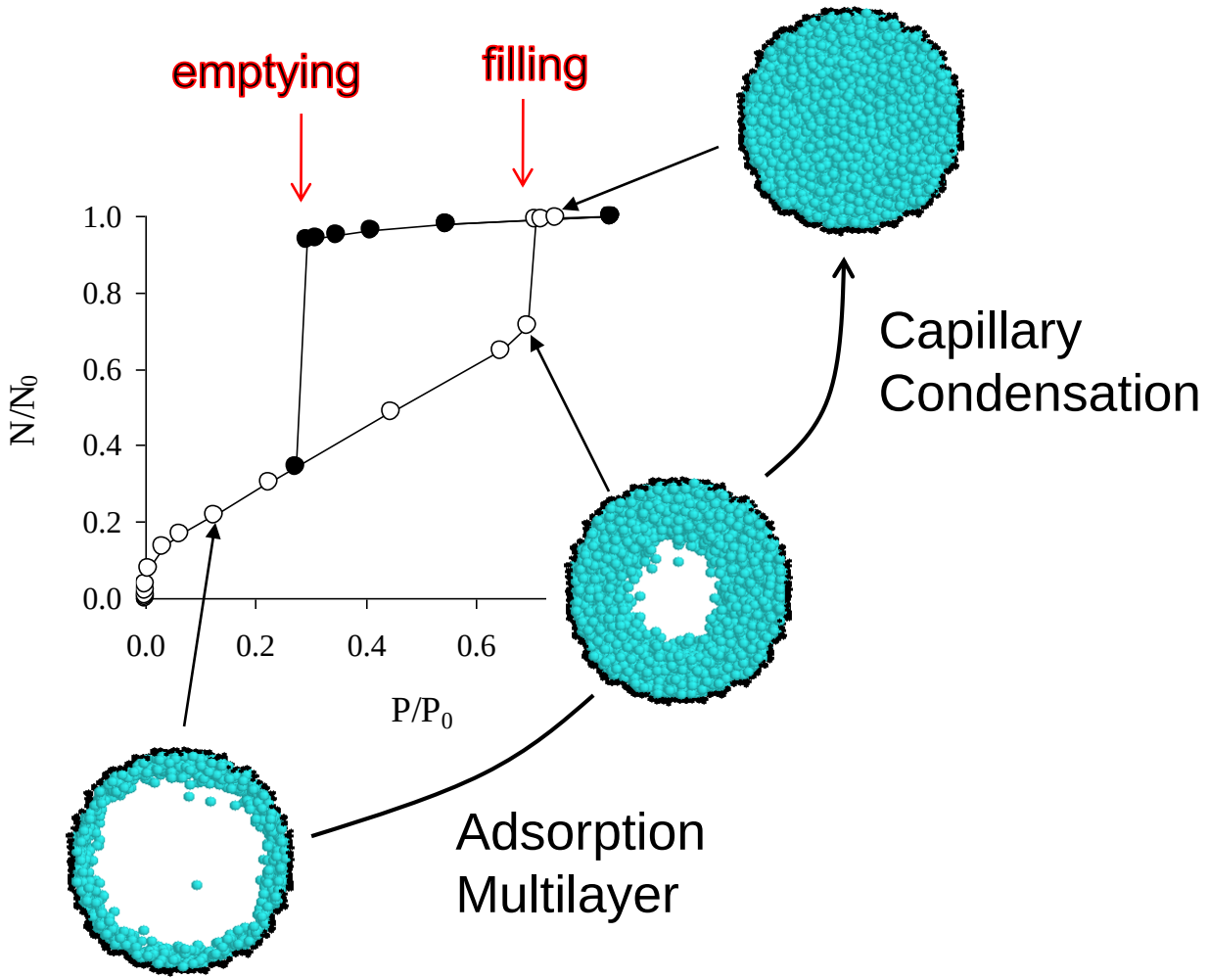


(1) and (2) means that the radius ($r_{k,1}$ and $r_{k,2}$) and are defined along two perpendicular planes (a section plane and a plane perpendicular to the section)

Capillary condensation in the mesopores

Adsorption Argon a 87 K





Adsorption / Desorption

Capillary condensation

Adsorption =

multilayer formation

Desorption =

Meniscus development

Isotherm Hysteresis

- At adsorption, if liquid wet the surface $0° < \theta_{ads.} < 90°$. Upon desorption, as condensed adsorbate contact to a wetted surface, the contact angle value is almost $\theta_{des.} = 0°$.

  So that $P_{des.}/P_0 = \exp(-2\gamma V/(r_K RT)) < P_{ads.}/P_0$

  and an hysteresis loop appear in the adsorption- desorption isotherms.

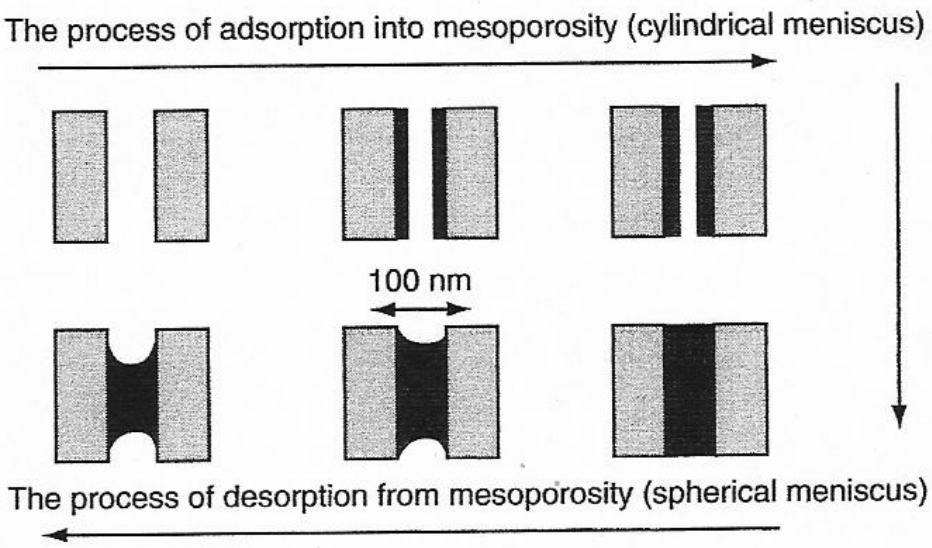
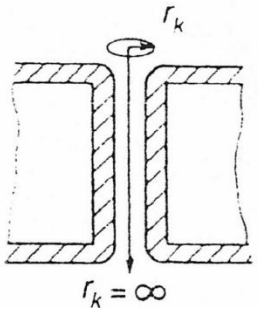


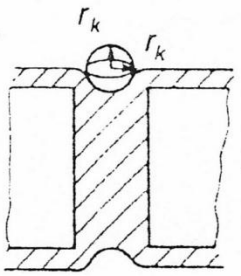
Figure 4.59. Adsorption in mesoporosity: a possible cause of hysteresis.

- Hypothesis of a cylindrical pore



for adsorption, vacuumed pore $(1/r_k)_{eff} = 1/r_k + 1/\infty$

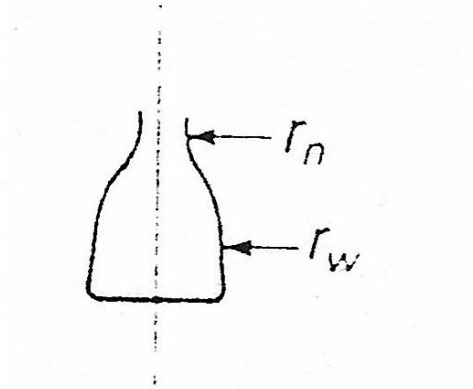
for desorption, full pore $(1/r_k)_{eff} = 1/r_k + 1/r_k$ thus,

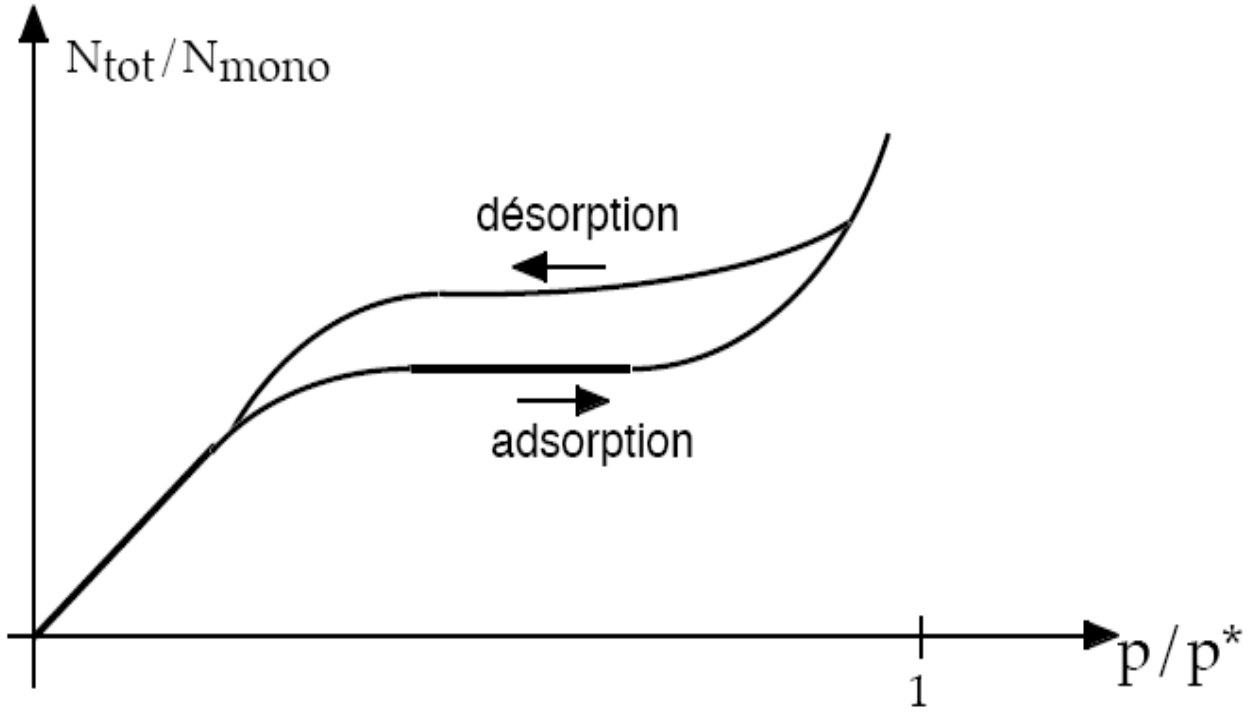


$r_K = -\gamma V \cos(\theta)/[RT \ln (P/P_0]$

and $P_{ads.}/P_0 > P_{des.}/P_0 = \exp(-2\gamma V/(r_k RT))$

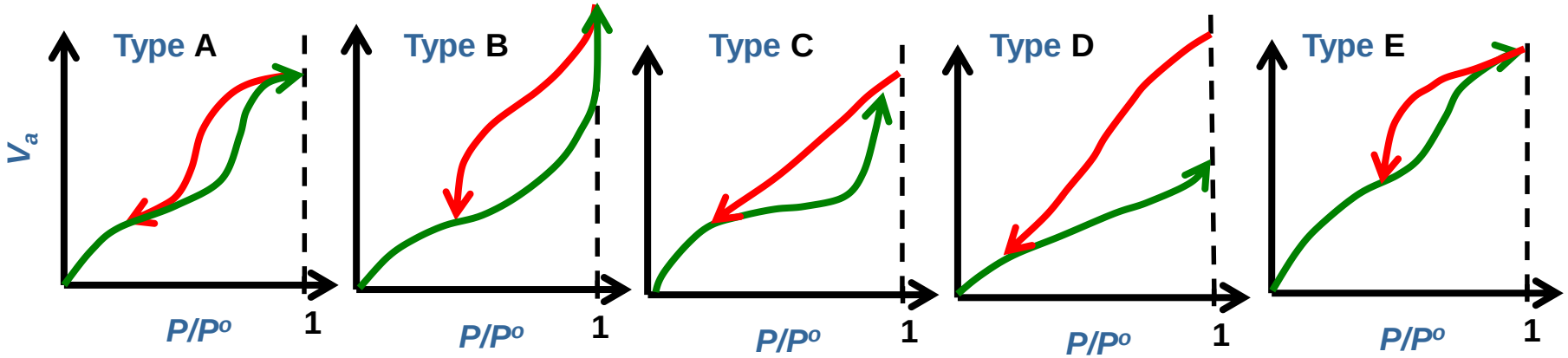
- Ink bottle pores are filled (Kelvin law) when the relative pressure corresponds to the internal radius (r_w), and empties as it corresponds to radius of the bottle neck.

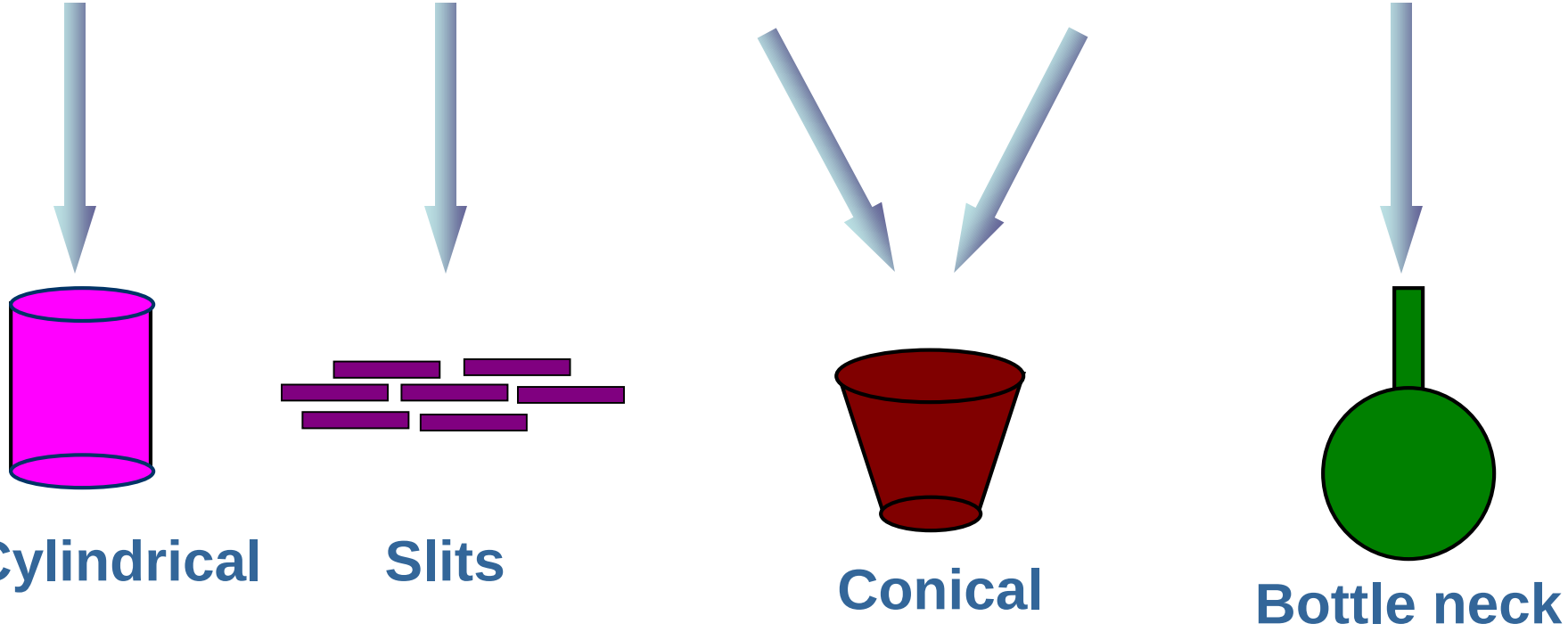


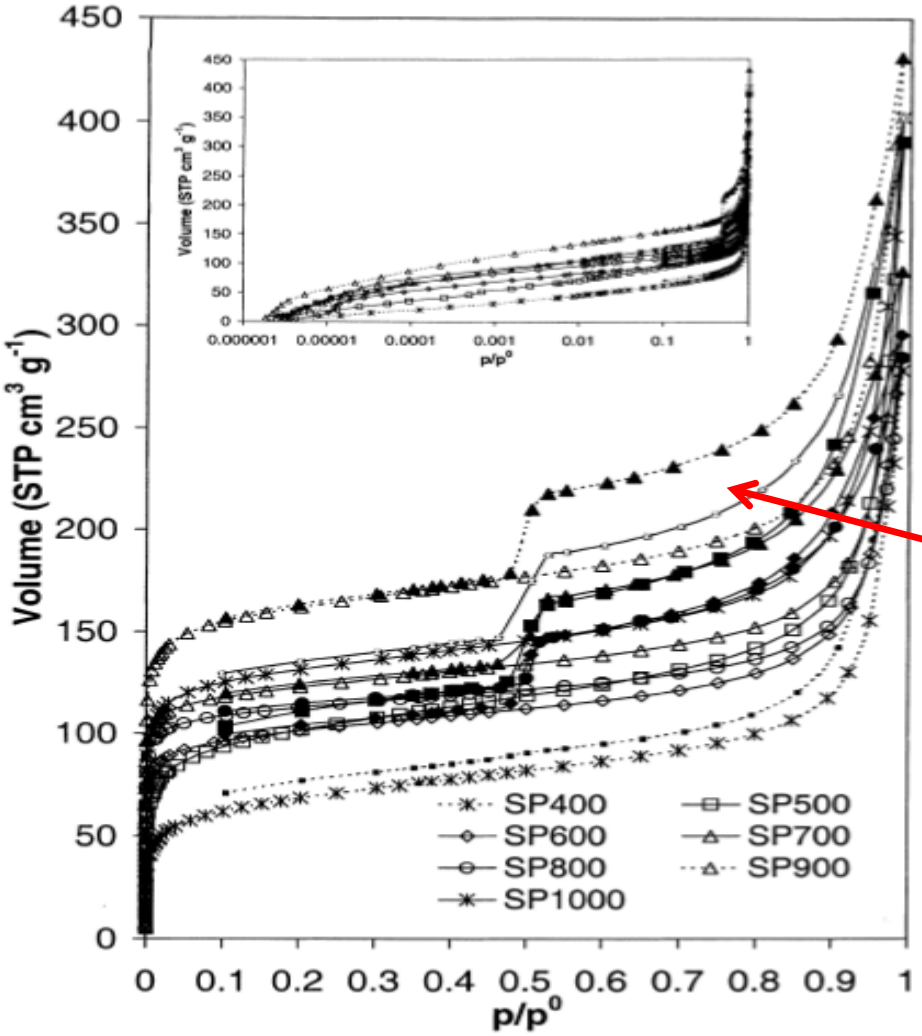


In a porous divided solid, the capillary condensation of the liquid phase can occur in the mesopores (2-50 nm diameter)

Gas Sorption: Hysteresis







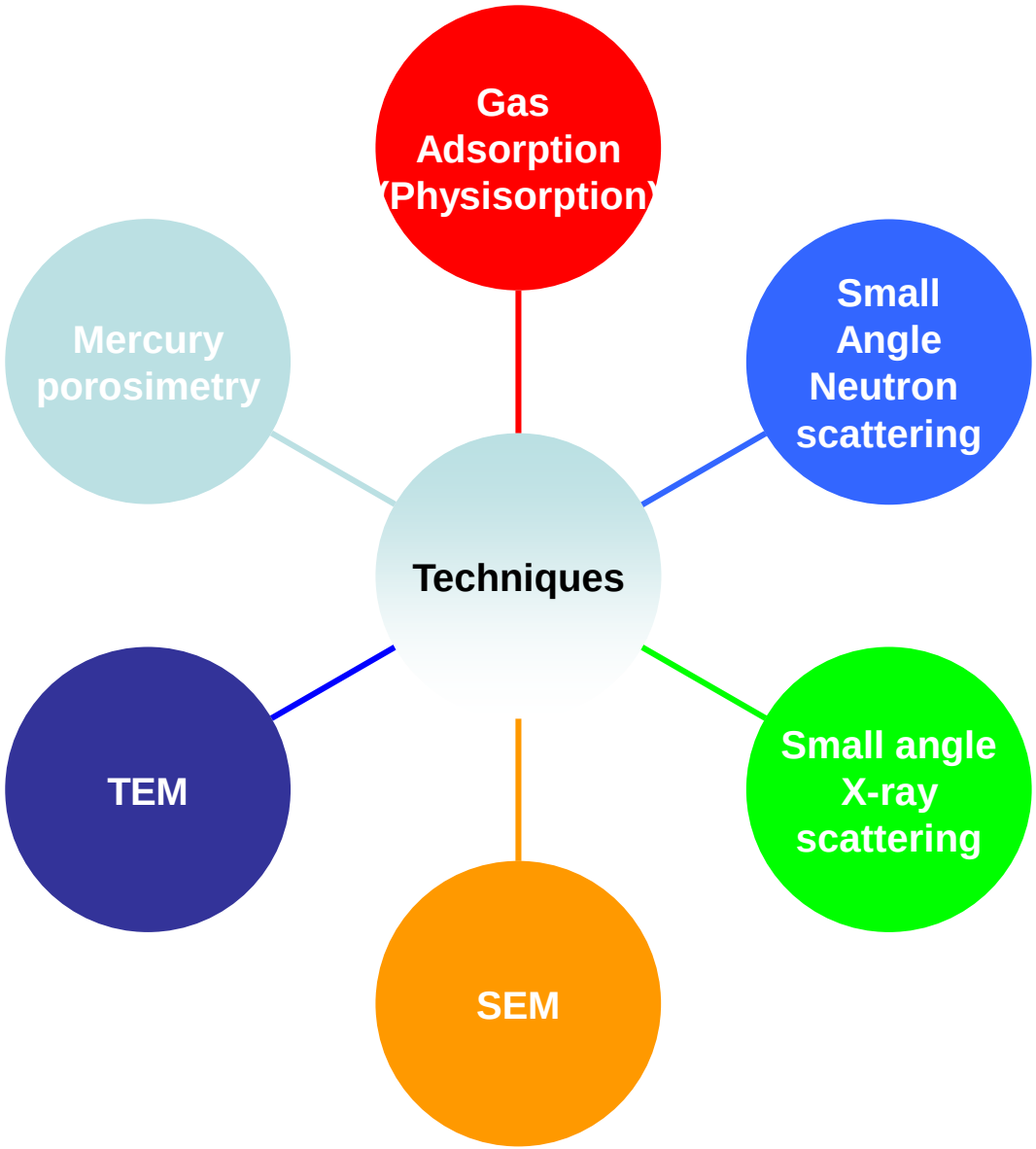
Presence of mesopores

Fig. 1. Nitrogen adsorption–desorption isotherms at −196 °C on synthetic activated carbons prepared at different temperatures. Full symbols, adsorption; open symbols, desorption. Insert, semilogarithmic scale isotherms.

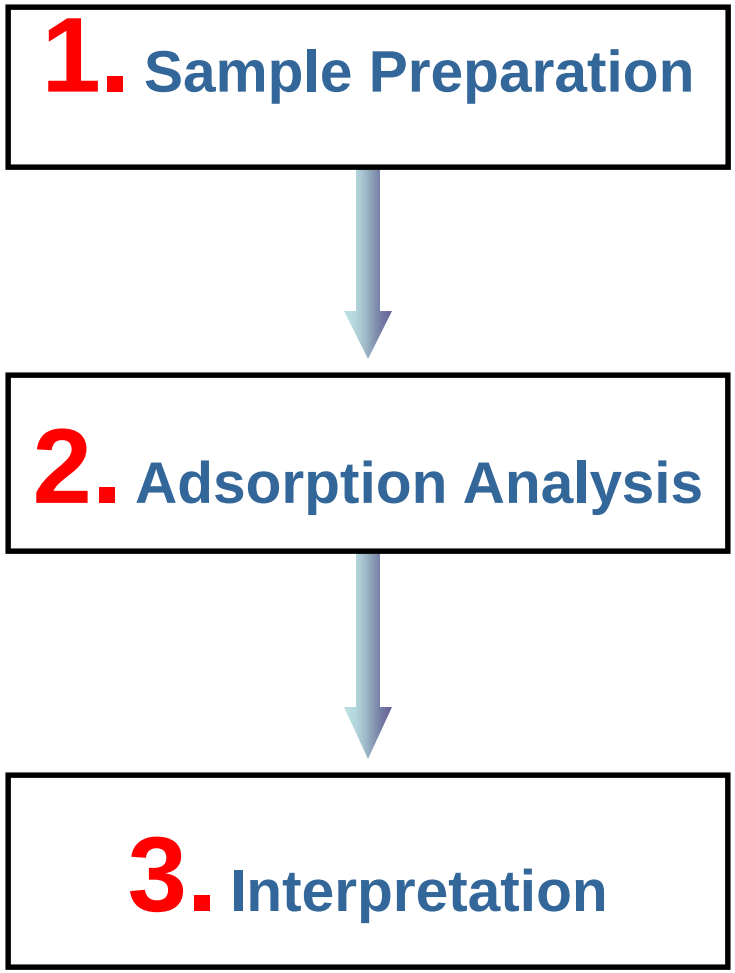
I.5.3 Classification of physisorption isotherms

IUPAC Classification of pores

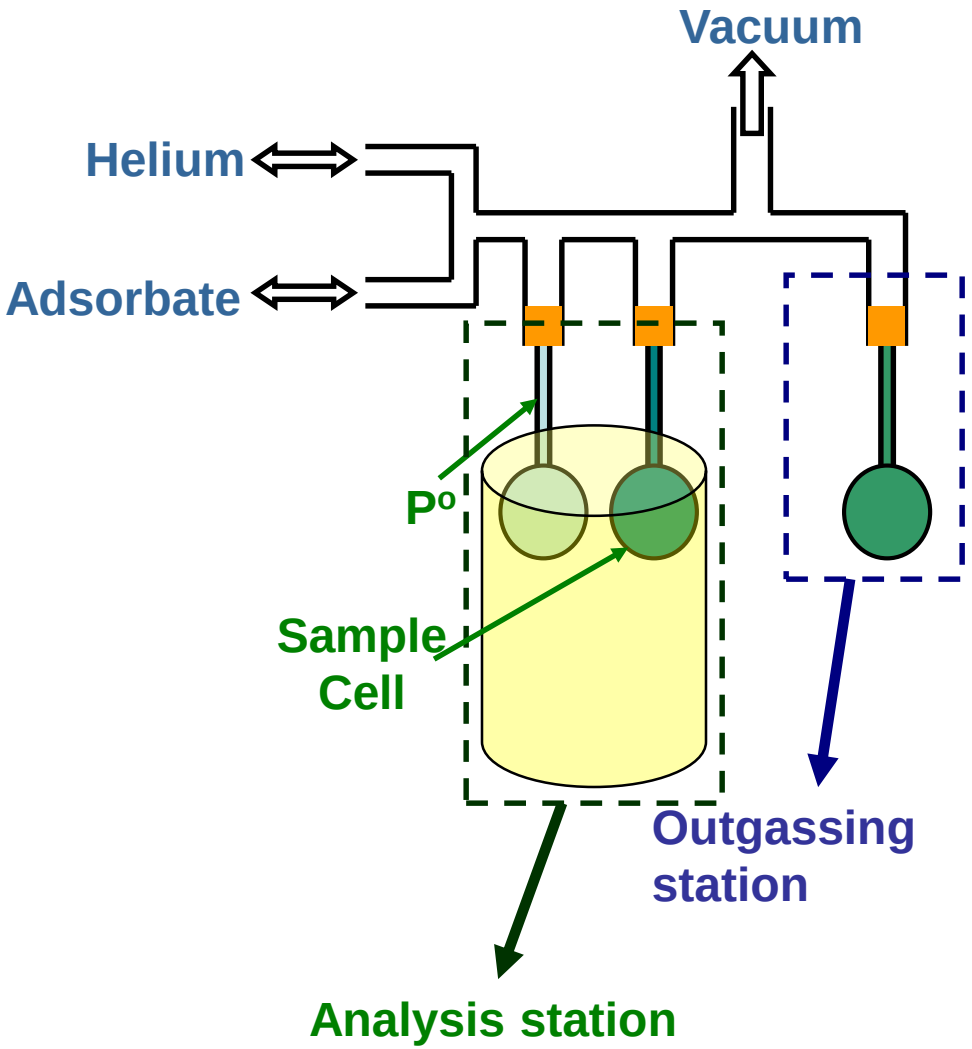
Techniques for Porosity Analysis



Porosity Analysis by gas physisorption

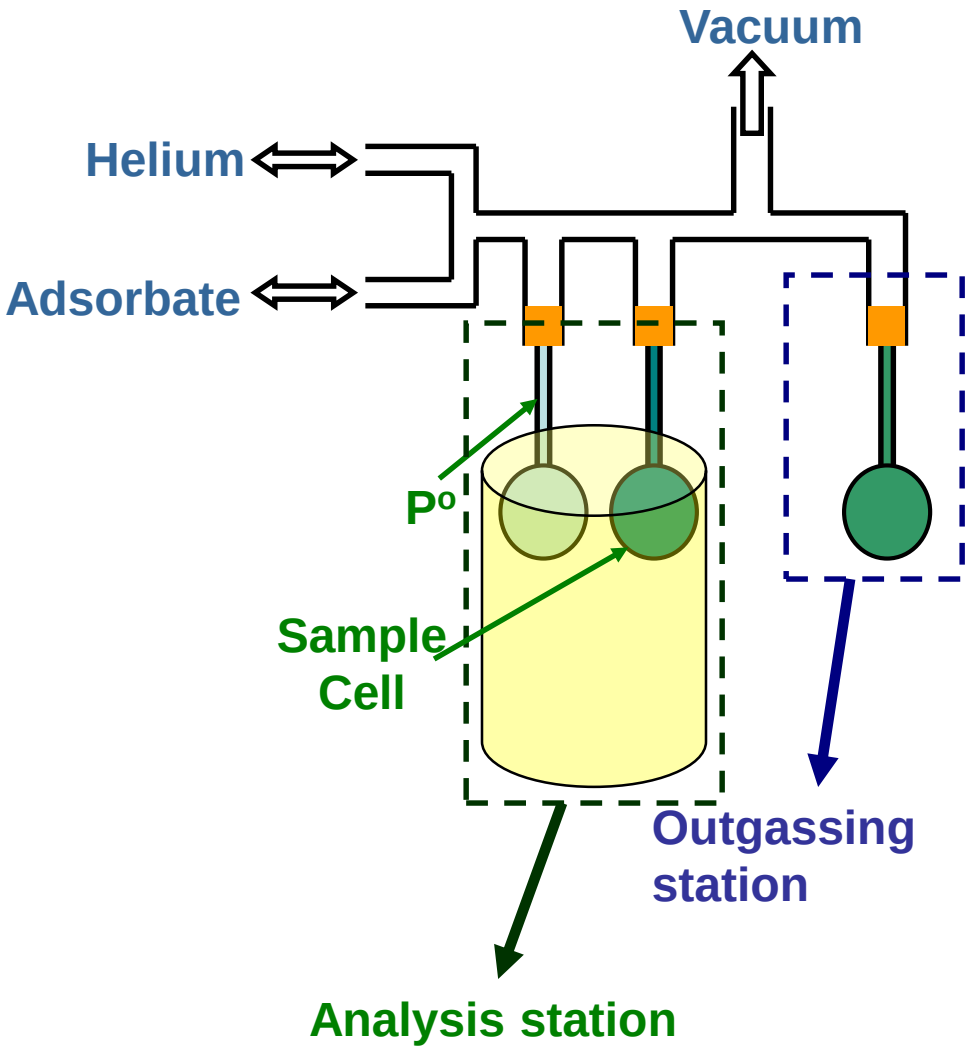


Sample Preparation (Outgassing)



- Surface contamination is removed by application of:
  - Temperature
  - Flowing gas (helium or nitrogen) or vacuum
- Backfill can be done using helium or adsorbate gas.
- According to IUPAC standards, materials should be outgassed for **at least 16 hours**.

Adsorption Analysis

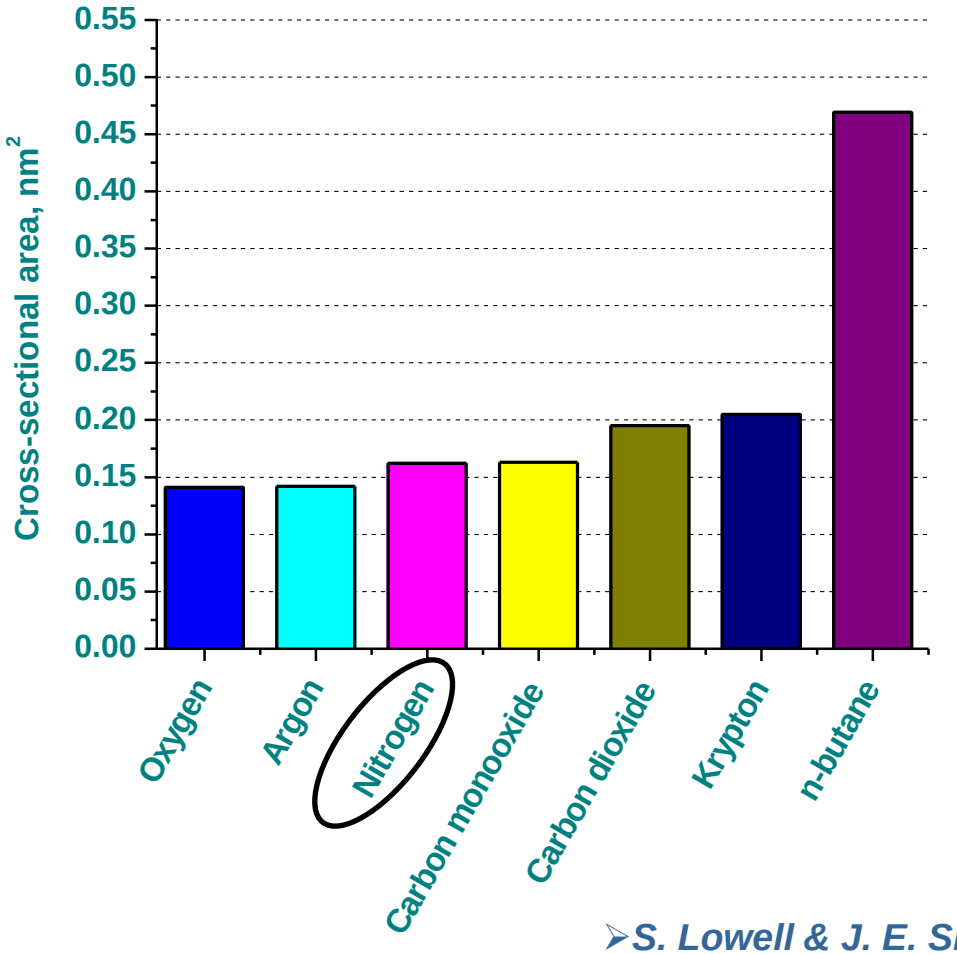


- Adsorbate (nitrogen, argon, carbon dioxide, krypton)
- Analysis temperature (liquid nitrogen, liquid argon, 0 °C)
- Quantity of sample (1 mg sample is sufficient)
- Number of points (single point, five points, seven points, eleven points, full analysis)

Common Adsorbates

Gas	Temperature	Cross sectional area (nm^2)
N_2	➢ -195.8 ^oC (liquid nitrogen) ➢ -183 ^oC (liquid argon).	0.162
Ar	➢ -183 ^oC (liquid argon). ➢ -195.8 ^oC (liquid nitrogen)	0.142
CO_2	➢ -78 ^oC, -25 ^oC, 0 ^oC	0.195
CO	➢ -183 ^oC (liquid argon)	0.163
Kr	➢ -195.8 ^oC (liquid nitrogen)	0.205
O_2	➢ -183 ^oC (liquid argon)	0.141
C_4H_{10}	➢ 0 ^oC, 25 ^oC	0.469

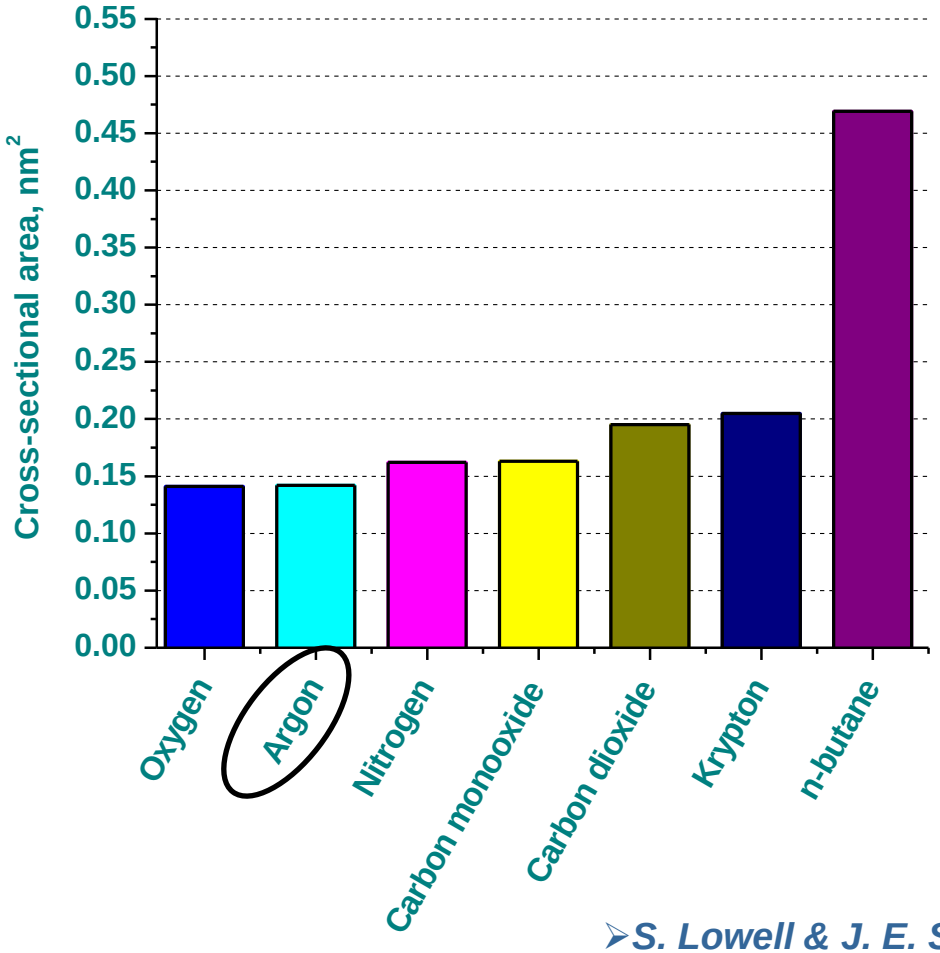
Choice of Adsorptive



- $N_{2(g)}$ in $N_{2(l)}$ is the most commonly used adsorbate.
- Not completely inert.
- Dipole movement and thus can have localized adsorption.
- Cross-sectional area of 0.162 nm^2 is questionable.

- *S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991*
- *Quantachrome Autosorb-I Operational Manual*

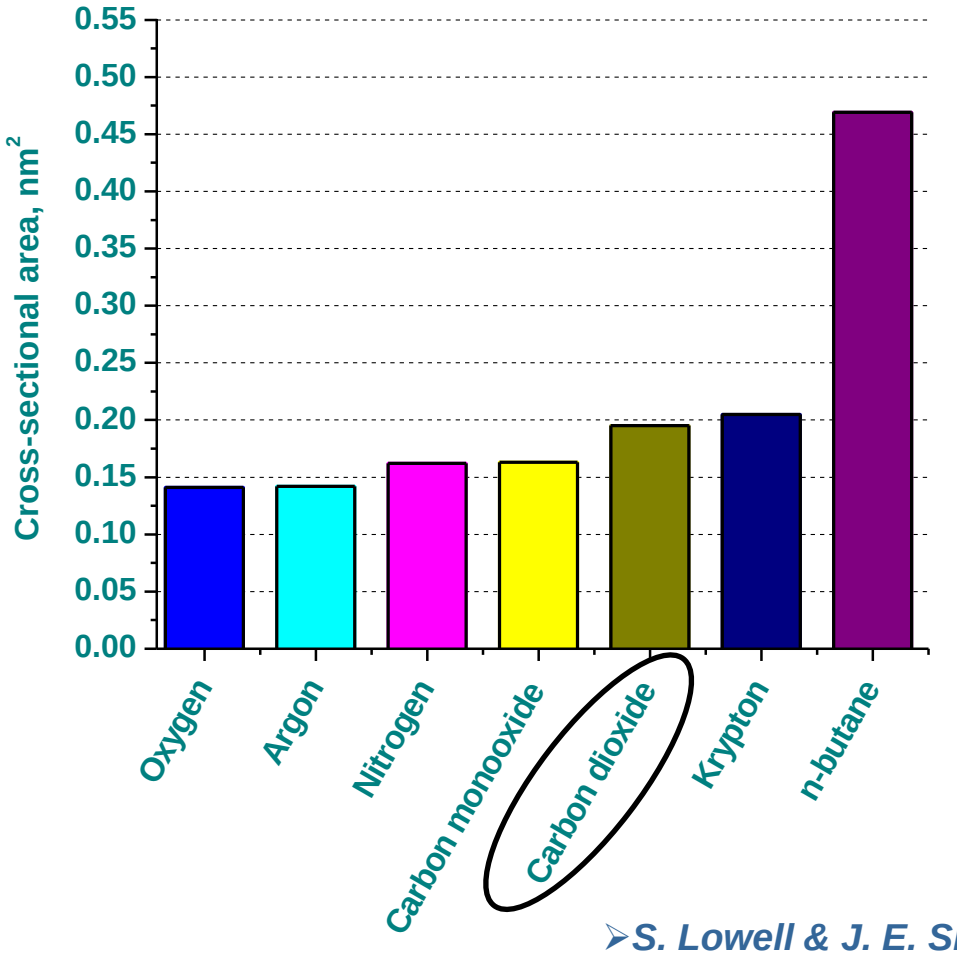
Choice of Adsorptive



- $Ar_{(g)}$ in $Ar_{(l)}$ is preferable but because of unavailability of $Ar_{(l)}$ (87K), $N_{2(l)}$ (77 K) is used.
- Ar can reach to somewhat smaller pores than N_2.
- Accurate measurement of micropores is possible using Ar.

- *S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991*
- *Quantachrome Autosorb-I Operational Manual*

Choice of Adsorptive



- **In case of activated carbon, CO_2 is often the most preferred adsorbate.**
- **Adsorption analysis of CO_2 takes less time.**
- **Limited to micropore analysis.**

- *S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991*
- *Quantachrome Autosorb-I Operational Manual*

Six isotherm main types according to IUPAC

M. Thommes et al., Pure Appl. Chem. 2015; 57(9-10): 1051-1069

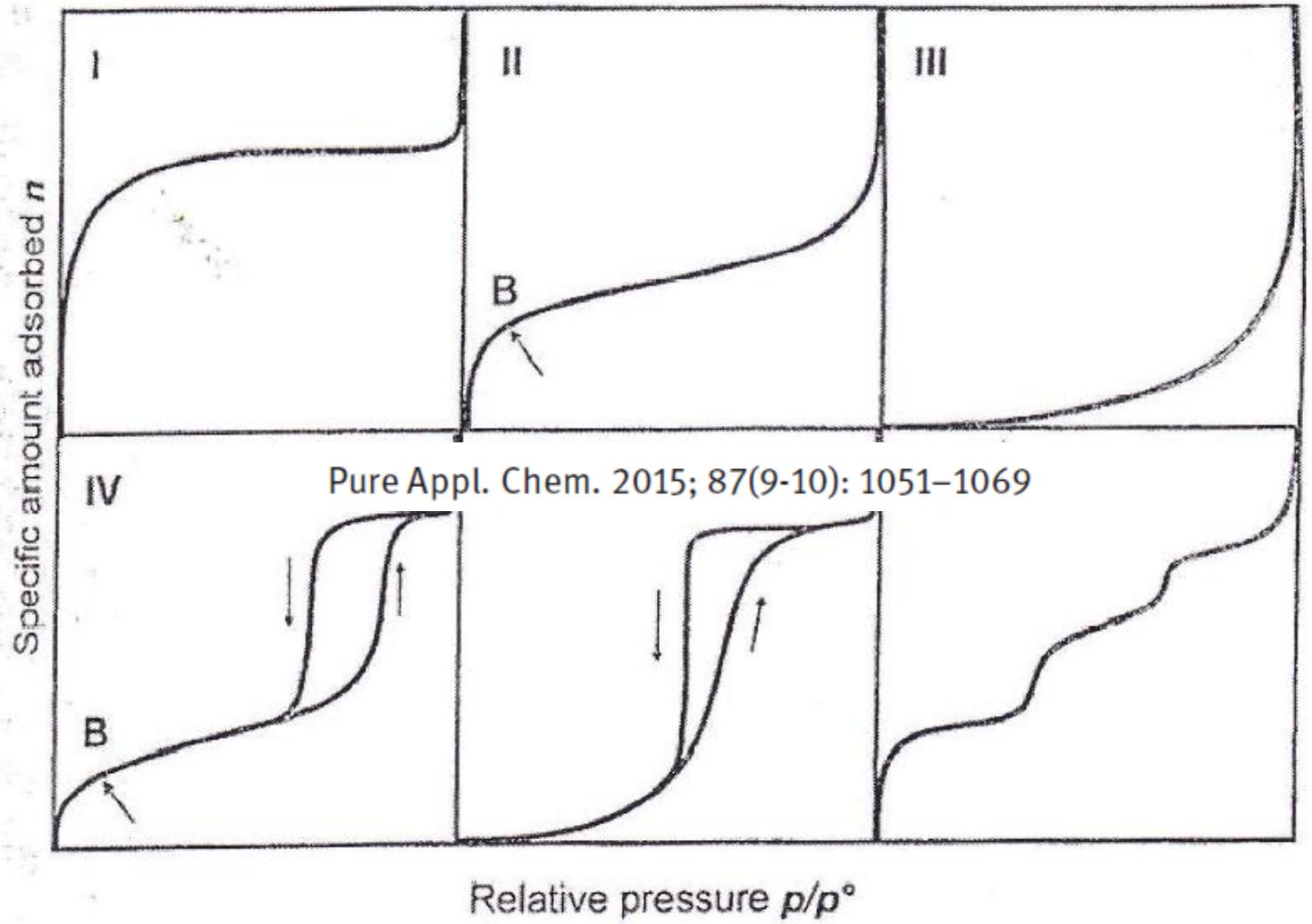
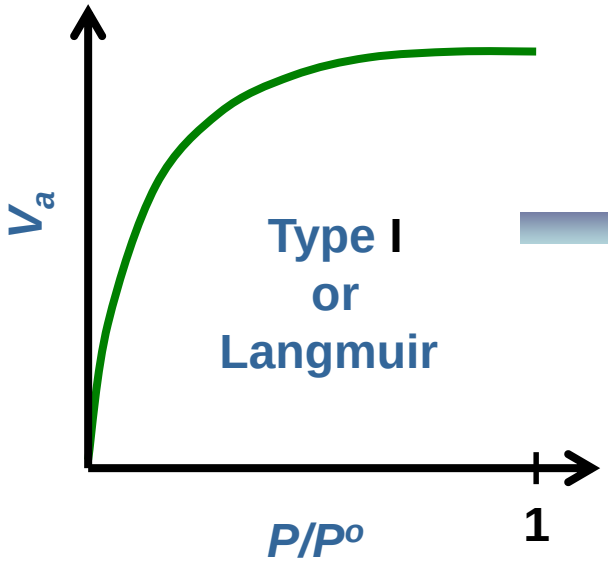
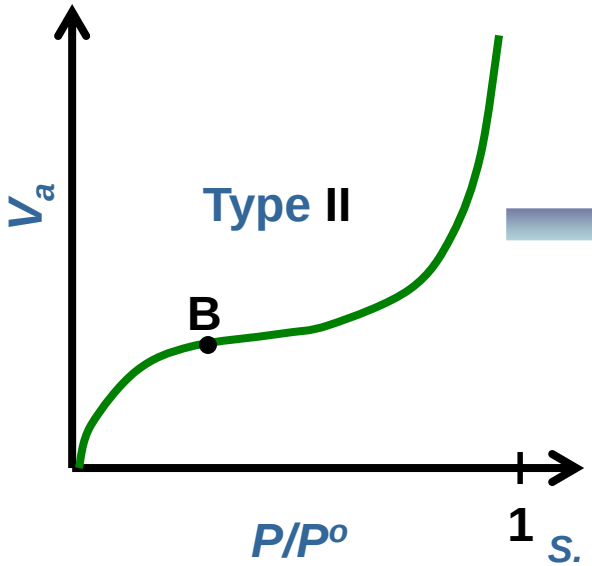


Figure 1.7. The six main types of gas physisorption isotherms, according to the IUPAC classification (after Sing *et al.*, 1985).

Isotherm type



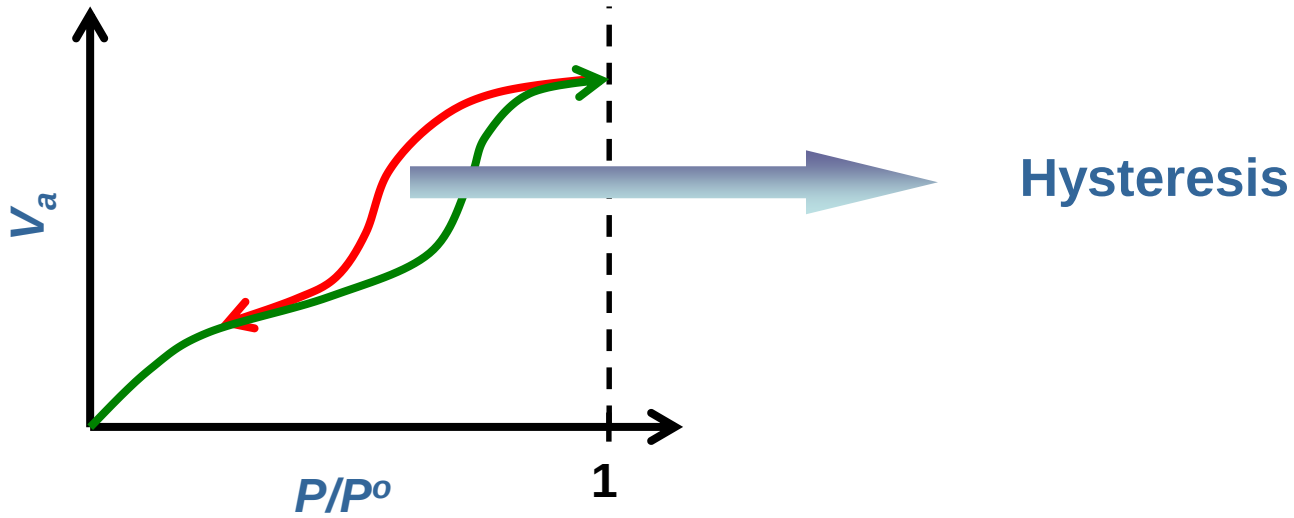
- Exhibited by microporous solids (< 2nm)
- Limiting value (plateau) due to filled pores and essentially zero external area.
- Steep initial region due to very strong adsorption, for example in micropores



- Exhibited by nonporous or macroporous solids (> 50nm)
- Unrestricted monolayer-multilayer adsorption
- Point B indicates the relative pressure at which monolayer coverage is complete

S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991

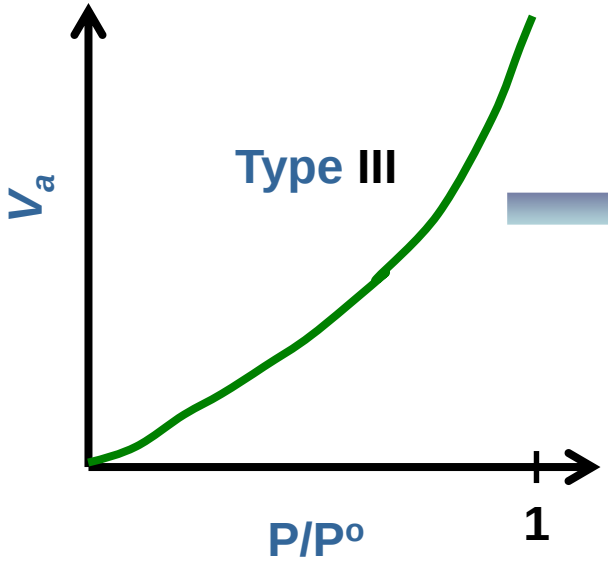
Hysteresis



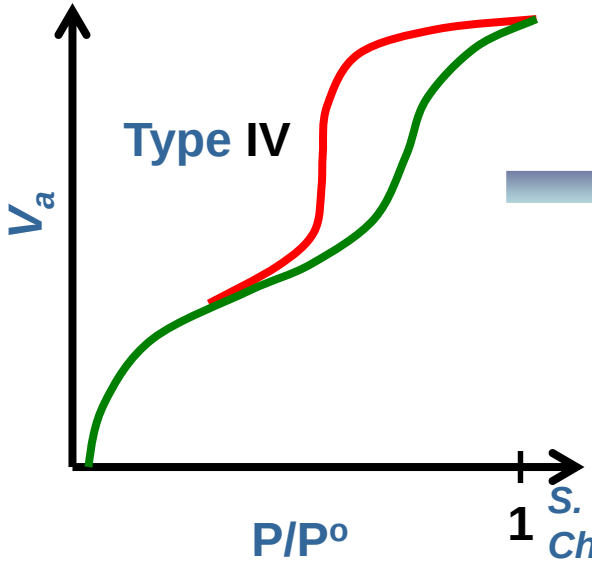
- Hysteresis indicates the presence of mesopores as the hysteresis is due to the liquid condensation into the mesopores
- Hysteresis gives information regarding pore shapes .
- Types I, II and III isotherms are generally reversible but type I can have a hysteresis. Types IV and V exhibit hysteresis.

S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991

Isotherm type



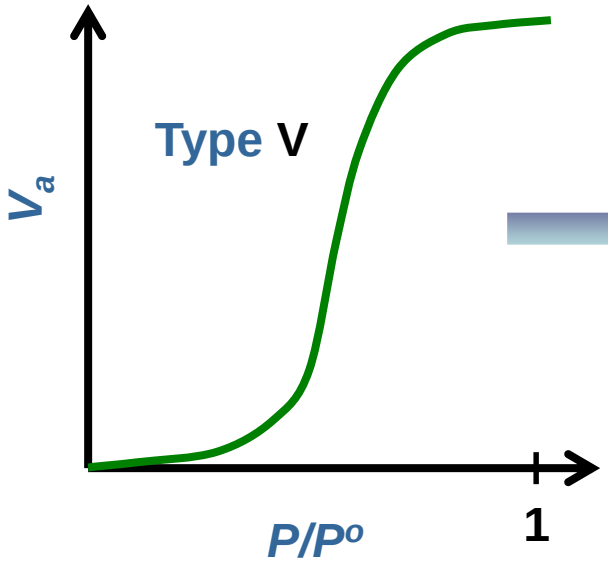
- Convex to the P/P_o axis
- Exhibited by nonporous solids
- Lack of knee represents extremely weak adsorbate-adsorbent interaction
- BET is not applicable



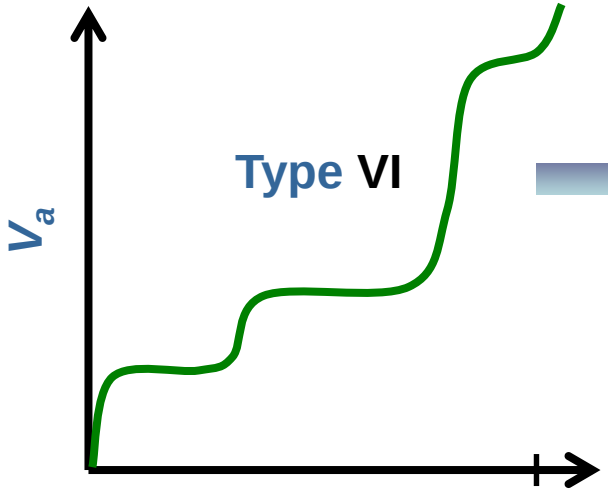
- Exhibited by mesoporous solids
- Initial part of the type IV follows the same path as the type II
- Hysteresis indicates capillary condensation in meso and macropores

S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991

Isotherm type



- Highly uncommon
- Exhibited by mesoporous solids
- Lack of knee represents extremely weak adsorbate-adsorbent interaction



- Exhibited by nonporous solids with an almost completely uniform surface

S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991

Example of type VI isotherm

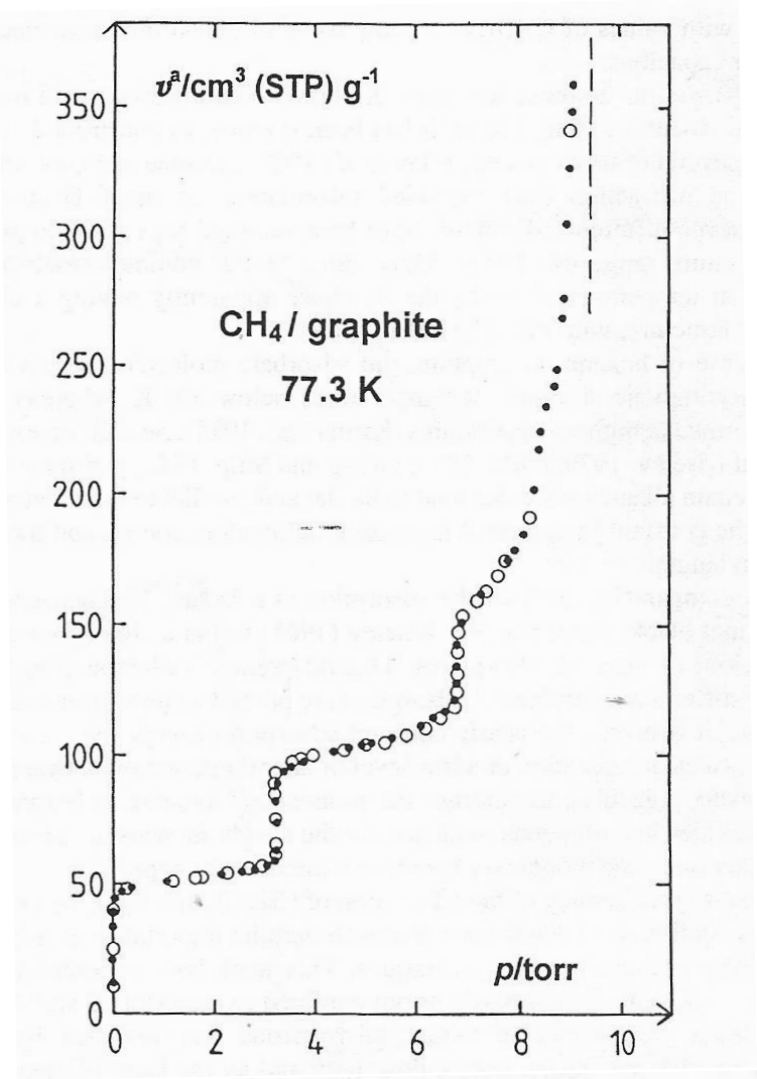


Figure 9.9. Stepwise isotherm of CH_4 on graphite foam (open circles) and exfoliated graphite (solid circles) at 77.3 K (reproduced courtesy of Bienfait *et al.*, 1990).

I.6 The heat of adsorption

Heat of Adsorption

Adsorption of gas on a solid is exothermic.

ΔH_{AD} is the isoteric (θ constant) enthalpy of adsorption.

Determining the thermal energy evolved when a known amount of gas is allowed to adsorb onto a clean surface (T rise of solid) can help to derive ΔH_{AD}.

$$\Delta G^\circ = -RT\ln K^\circ = \Delta H^\circ_{AD} - T\Delta S^\circ_{AD}$$

$$\boxed{\ln K^\circ = -\Delta H^\circ_{AD}/RT + \Delta S^\circ_{AD}/R}$$

Differentiate with respect to T at constant θ

Van t'Hoff equation $[\partial / \partial\, T(\ln K^\circ)]_\theta = \Delta H^\circ_{AD}/RT^2$

Remember: $KP = \theta/(1-\theta)$

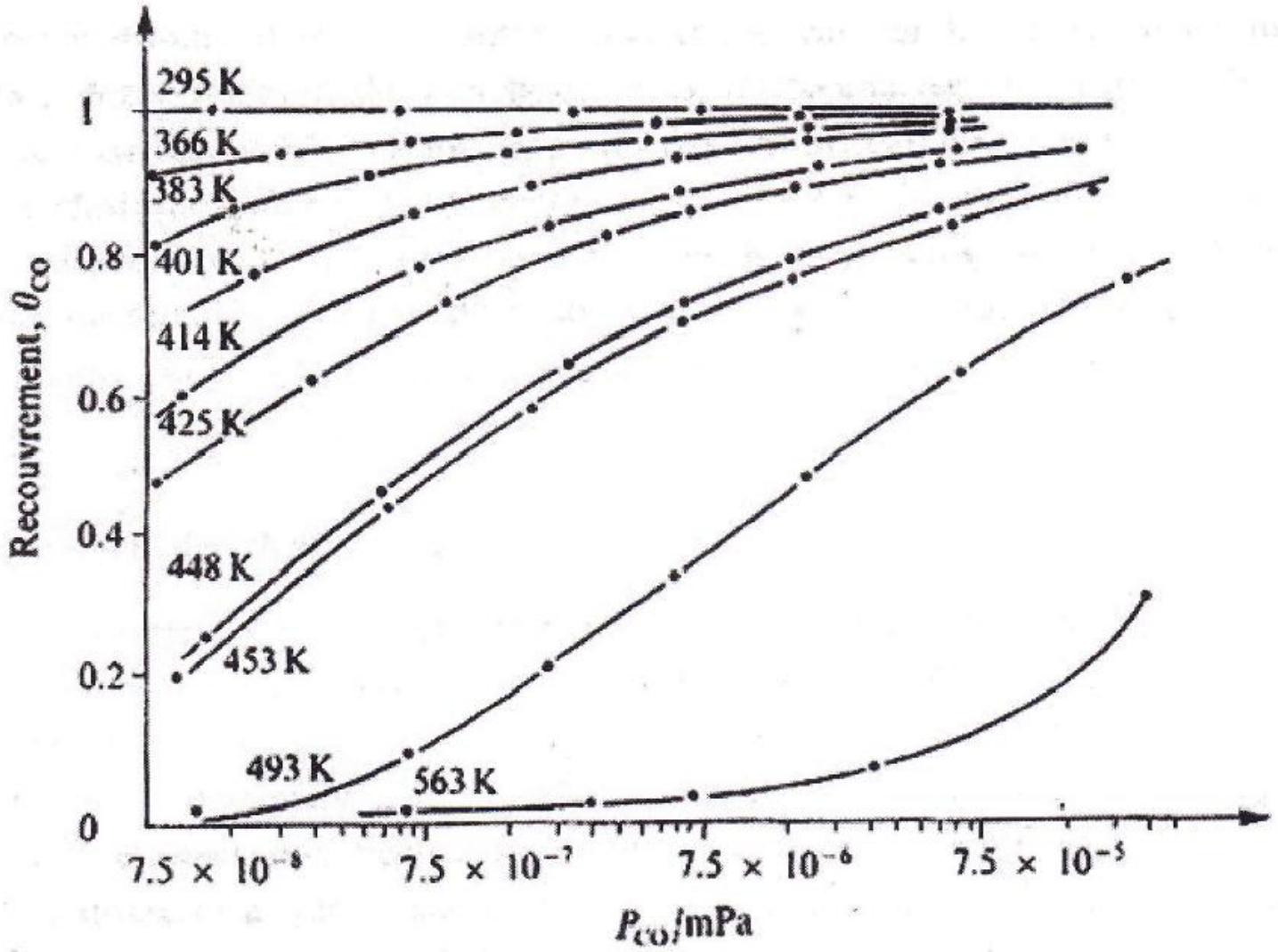
$$\ln K + \ln P = \ln(\theta/(1-\theta))$$

$$[\partial / \partial\, T(\ln K)]_\theta + [\partial / \partial\, T(\ln P)]_\theta = 0$$

$$[\partial / \partial\, T(\ln K)]_\theta = [\partial / \partial\, T(\ln K^\circ)]_\theta$$

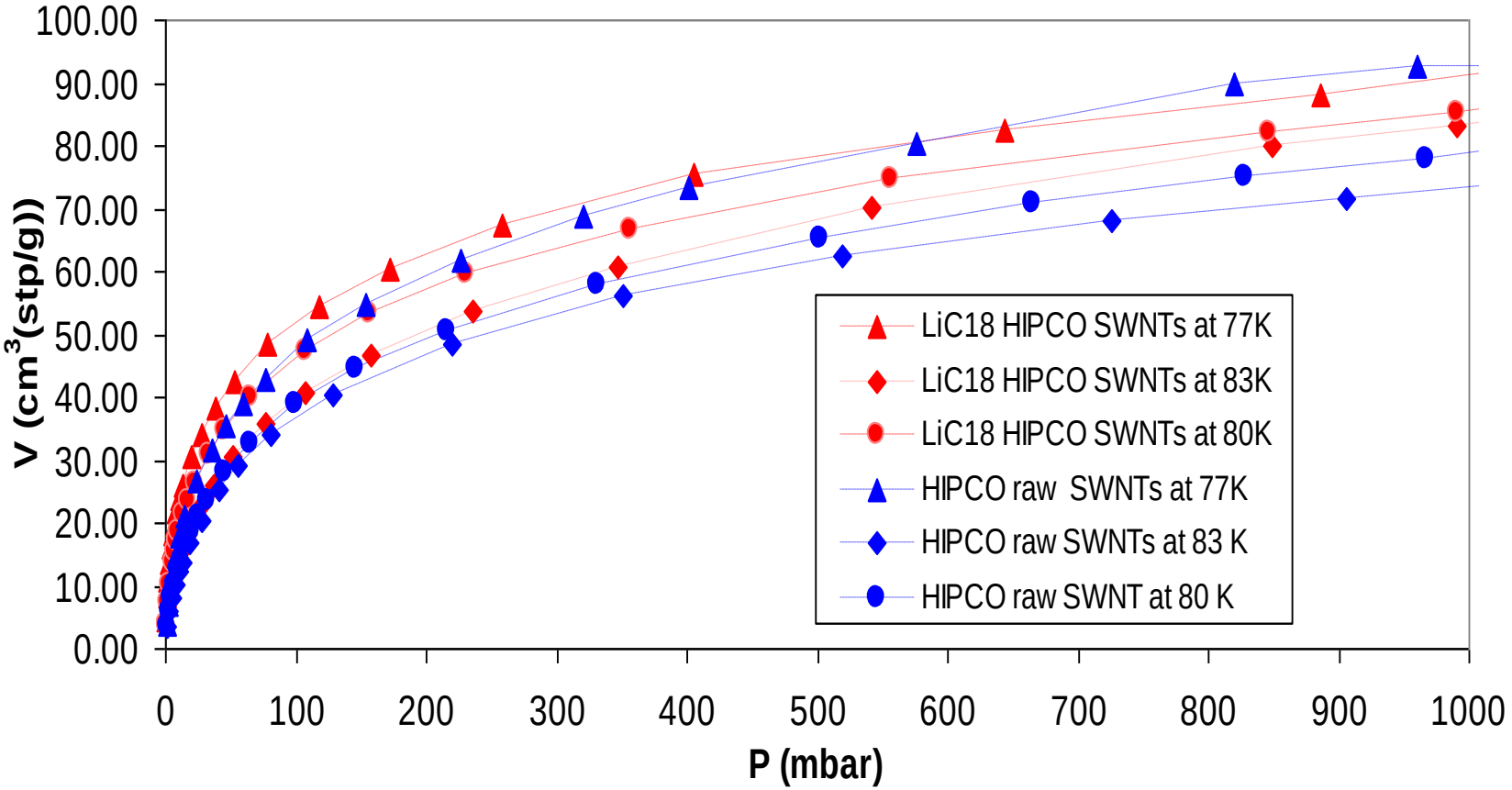
$$[\partial / \partial\, T(\ln P)]_\theta = \Delta H_{AD}/RT^2$$

$$\boxed{[\ln(P_1/P_2)]_\theta = (\Delta H_{AD}/R)(1/T_1 - 1/T_2)}$$



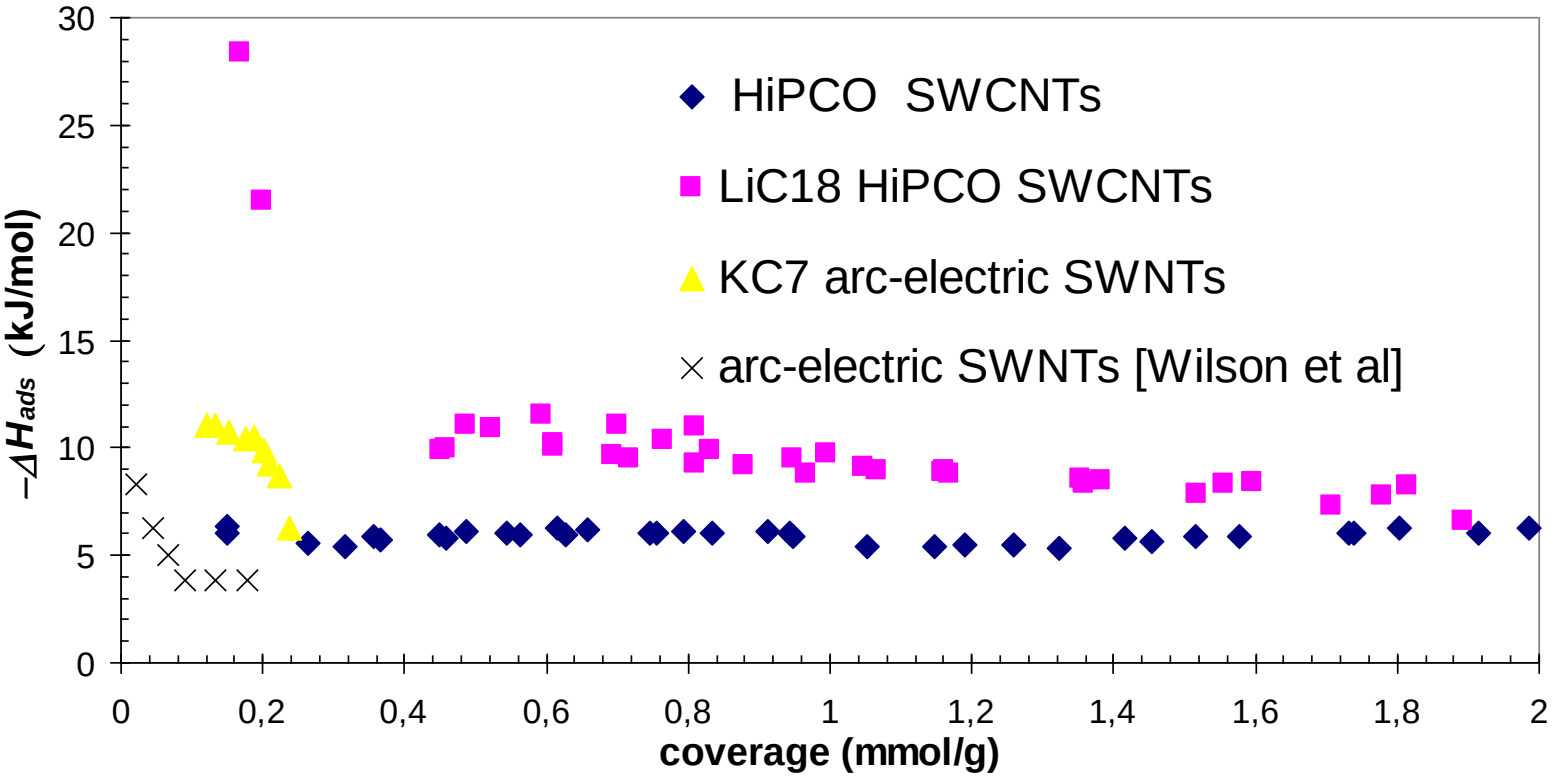
Isotherm of adsorption of CO on the (111) surface of platinum

D_2 adsorption isotherms of pristine and doped (LiC_{18}) HiPCO nanotubes at 83 K, 80 K et 77 K



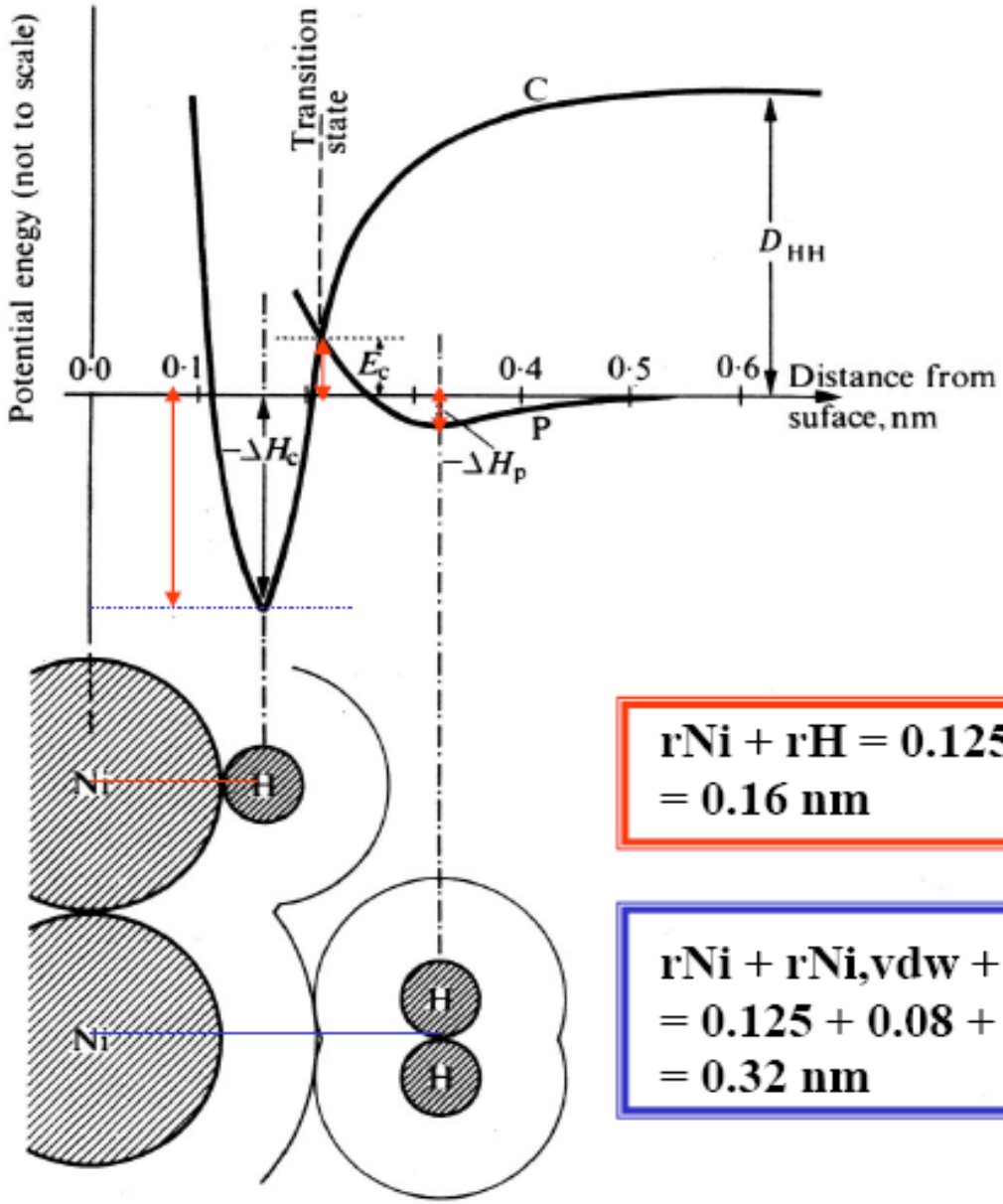
Isosteric heats of D_2 adsorption in doped and pristine SWNTs from the isotherms at T~80K

Clausius Clapeyron Law : $Ln(P)=q_{st}/RT+\Delta S°/R$



[T. Wilson, A. Tyburski, M. M. R. DePies, O. E. Vilches, D. Becquet, M. Bienfait, J. Low Temperature Phys. 126 (2002) 403-408.]

Appendix



rNi + rH = 0.125 + 0.035 = 0.16 nm

rNi + rNi,vdw + rH + rH,vdw = 0.125 + 0.08 + 0.035 + 0.08 = 0.32 nm

FIG. 3.2. **Potential-energy curves for the adsorption of hydrogen on nickel, and pictorial representation of the adsorbed states.**

The transition metals can chemisorb simple molecules

TABLE 3.1

A classification of metals according to their abilities in chemisorption

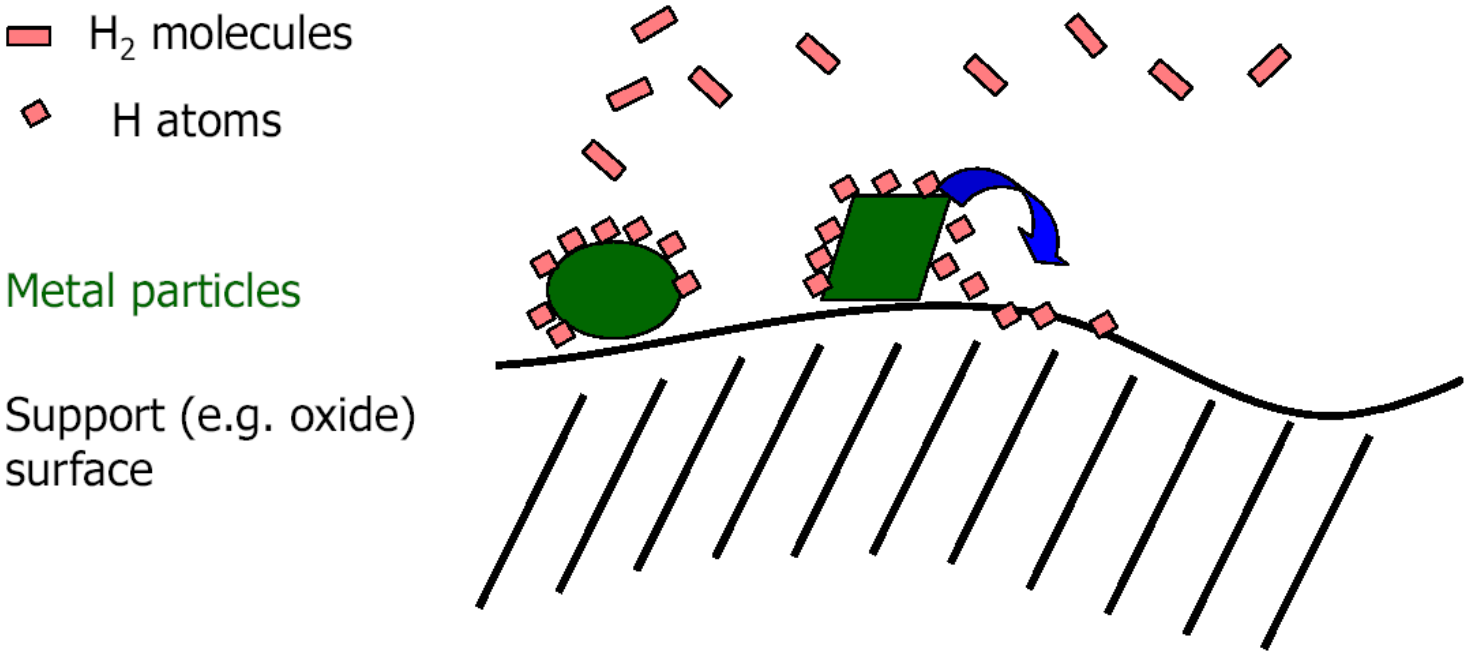
Group	Metals	Gases						
		O_2	C_2H_2	C_2H_4	CO	H_2	CO_2	N_2
A	Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os	+	+	+	+	+	+	+
B_1	Ni, Co	+	+	+	+	+	+	−
B_2	Rh, Pd, Pt, Ir	+	+	+	+	+	−	−
B_3	Mn, Cu	+	+	+	+	±	−	−
C	Al, Au	+	+	+	+	−	−	−
D	Li, Na, K	+	+	−	−	−	−	−
E	Mg, Ag, Zn, Cd, In, Si, Ge, Sn, Pb, As, Sb, Bi	+	−	−	−	−	−	−

(+ means that strong chemisorption occurs; ± means that it is weak; −means unobservable.)

The chemisorption of a number gases of practical interest has been investigated on many metals. It is found that, with few exceptions, the strength with which they are chemisorbed falls in the following sequence:

$$O_2 > C_2H_2 > C_2H_4 > CO > H_2 > CO_2 > N_2.$$

Spillover effect (example H_2)



The H_2 molecule firstly chemisorbed on the metals and then chemisorbed on the support from the metallic particles by « spillover ».

London Dispersion Forces

- London dispersion forces increase as molecular weight increases.
- London dispersion forces exist between all molecules.
- London dispersion forces depend on the shape of the molecule.
- The greater the surface area available for contact, the greater the dispersion forces.
- London dispersion forces between spherical molecules are lower than between sausage-like molecules.

Adsorption Process

$$V_a = f(W, T, I, P)$$

where

V_a = volume of gas adsorbed;

W = weight of adsorbent;

P = pressure of the adsorbate;

T = temperature;

I = interaction between adsorbate and adsorbent.

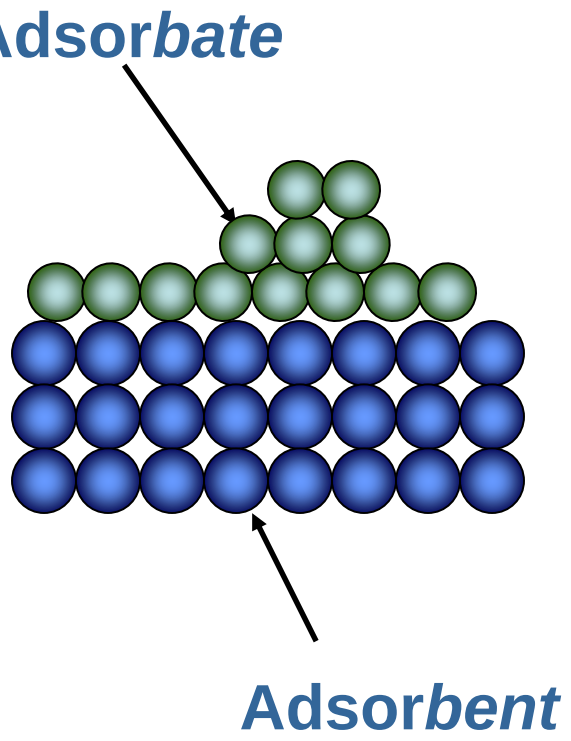
If W, T, and I are made constant, the above equation can be written as :

$$V_a = f\left(\frac{p}{p^o}\right)$$

→ Equation of adsorption isotherm

where

$$\frac{p}{p^o} = \frac{\text{pressure of adsorbate}}{\text{saturated pressure of adsorptive}}$$



S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991

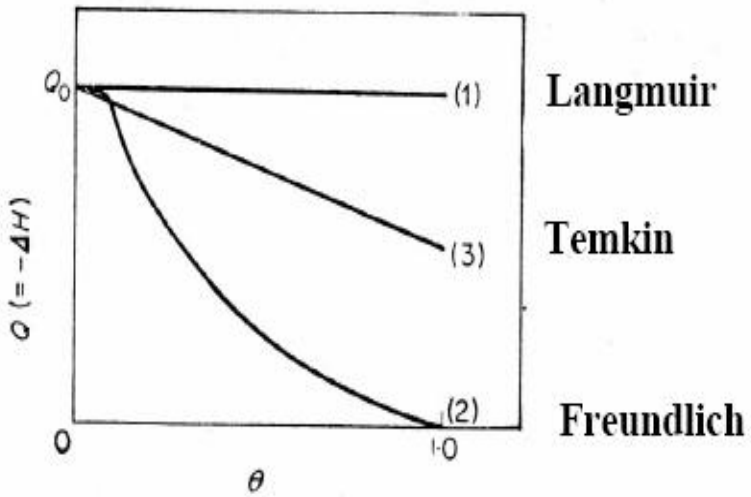


FIG. 11. Schematic diagram illustrating (1), constant heat of adsorption; (2), logarithmic fall of heat of adsorption; and (3), linear fall of heat of adsorption with increasing coverage.

Table 5. Summary of Mono-layer Adsorption Isotherms

Name	Fundamental equation of isotherm	Linear form of the isotherm	Straight line plot for	Variation of Q with θ	Examples of application
Langmuir	$v = v_m\, bp/(1 + bp)$	$(p/v) = (1/v_m b) + p/v_m$	(p/v) vs P	Nil	Adsorption of hydrogen on copper powder at 298 K
Halsey-Taylor (Freundlich)	$v = v_m(b_0\, p)^{RT/Q_m}$	$\ln v = \ln v_m + (RT/Q_m) \ln b_0 + (RT/Q_m) \ln p$	$\log v$ vs $\log p$	Q proportional to $-\ln \theta$	Nitrogen on tungsten powder
Temkin (Slygin-Frumkin)	$v = v_m(RT/Q_0\alpha) \ln B_0 P$	$v = (v_m RT/Q_0\alpha) \ln B_0 + (v_m RT/Q_0\alpha) \ln p$	v vs $\log p$	Q is proportional to $-\theta$	Adsorption of hydrogen on iron films
Henry	$v = k'p$	$v = k'p$	v vs p		Nitrogen on charcoal at 298 K

TABLE 2.3. A selection of adsorption isotherms†

Name	Isotherm equation	Applicability	Equation number
Langmuir	$\frac{v}{v_m} = \theta = \frac{bp}{1 + bp}$	Chemisorption and physical adsorption	(23)
Freundlich	$v = kp^{1/n}, (n > 1)$	Chemisorption and physical adsorption	(24)
Henry	$v = k'p$	Chemisorption and physical adsorption	(25)
Slygin-Frumkin‡ (Temkin)	$\frac{v}{v_m} = \theta = \frac{1}{a} \ln c_0 p$	Chemisorption	(26)
Brunauer-Emmett-Teller (BET)	$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c - 1)}{v_m c} \frac{p}{p_0}$	Multilayer physical adsorption	(27)

Hysteresis loop : evaporation of condensed gas in fine pores does not occur as easily as its condensation; this is because a molecule evaporating from a highly curved meniscus has a higher probability of re-condensing than one evaporating from a plane surface.

Lord Kelvin

$$\ln(P/P_0) = -\frac{2V\gamma}{rRT}\cos\phi,$$

where V is the molar volume of the liquid, γ its surface tension, r the pore radius and ϕ the contact angle (usually taken to be zero): the other symbols have their usual significance. The relative pressure at which condensation will occur in a pore of a given size can thus be determined, and the isotherm then used to obtain a pore size distribution.

Gas Sorption: Hysteresis