

Calorimetry for gas adsorption: fundamentals and applications

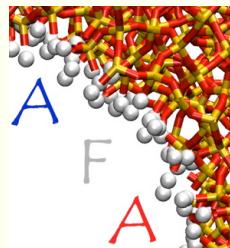
JP Bellat

Laboratoire Interdisciplinaire Carnot de Bourgogne UMR 6303 CNRS

Group: Adsorption on Porous Solids

Université de Bourgogne Franche-Comté, 9 A. Savary BP 47870 Dijon – France

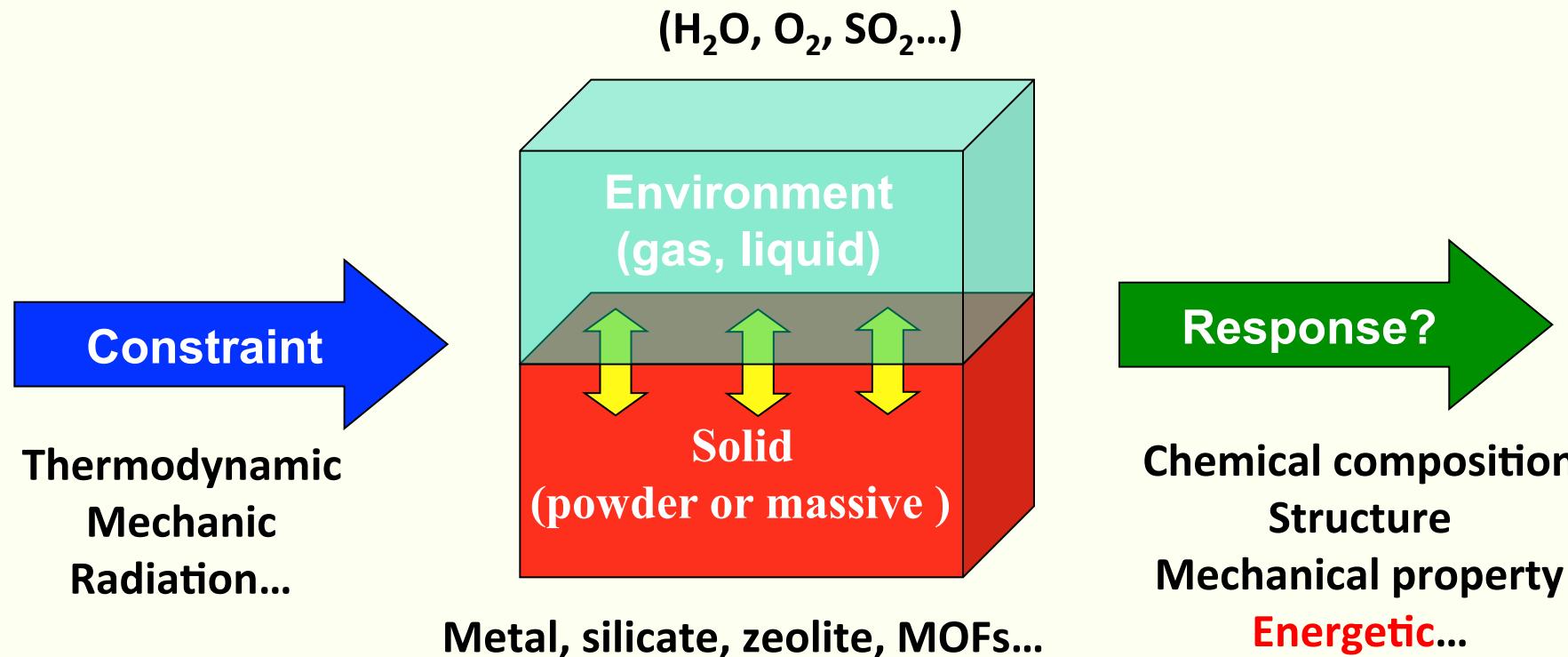
(jean-pierre.bellat@u-bourgogne.fr)



I – Fundamentals On Adsorption

Concepts and Thermodynamics

Why using the calorimetry?



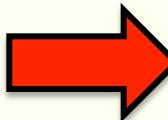
Q = heat exchanged

$p = \text{cte}$

$\Delta_r H$

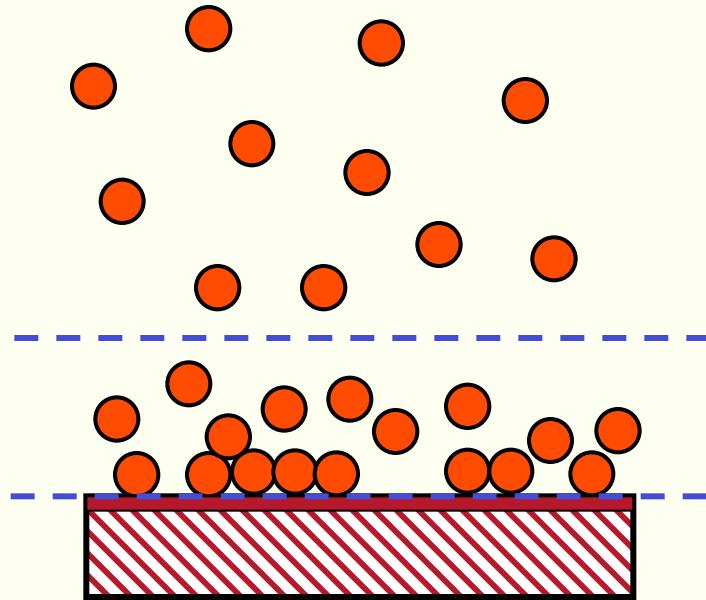
$V = \text{cte}$

$\Delta_r U$



surface chemistry
chemical reaction
gas - solid interaction
mechanism of reaction...

What is adsorption?



III- Gas phase = adsorptive

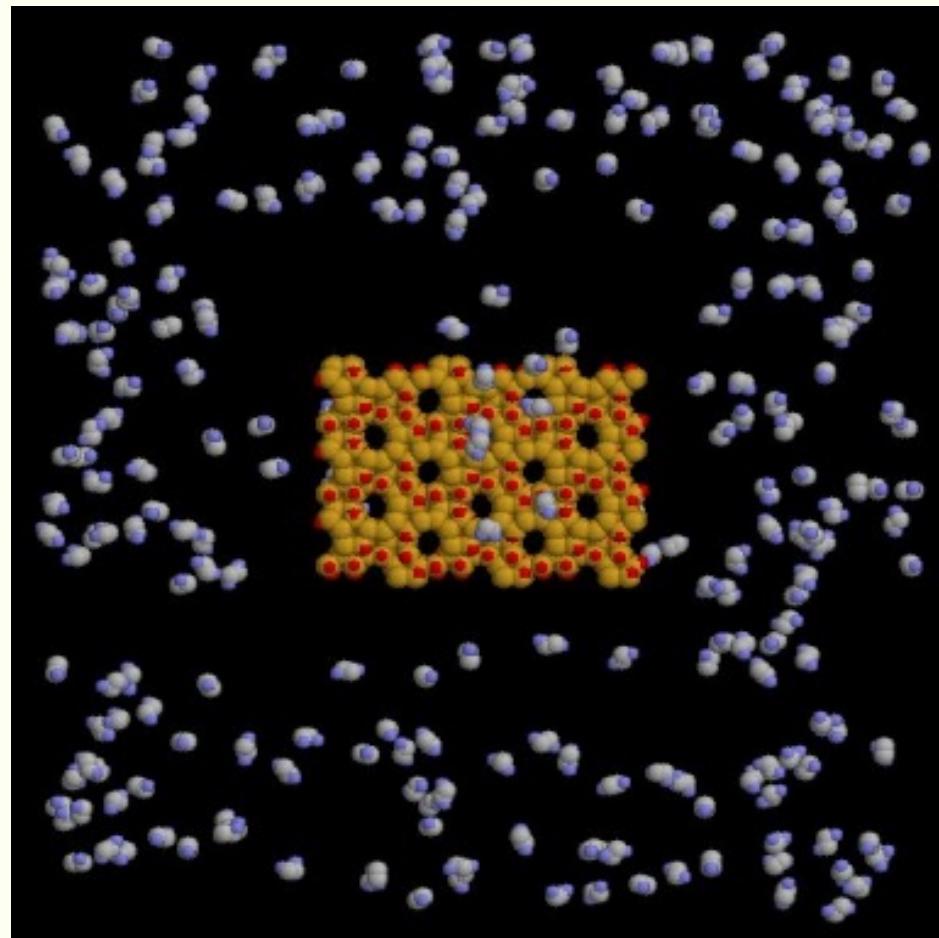
I - Adsorbed phase = adsorbate

II - Solid = adsorbent

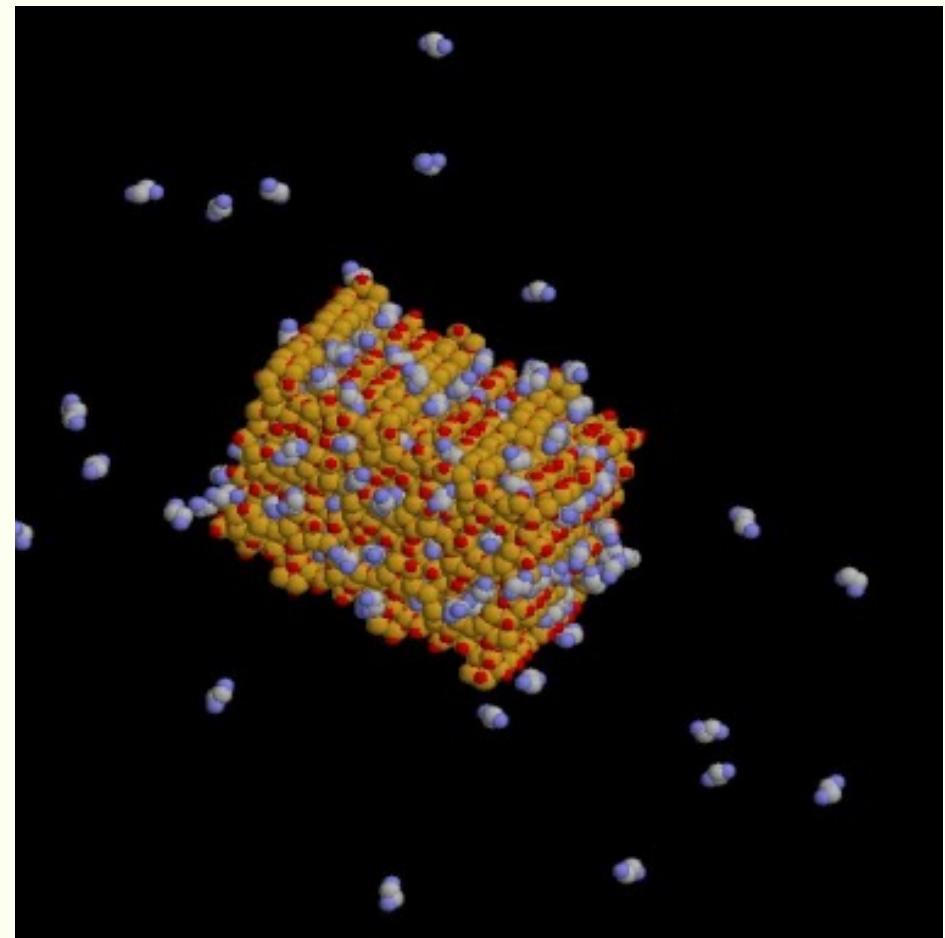
Virtual image of the adsorption process obtained by numerical simulation of molecular dynamics

Butane / Silicalite à 298 K

Initial configuration



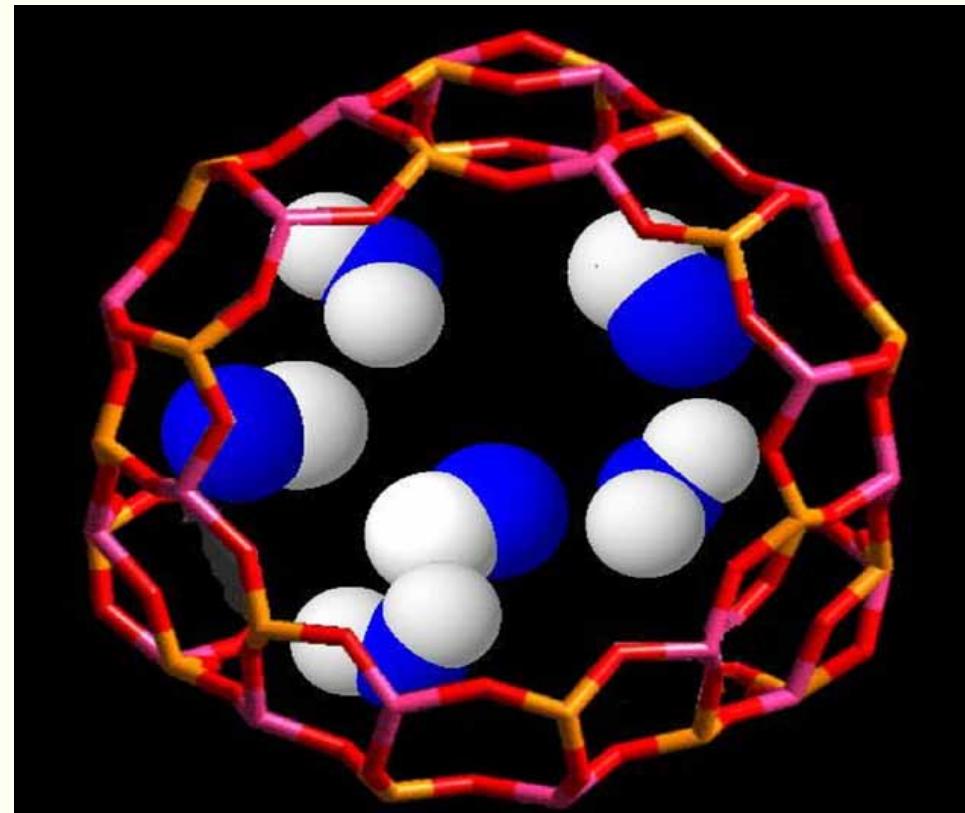
Equilibrium configuration



The accumulation of molecules on a plane surface is a restrictive image of the adsorption process.

Molecules can be adsorbed in a micropore which has a size close to that one of the molecules.

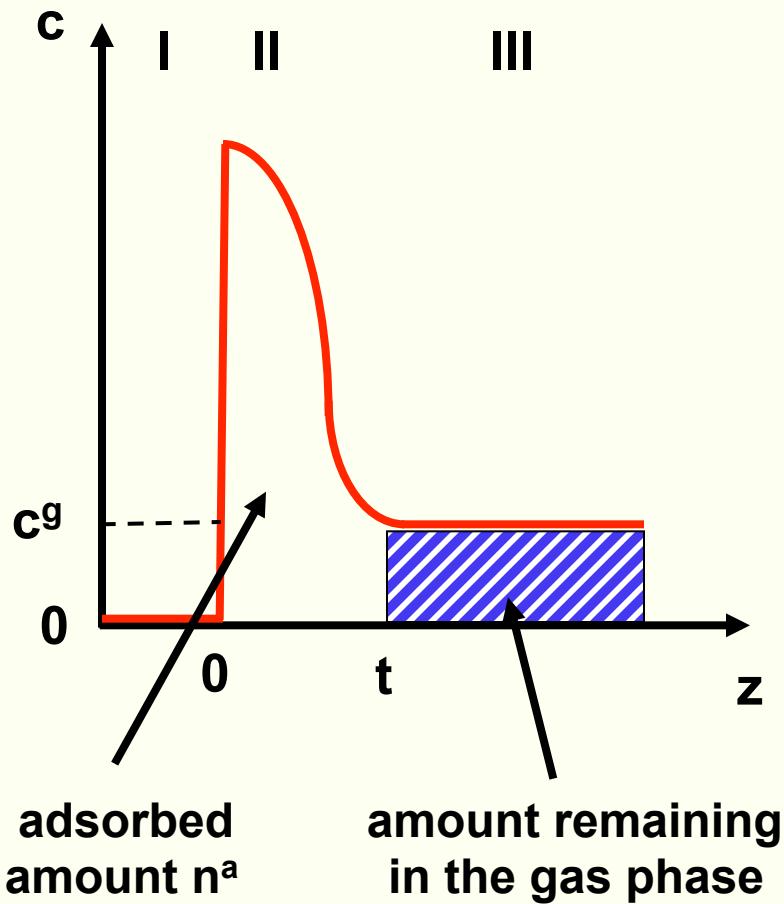
(Confinement of molecules inside a cavity)



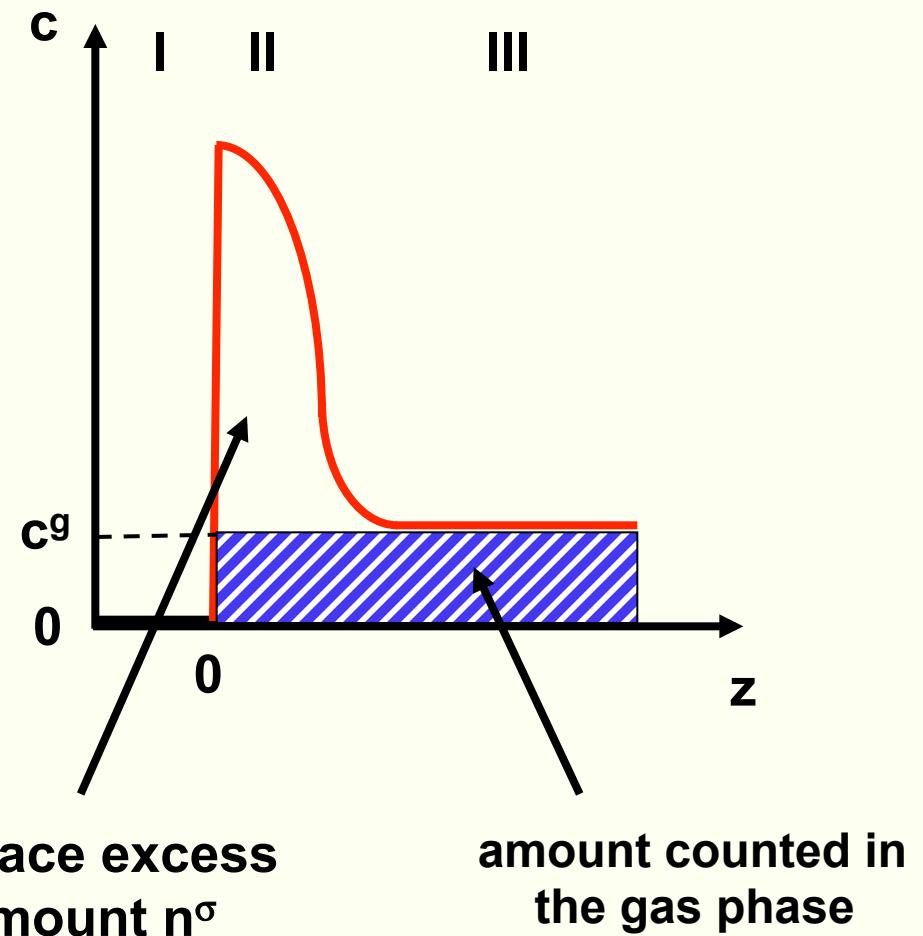
NOx molecules inside a zeolitic cage

Adsorbed amount n^a and surface excess amount n^σ

Layer model



Gibbs representation



Adsorption is a universal phenomena

Gas + Solid  adsorption

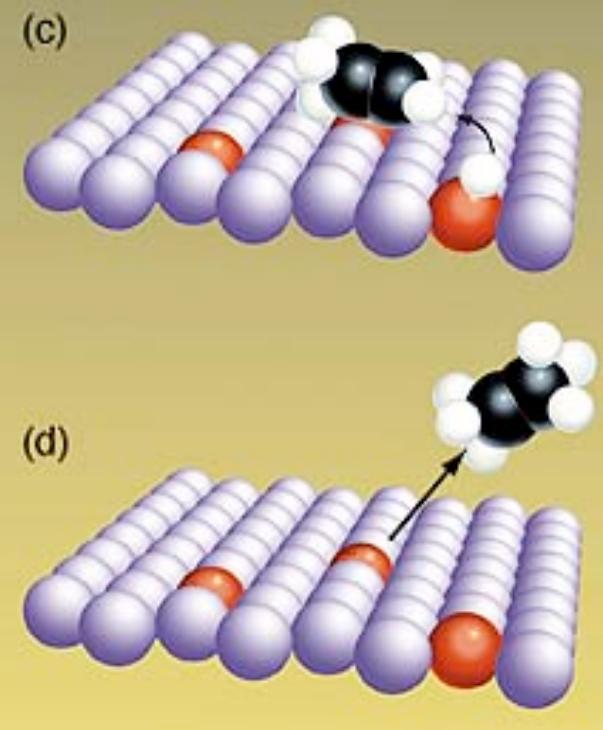
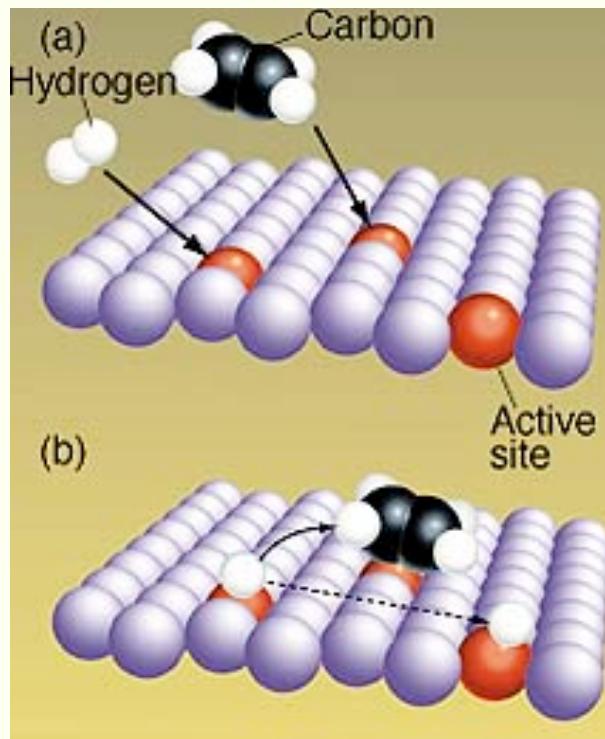
Adsorption occurs in any gas-solid reaction:

- oxidation of metal
 - hydration of salts
 - heterogeneous catalytic reaction
 - adsorption in porous media
- separation of gases, purification, storage of gases....

Example: catalytic reaction on solid

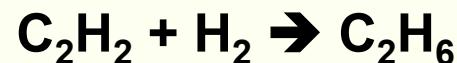
A gas-solid reaction always starts by an adsorption reaction
and ends by a desorption reaction.

Adsorption



Desorption

Hydrogenation of ethylene on a catalytic surface



Difference between adsorption and absorption

ADsorption

Molecules located on
the surface

ABsorption

Molecules dispersed
inside the matter

Adsorption versus Absorption



Major differences between chemisorption and physisorption:

Chemisorption

- chemical bonds between adsorbate and adsorbent (electronic transfer): « reactive adsorption »

- **high energy of interaction**

$$(E > E_{liquefaction} \quad E > 100 \text{ kJ.mol}^{-1})$$

- restricted to the monolayer

- specific process: molecules are fixed on different sites

- **irreversible** (non complete desorption, hysteresis)

- kinetics: slow

Physisorption

- no chemical bonds, van Der Waals interactions

- **low energy of interaction**

$$(E \approx E_{liquefaction} \quad E \leq 100 \text{ kJ.mol}^{-1})$$

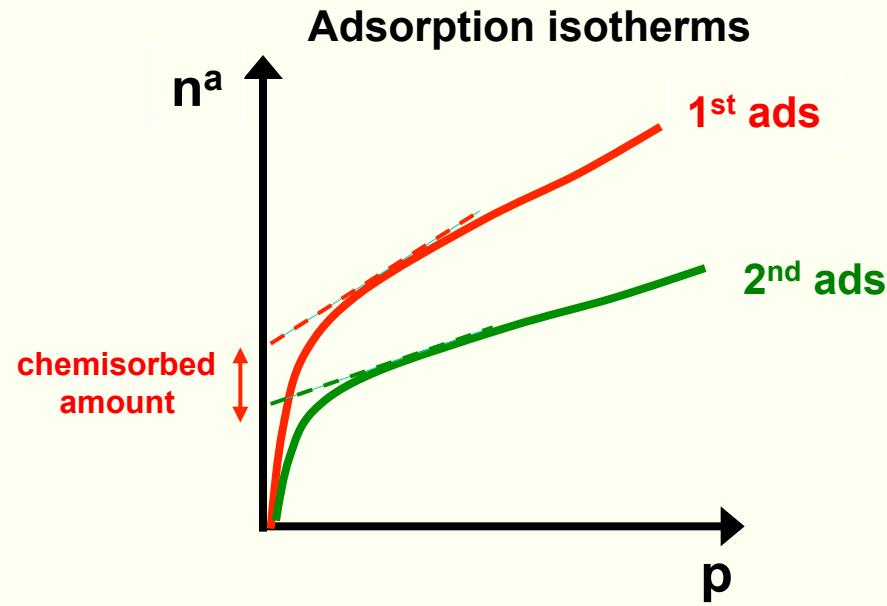
- multilayer adsorption possible

- not very specific
(molecules can move on the surface)

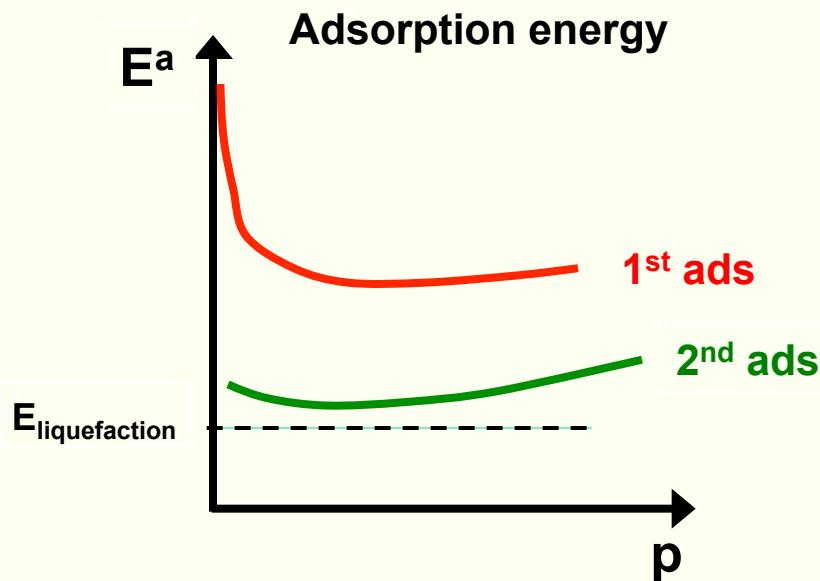
- generally **reversible**

- kinetics: rather fast

How to distinguish physisorption and chemisorption?

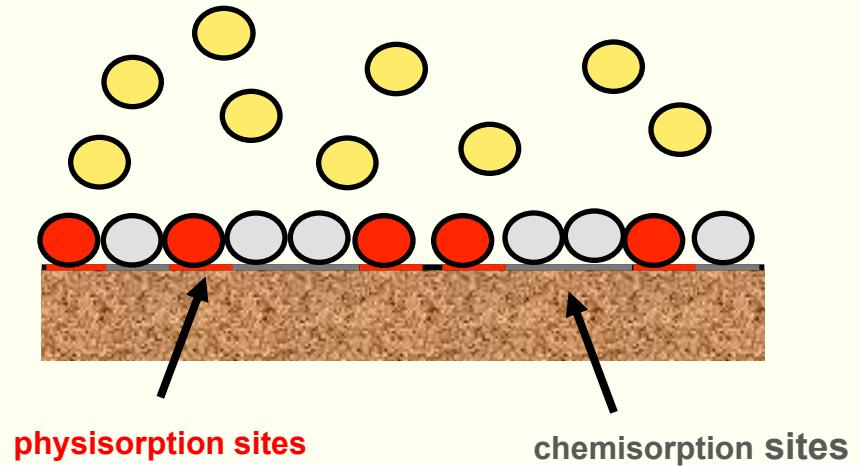


1st adsorption
 $E^a \gg E_{\text{liquefaction}}$



Desorption under vaccum

2nd adsorption
 $E^a \approx E_{\text{liquefaction}}$



Interactions in physisorption?

Energy of adsorption :

$$U_{\text{total}} = \underbrace{U_D + U_R + U_P}_{\text{non-specific}} + \underbrace{U_{Fm} + U_{F'Q} + U_{aa}}_{\text{specific}}$$

U_D : dispersion energy (attractive)

U_R : repulsion energy

U_P : polarization energy (attractive)

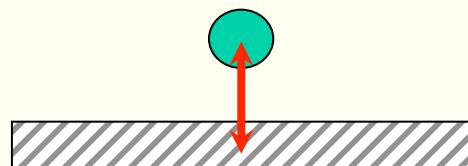
U_{Fm} : electrical field – dipole interaction

U_{FQ} : electrical field gradient – quadrupole interaction

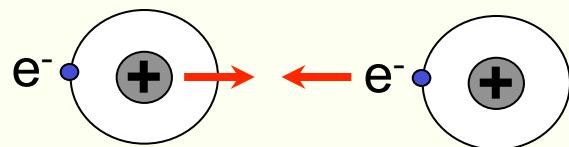
U_{aa} : adsorbate – adsorbate interaction

Adsorption interactions

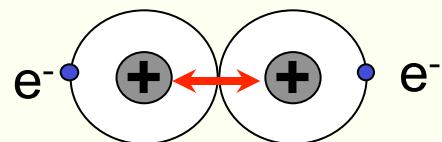
a – A Interactions adsorbate - Adsorbent



Non-specific interactions
(dispersion-repulsion forces)



Non-specific attraction

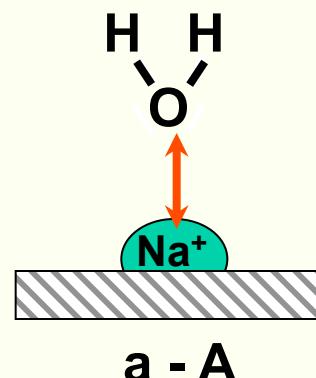


Non-specific repulsion

a – a Interactions adsorbate - adsorbate



Specific interaction
(heterogeneous distribution of charges)



a - A



a - a

Classification of adsorptives and adsorbents proposed by KISELEV and based on gas / solid interactions

		I No reactive chemical fonction or ion (neutral)	II Localized positive charges	III Localized negative charges
Adsorbent				
Adsorptive				
A	Spherical symetry σ bonds	n.s		n.s
B	Molecules with non-bonding electrons or π bonds	n.s		n.s + s
C	Localized positive charges (cations)	n.s		n.s + s
D	Chemical fonction with localized positive charges	n.s		n.s + s

Adsorption equilibrium of single component

Gas = Adsorbate

$$\Delta G^a = \Delta H^a - T\Delta S^a < 0$$

$$K_T = \frac{\gamma \theta}{P/P^0}$$

(θ = filling coefficient, γ = activity coefficient et P^0 = standard pressure 10^5 Pa)

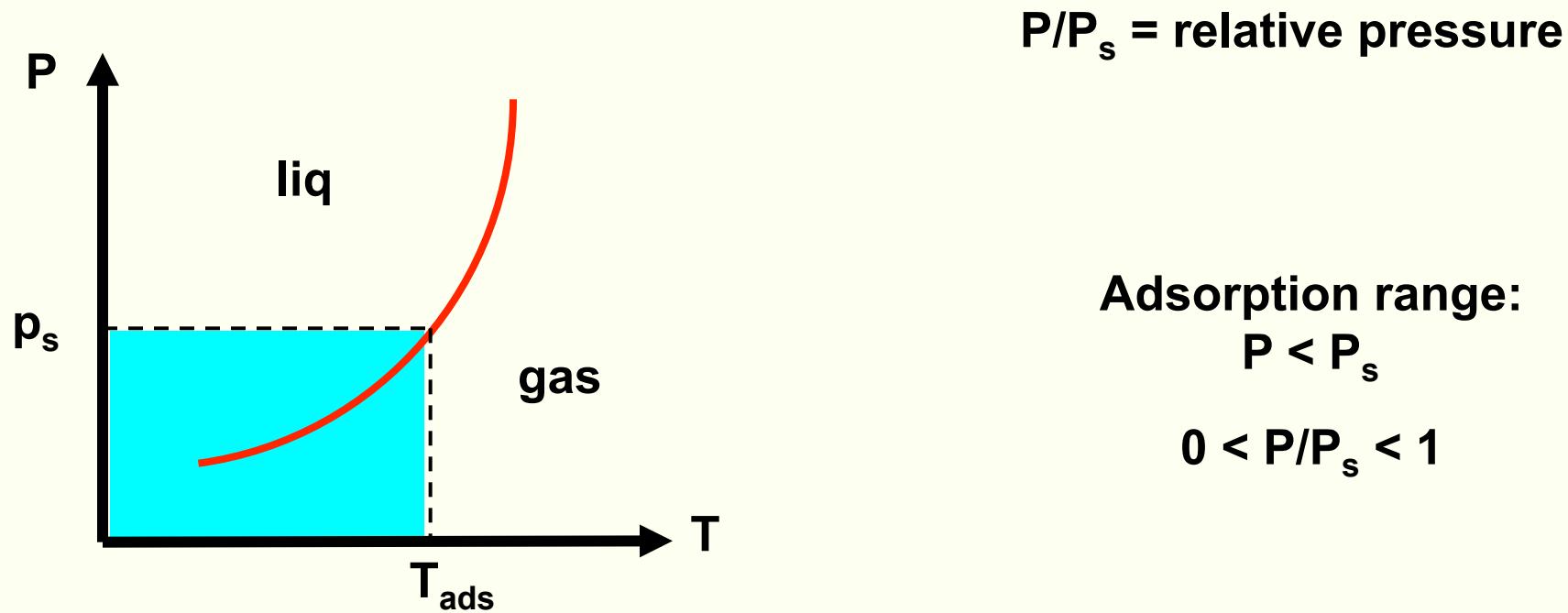
$$\theta = \frac{n^a}{n_s^a} \quad n_s^a \text{ is the maximal amount adsorbed at the saturation pressure } P_s$$

Intensive parameters of state:

- temperature T
- gas pressure P
- spreading pressure π

At constante temperature, the adsorption occurs for pressure lower than the saturated vapor pressure P_s of the fluid at the same temperature as the adsorption temperature.

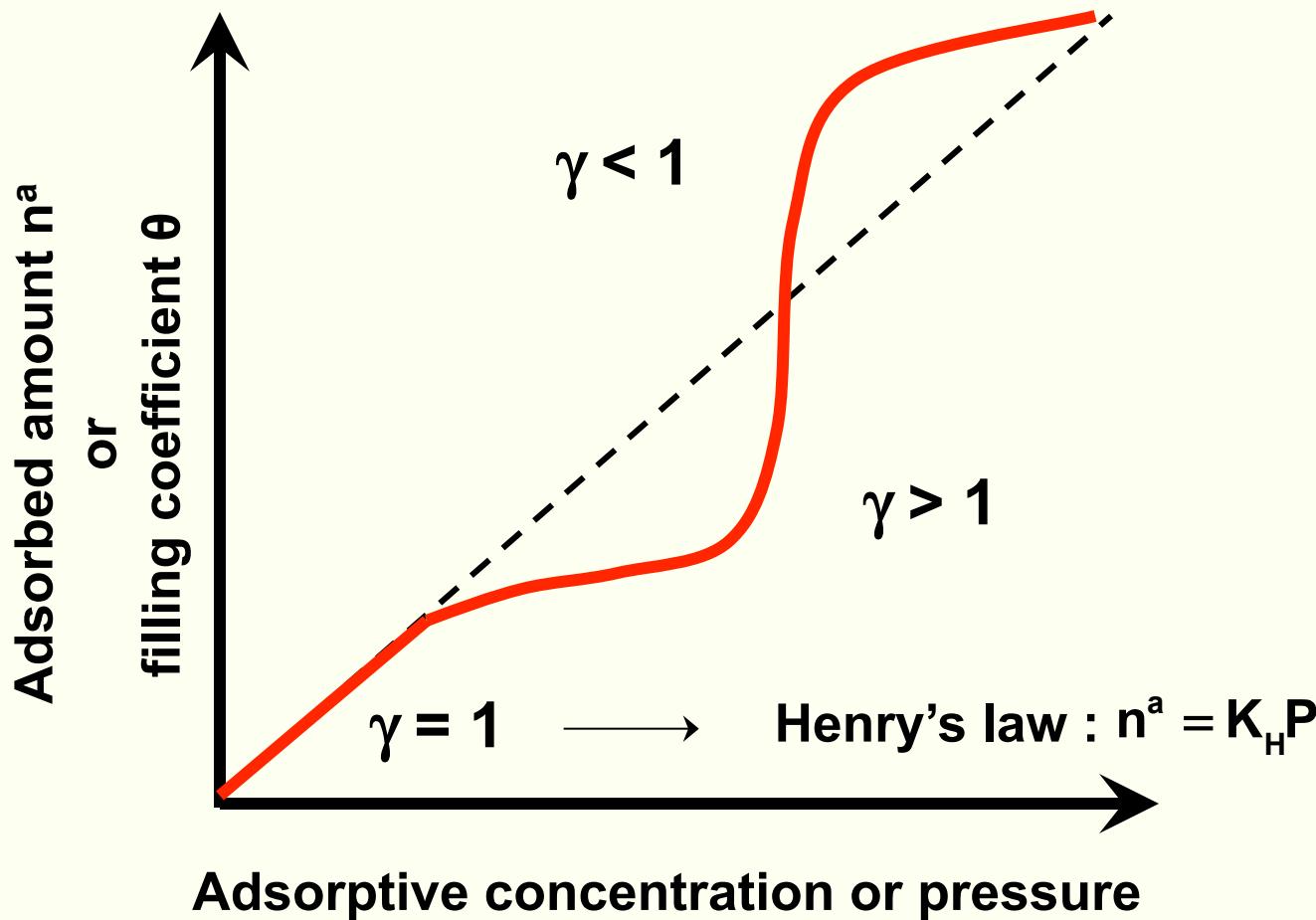
If $P > P_s$, then adsorption is replaced by liquefaction.



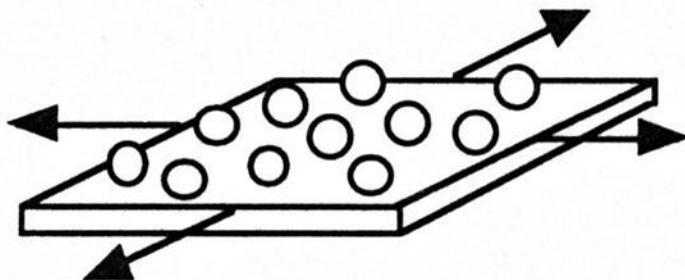
The activity coefficient γ indicates the deviation from ideality

$\gamma = 1$: ideal adsorption, linear isotherm (Henry's law)

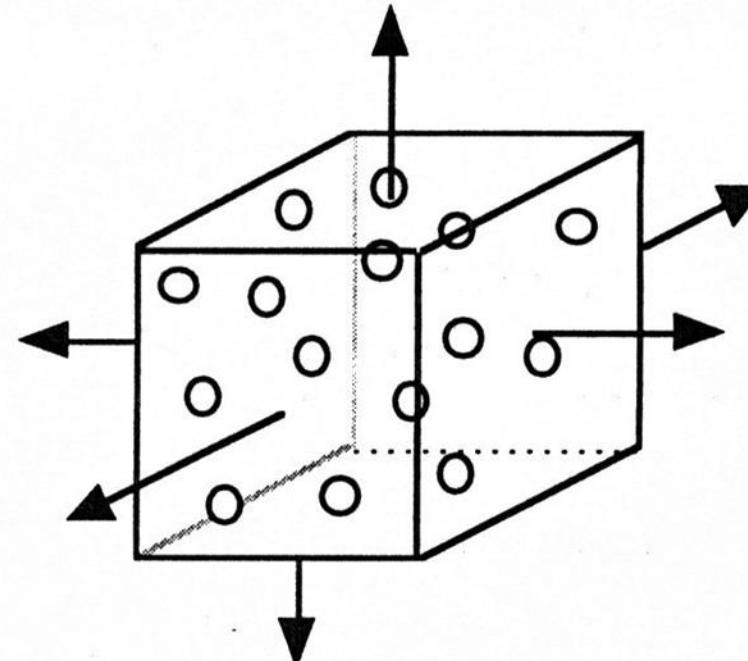
$\gamma \neq 1$: real adsorption, non-linear isotherm



What is the spreading pressure π ?



Adsorbed phase
 π : spreading pressure
2 dimensions (surface)



Gas phase
 P : pressure
3 dimensions (volume)

$$\delta W = -\pi dA$$

$$\delta W = -PdV$$

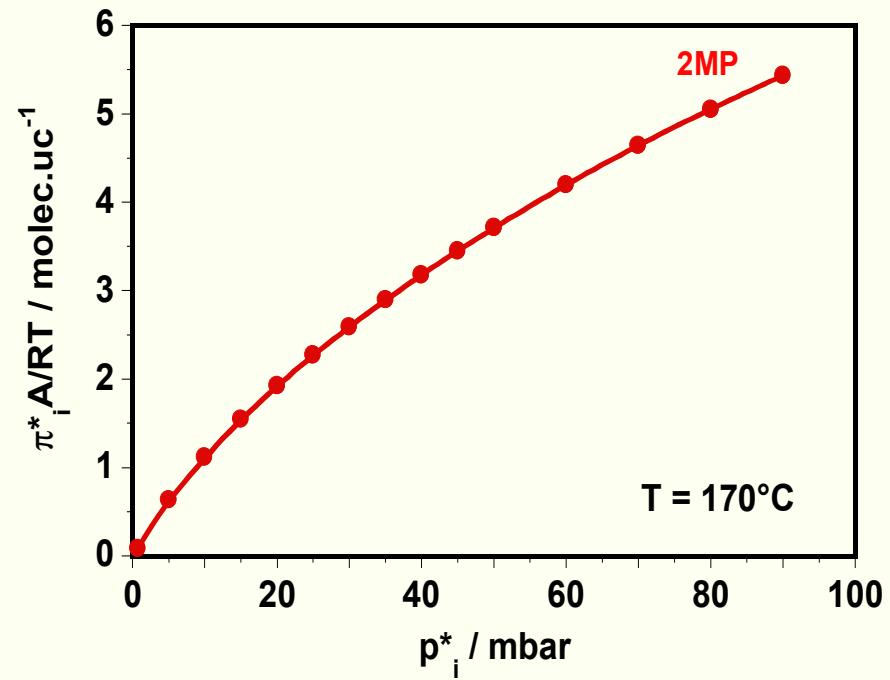
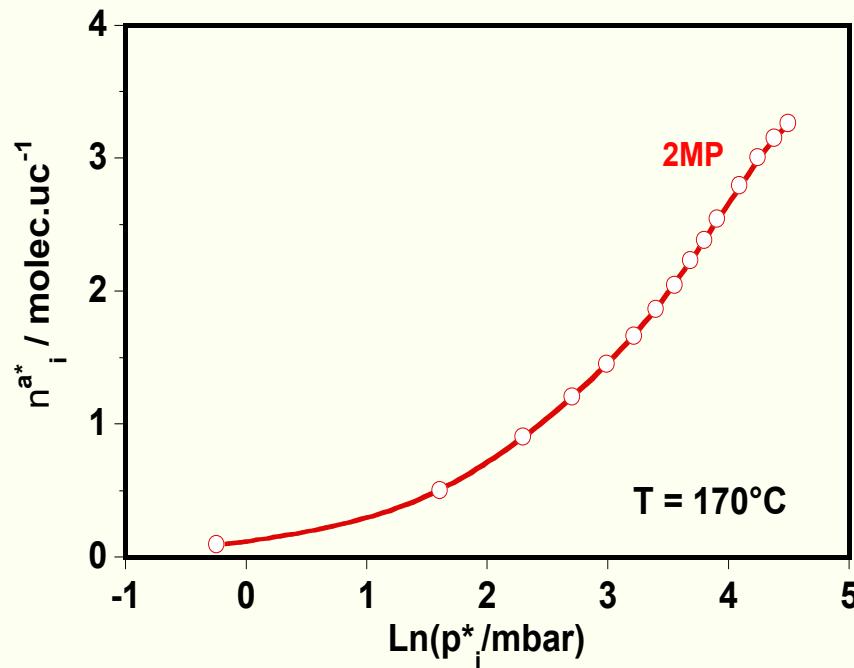
π is related to the surface tension of the solid: $\pi = \gamma_0 - \gamma$

The spreading pressure is related to the adsorbed amount by the relation:

$$\pi(T, P) = \frac{RT}{A} \int_0^P n^a d\ln(P)$$

This is the Gibbs adsorption isotherm

π can be calculated by integration of the adsorption isotherm



Variance of the adsorbate / adsorbent system

Gas = Adsorbate

Phases rule of Gibbs: $v = N - r + X - \varphi$

$N = 3$ (gas, adsorbate and adsorbent)

$r = 1$ (equilibrium constant)

$X = 3$ (P, T and π)

$\varphi = 3$ (gas, adsorbate and adsorbent)

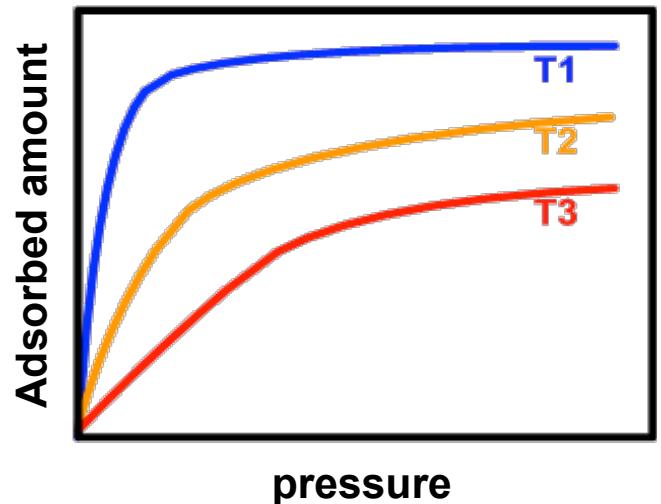


Degree of freedom: $v = 2$

Representation of adsorption equilibria

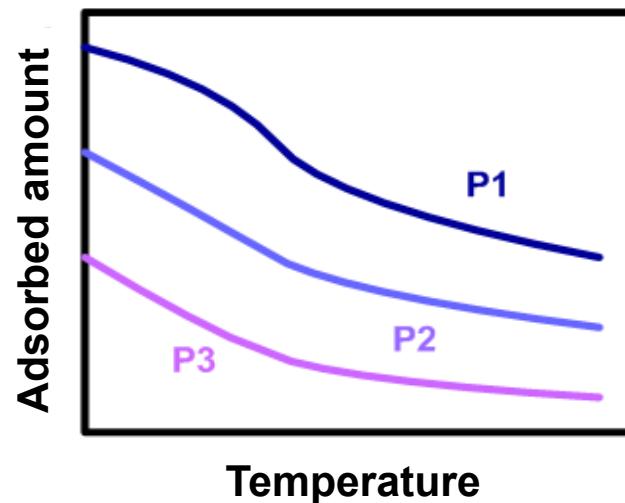
Divariant equilibrium

Isotherm

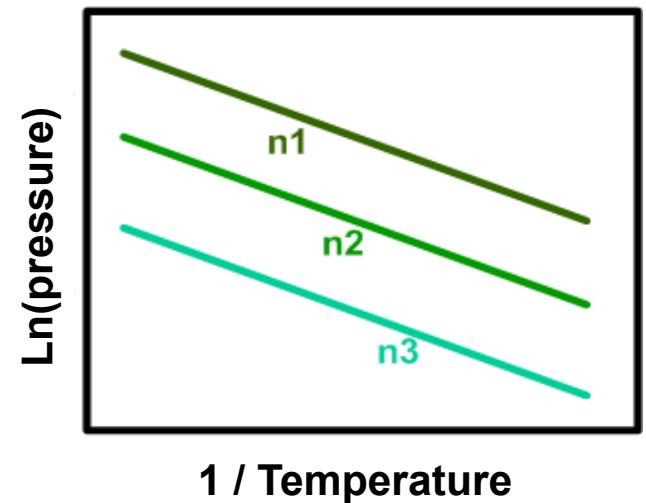


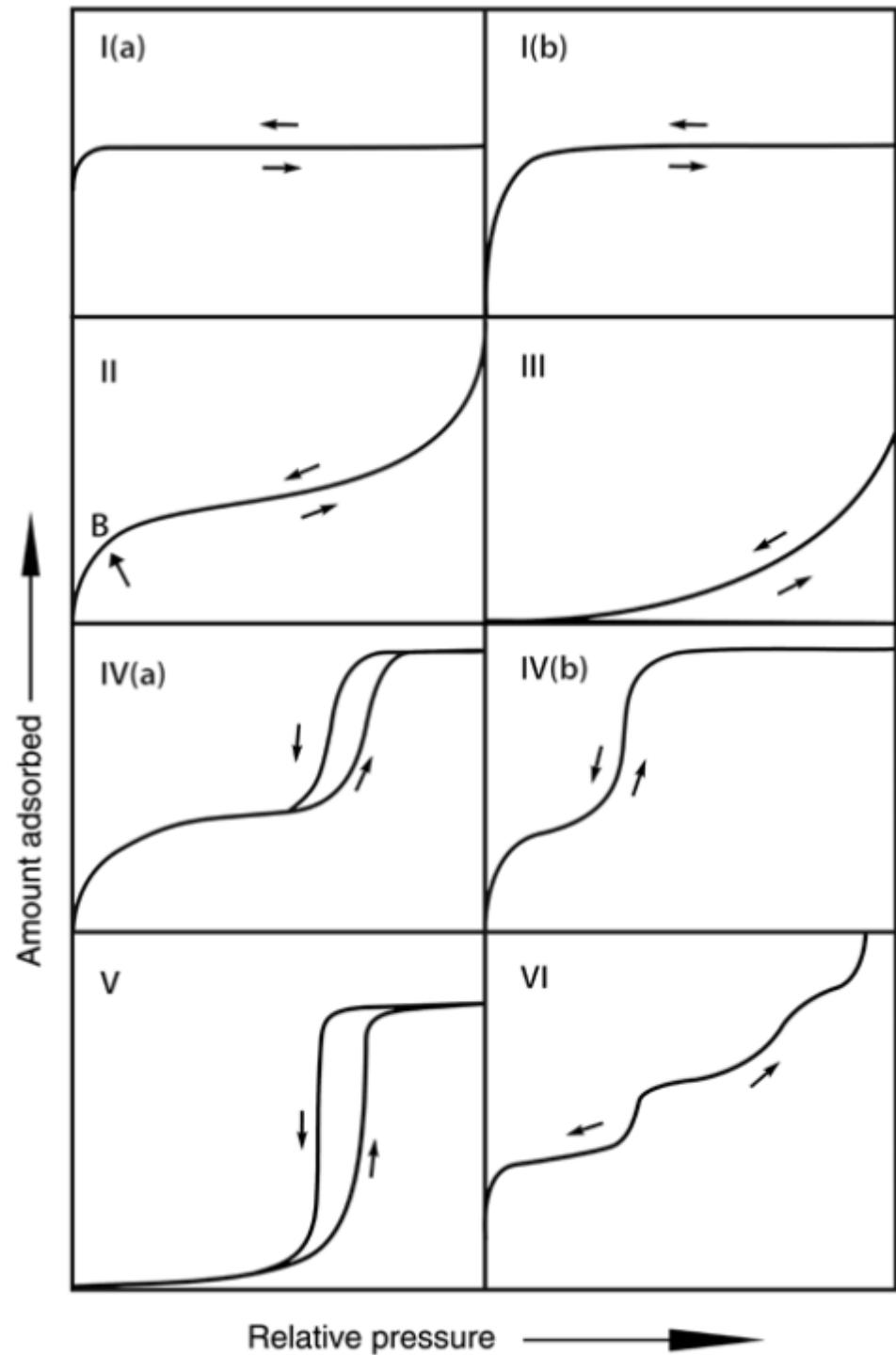
(the more often used)

Isobar



Isoster





New classification since 2015

M. Thommes et al.

Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)

Pure Appl. Chem. 87(9-10) (2015) 1051-1069.

Models derived from the Gibbs adsorption theory

$$\text{Model} = \pi = \frac{RT}{A} \int_0^P n^a d\ln(p) + \text{equation of state } \pi = f(A, T)$$

Table 2.3.1: Isotherm Equations derived from the Gibbs Equation

Equation of state	Isotherm	Name	Type of adsorption
$\pi\sigma = R_g T$	$bP = \theta$	Henry law	mobile
$\pi\sigma = R_g T \frac{\sigma}{\sigma_0} \ln\left(\frac{\sigma}{\sigma - \sigma_0}\right)$	$bP = \frac{\theta}{1 - \theta}$	Langmuir	mobile
$\pi(\sigma - \sigma_0) = R_g T$	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right)$	Volmer	localized without a – a interaction
$\pi\sigma = R_g T \frac{\sigma}{\sigma_0} \ln\left(\frac{\sigma}{\sigma - \sigma_0}\right) - \frac{cw}{2} \frac{\sigma_0}{\sigma}$	$bP = \frac{\theta}{1 - \theta} \exp\left(-\frac{cw\theta}{RT}\right)$	Fowler-Guggenheim	mobile
$\left(\pi + \frac{a}{\sigma^2}\right)(\sigma - \sigma_0) = R_g T$	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right) \exp(-c\theta)$	Hill-deBoer	mobile
$\left(\pi + \frac{a}{\sigma^3}\right)(\sigma - \sigma_0) = R_g T$	$bP = \frac{\theta}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta}\right) \exp(-c\theta^2)$		mobile
$\left(\pi + \frac{a}{\sigma^3}\right)\left(\sigma - \frac{\sigma_0}{\sigma}\right) = R_g T$	$bP = \sqrt{\frac{\theta}{1 - \theta}} \exp\left(\frac{1}{1 - \theta}\right) \exp(-c\theta)$		mobile

($\sigma = A/n^a$: surface area recovered per adsorbed molecule)

Some empirical models

Table 3.2-12 Summary of commonly used empirical isotherm equations

Isotherm	Functional form	Remarks
Frendlich	$C_\mu = KP^{1/n}$	Does not have Henry law limit and no saturation limit
Sips (LF)	$C_\mu = C_{\mu s} \frac{(bP)^{1/n}}{1 + (bP)^{1/n}}$	Does not have Henry law limit, but it has finite saturation limit
Toth	$C_\mu = C_{\mu s} \frac{bP}{[1 + (bP)^t]^{1/t}}$	Has Henry law limit and finite saturation limit
Unilan	$C_\mu = \frac{C_{\mu s}}{2s} \ln \left(\frac{1 + \bar{b}e^s P}{1 + \bar{b}e^{-s} P} \right)$	Has Henry law limit and finite saturation limit
Keller et al.	$C_\mu = C_{\mu s} \alpha_m \frac{bP}{[1 + (bP)^\alpha]^{1/\alpha}}$	Has Henry law limit and finite saturation limit
DR	$V = V_0 \exp \left[-\frac{1}{(\beta E_0)^2} \left(R_g T \ln \frac{P}{P_0} \right)^2 \right]$	Does not have Henry law limit, but reach a finite limit when P approaches P_0
Jovanovich	$C_\mu = C_{\mu s} [1 - e^{-bP}]$	Has Henry law limit and finite saturation limit
Temkin	$v(P) = C \ln(cP)$	Same as Freundlich. It does not have correct Henry law limit &finite saturation limit

Adsorption Analysis: Equilibria and Kinetics, D. D. Do, Imperial College Press (1998).

The most often used model: the Langmuir model

Adsorption rate = Desorption rate

$$v^a = v^d$$

$$\frac{P}{\sqrt{2\pi MRT}} \alpha(1 - \theta) = k_\infty^d \theta e^{\frac{-Q^a}{RT}}$$

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

avec $b = \frac{\alpha}{k_\infty^d \sqrt{2\pi MRT}} e^{\frac{Q^a}{RT}}$

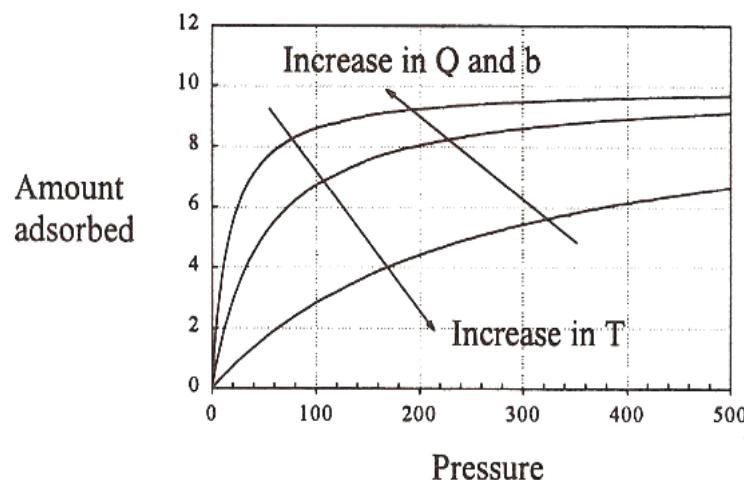
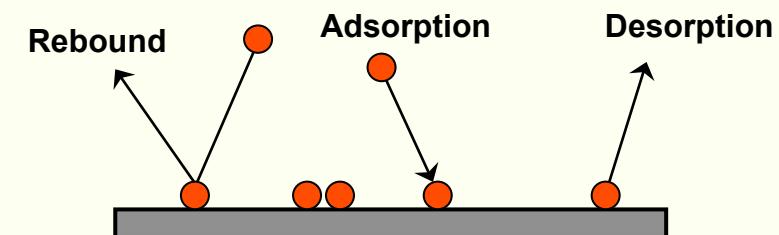
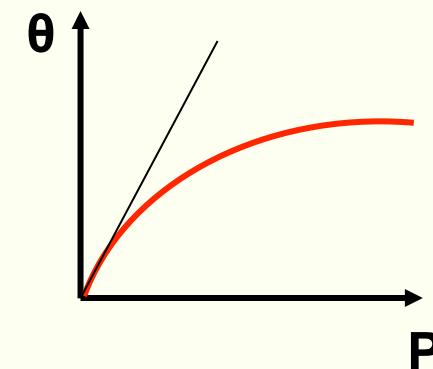


Figure 2.2-2: Behaviour of the Langmuir equation
(from D.D. Do)

When $P \rightarrow 0$, $bP \ll 1$
 $\theta = bP$ Henry's law

Isotherm of type I



Energies of adsorption

Adsorption of gas on a solid is a spontaneous process:

$$\Delta G^a = \Delta H^a - T\Delta S^a < 0$$

$\Delta H^a < 0$ adsorption is exothermic

$\Delta S^a < 0$ disorder is lower in adsorbate than in gas

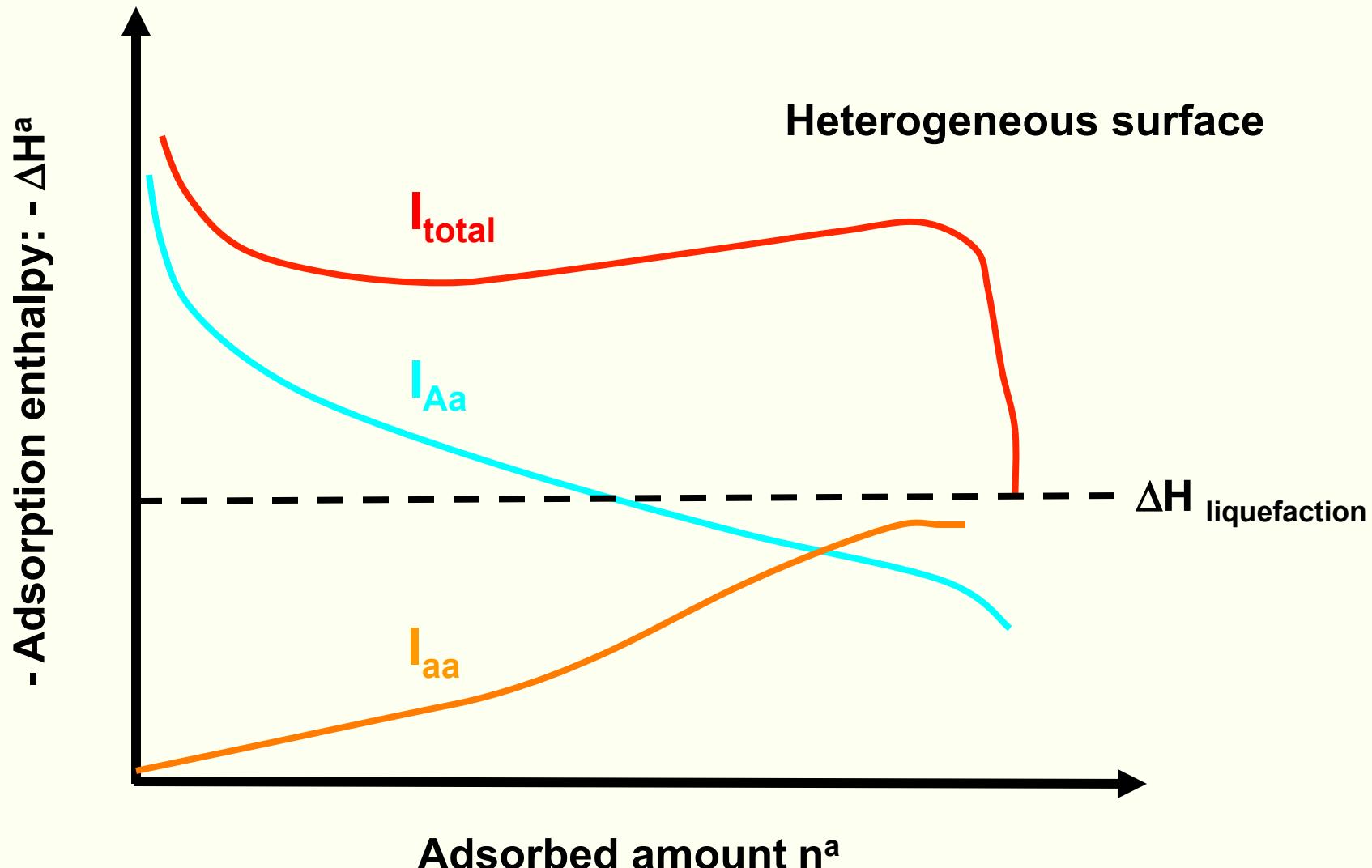
ΔH^a and ΔS^a give information about the adsorption process:

ΔH^a → adsorbate / adsorbent and adsorbate / adsorbate interactions

ΔS^a → physical state of matter confined in pores

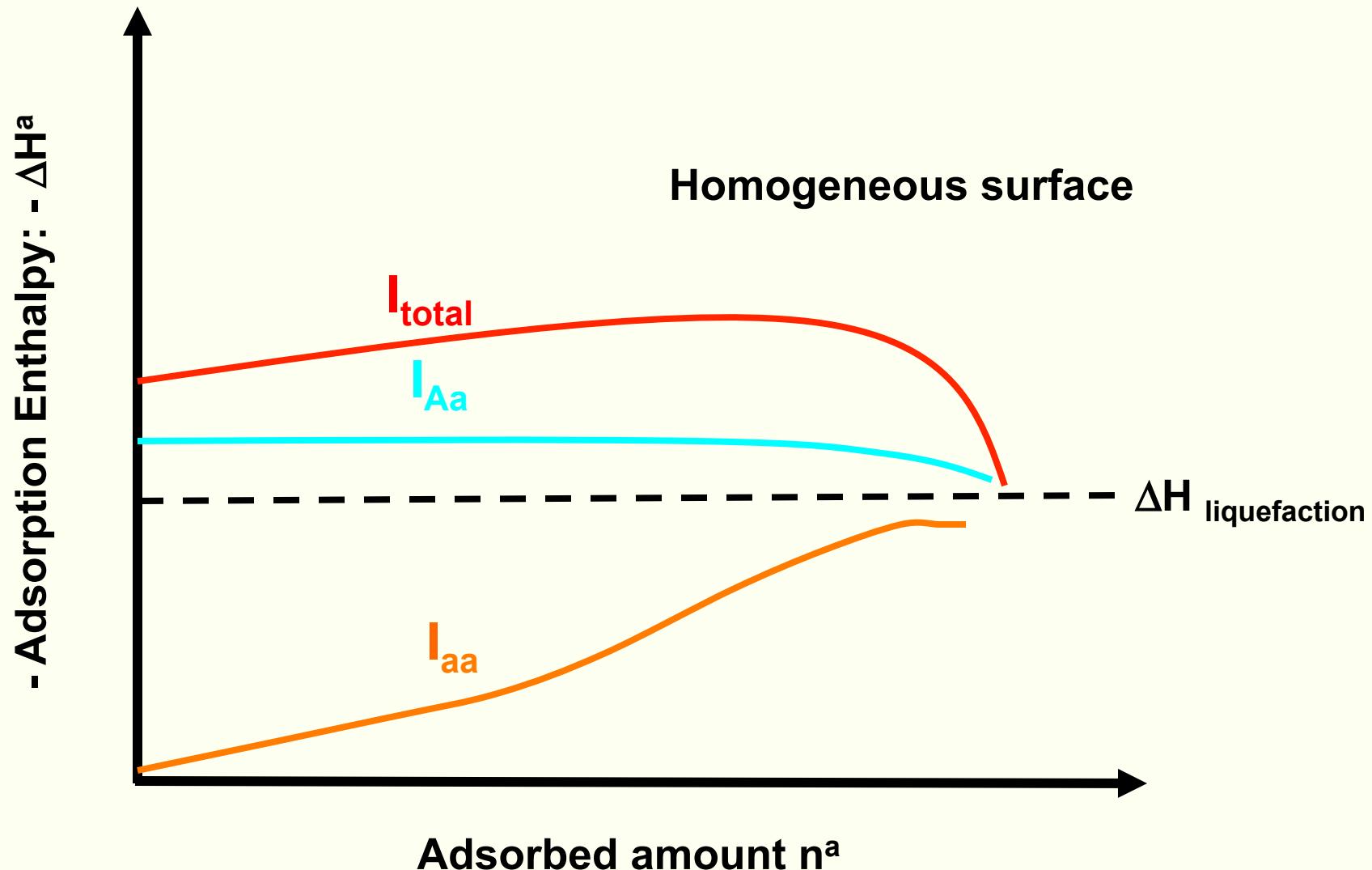
Adsorption enthalpy $\Delta H^a < 0$

→ Adsorbate / adsorbent + adsorbate / adsorbate interactions



Adsorption enthalpy $\Delta H^a < 0$

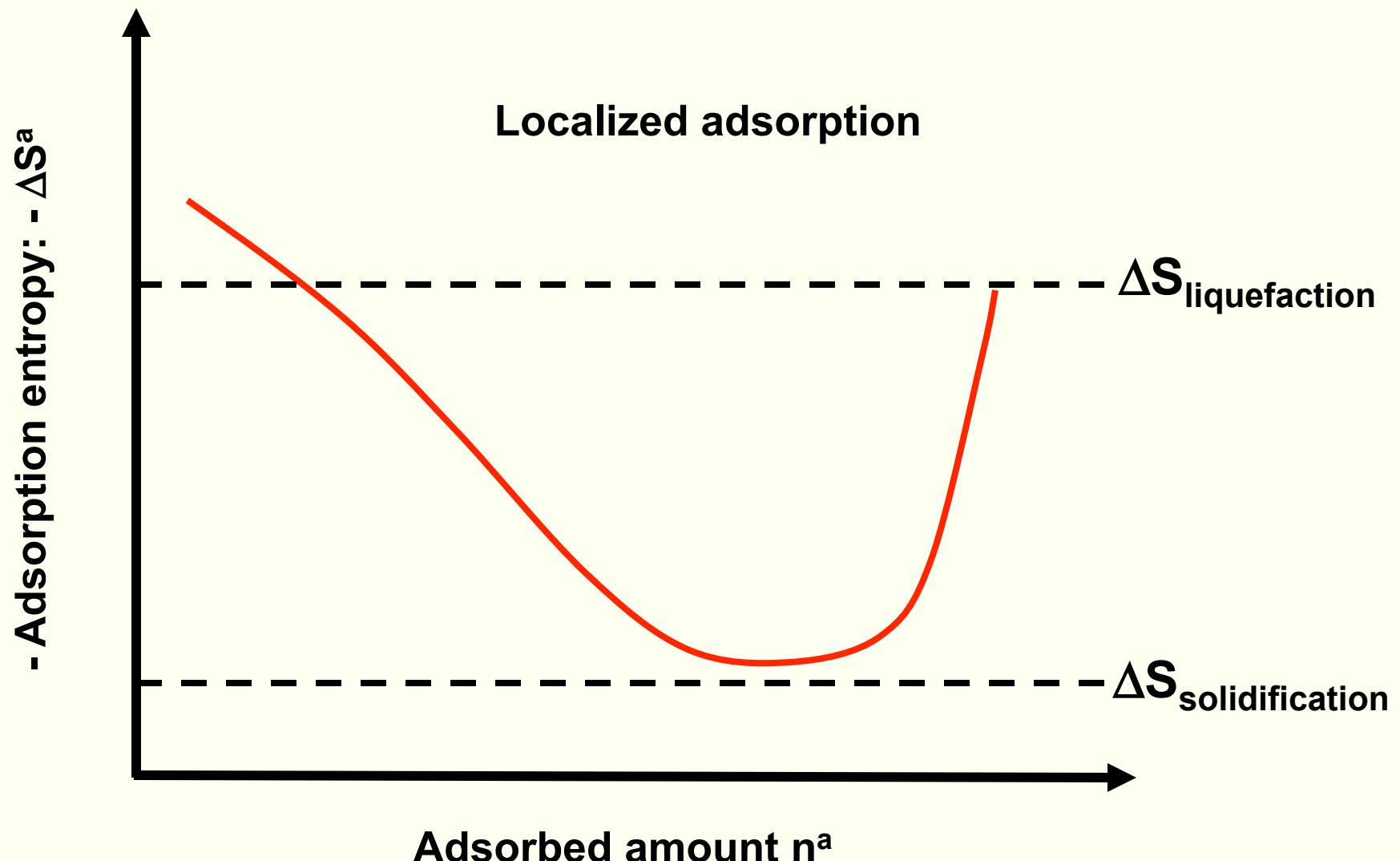
→ Adsorbate / adsorbent + adsorbate / adsorbate interactions



Adsorption entropy $\Delta S^a < 0$



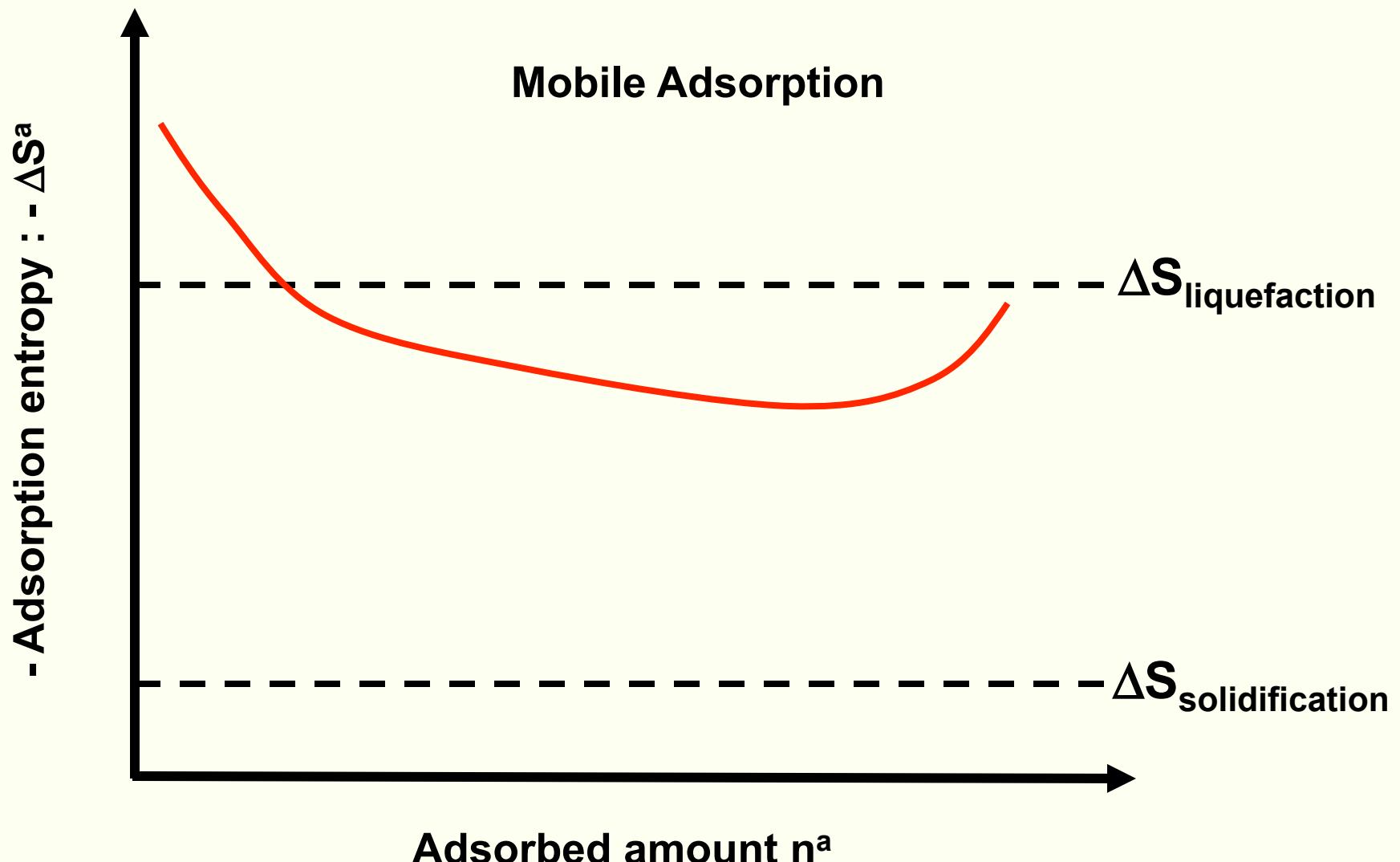
Physical state of adsorbate (confinement effect)



Adsorption entropy $\Delta S^a < 0$



Physical state of adsorbate (confinement effect)



How can we determine ΔH^a and ΔS^a ?

From adsorption isotherms measured at different temperatures

Van't Hoff equation

Isosteric plot

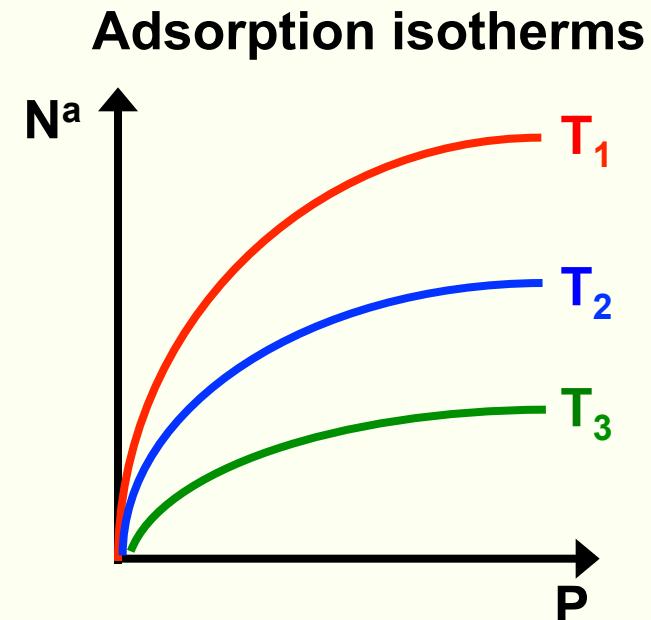
ΔH^a and ΔS^a

From calorimetric measurements

Q^a = heat of adsorption = ΔH^a

$\Delta S^a = S^g - S^a$

From Van't Hoff equation: $\ln(K_T) = -\frac{\Delta H^a}{R} \frac{1}{T} + \frac{\Delta S^a}{R}$



$$K_T = \frac{K_{H,L}}{P^\circ}$$

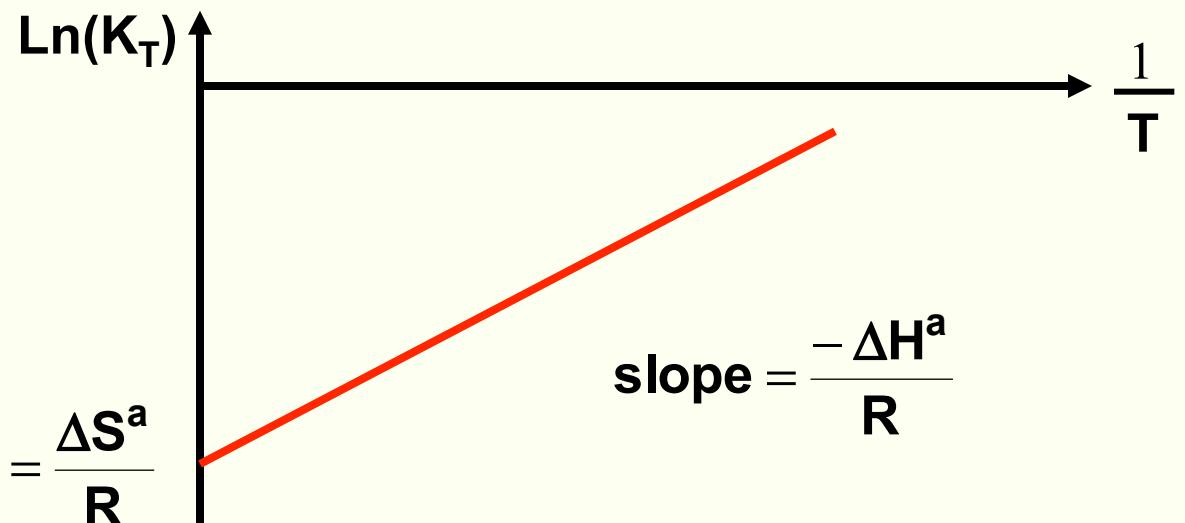
(P° = standard pressure = 10^5 Pa)

$$\text{intercept} = \frac{\Delta S^a}{R}$$

Thermodynamic model of adsorption:

Henry: $N^a = K_H P$

Langmuir: $N^a = N_s^a \frac{K_L P}{1 + K_L P}$



From isosteric plots:

gas = adsorbate

At equilibrium and constant adsorbed amount: $\mu^g = \mu^a$

$$\mu^{g^\circ}(T) + RT \ln\left(\frac{P}{P^\circ}\right) = \mu^a(T, n^a) \quad (P^\circ = \text{standard pressure} = 10^5 \text{ Pa})$$

with: $\mu^{g^\circ}(T) = H_m^{g^\circ}(T) - TS_m^{g^\circ}(T)$ and $\mu^a(T, n^a) = H_m^a(T, n^a) - TS_m^a(T, n^a)$

Let us define at constant n^a :

$$\Delta H_{\text{iso}}^a = H_m^a(T, n^a) - H_m^{g^\circ}(T) \quad \text{and} \quad \Delta S_{\text{iso}}^a = S_m^a(T, n^a) - S_m^{g^\circ}(T)$$

we obtain:

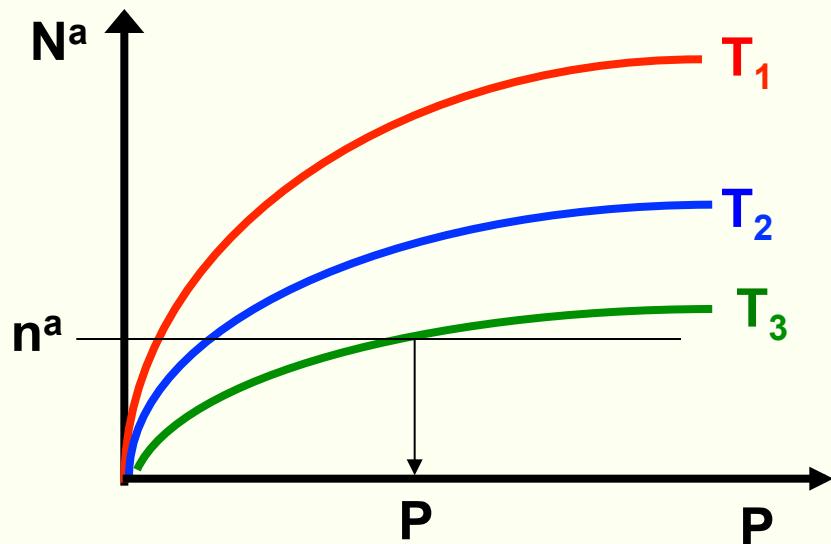
$$\ln\left(\frac{P}{P^\circ}\right)_{n^a} = \frac{\Delta H_{\text{iso}}^a}{R} \times \frac{1}{T} - \frac{\Delta S_{\text{iso}}^a}{R}$$

These are the molar isosteric enthalpy and entropy of adsorption.

ΔH_{iso} et ΔS_{iso} are determined from the isosteric plots

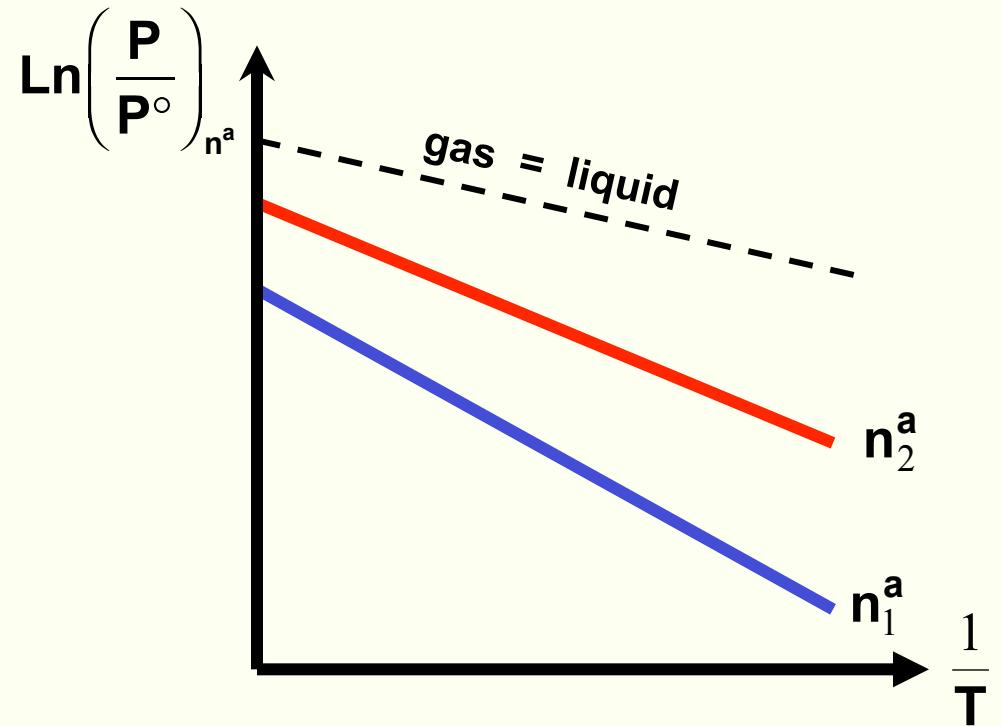
$$\ln\left(\frac{P}{P^\circ}\right)_{n^a} = f\left(\frac{1}{T}\right)$$

Adsorption isotherms

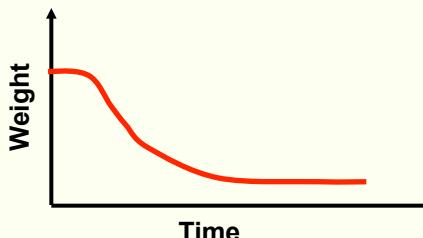
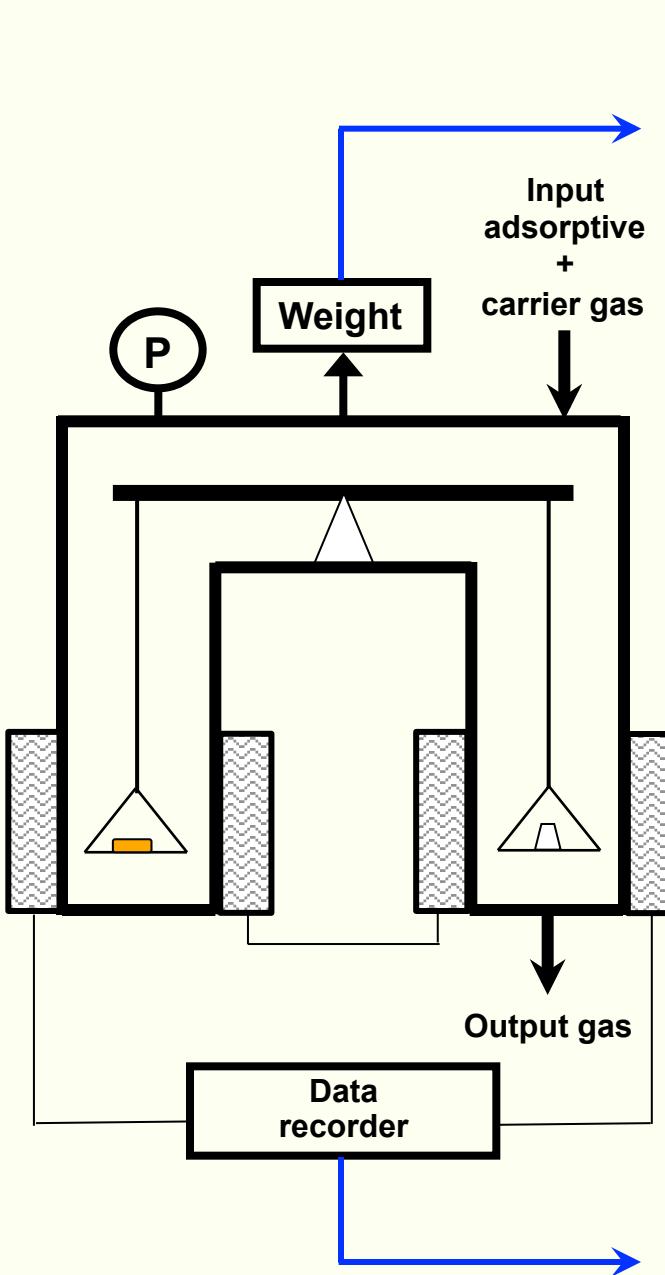


$$\text{slope} = \frac{\Delta H_{\text{iso}}}{R}$$

$$\text{intercept} = -\frac{\Delta S_{\text{iso}}}{R}$$



From calorimetric coupled with thermogravimetric measurements:



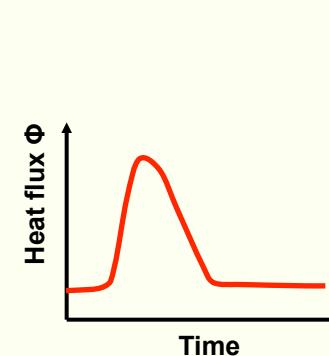
Adsorbed amount given by the thermobalance n^a

Pros:

- very high sensibility on the adsorbed amount
- small amount of sample (few mg)

Cons:

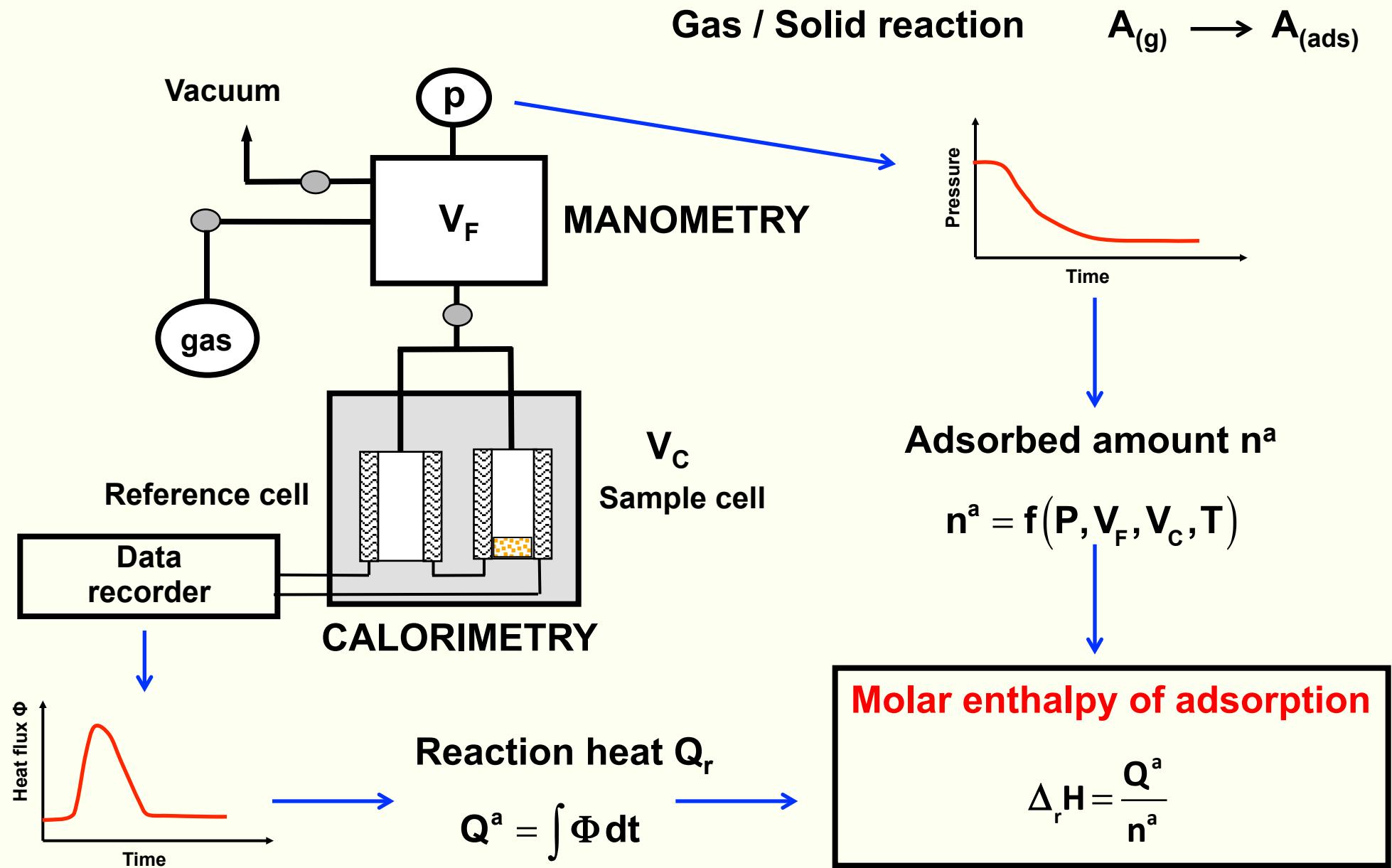
- need correction of buoyancy under high pressure (> 1 bar)
- measurements under flow gas:
 - thermodynamic equilibrium?
 - adsorption of carrier gas?
 - part of heat evacuated by the gas flow?



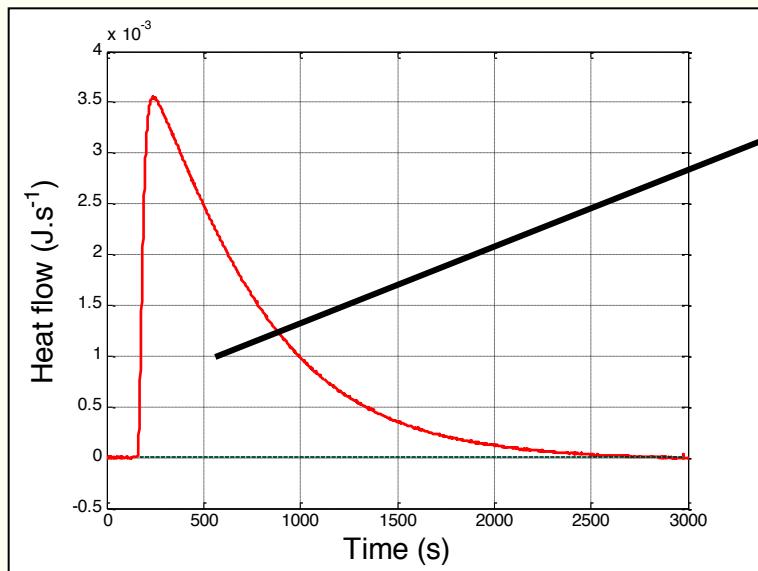
Molar enthalpy of adsorption $\Delta_r H = \frac{Q^a}{n^a}$

Adsorption heat given by the calorimeter Q^a

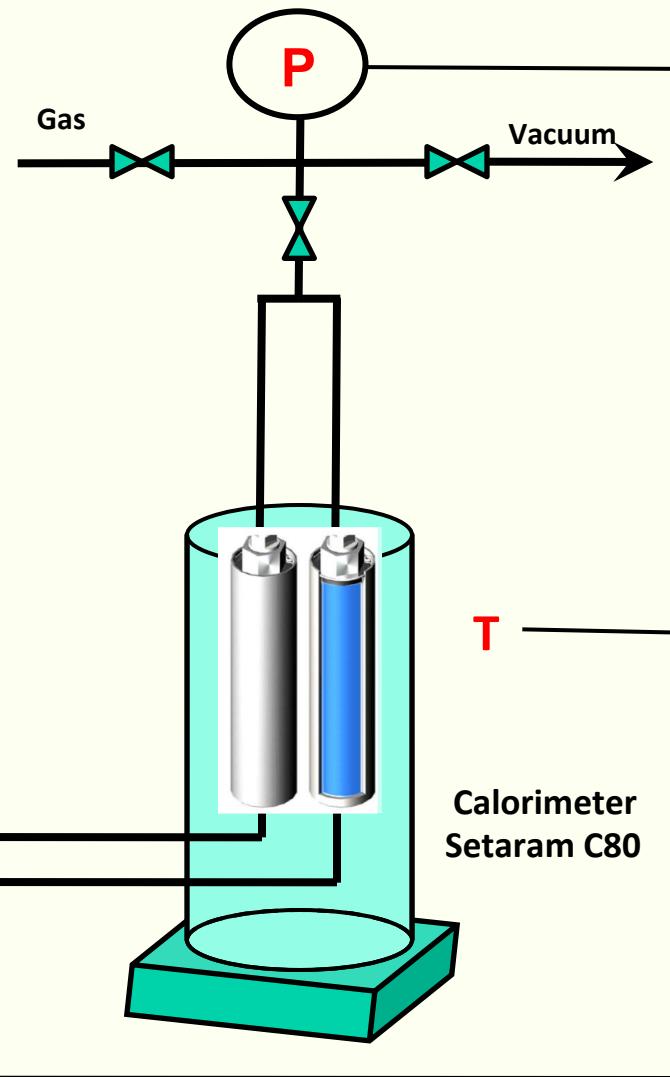
From calorimetric coupled with manometric measurements:



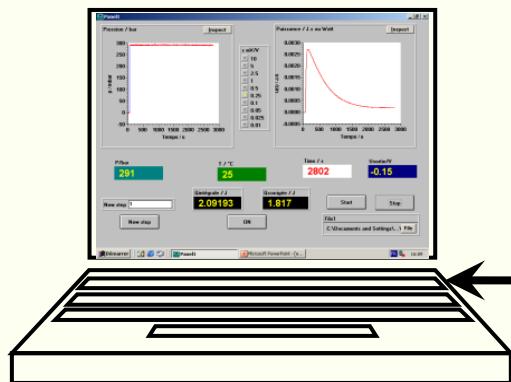
Procedure used by calorimetry and manometry



$$Q^a = \int (\text{HeatFlow}) dt$$



P, T, Heat Flow = f(t)



Interface
Testpoint, Labview

Experimental procedure

Introduction of a small dose of gas in the volume V_F

Measure of the initial pressure P_i of gas in the volume V_F

The gas is put in contact with the adsorbent

Measure of the final pressure P of gas at equilibrium in the volume V_F+V_c

Beside, measure of the heat flow versus time

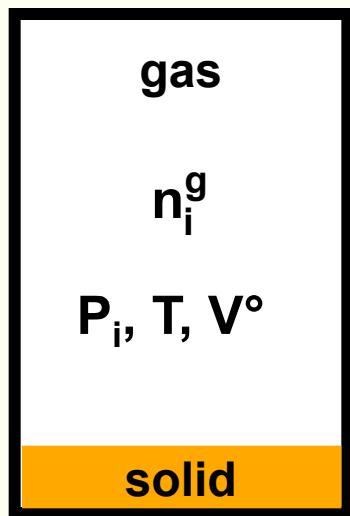
Calculation of the adsorbed amount

Calculation of the adsorption heat by integration of the heat flow versus time

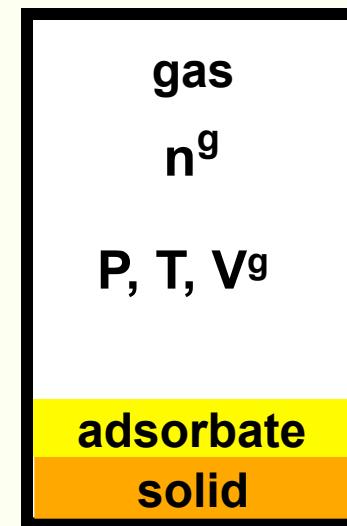
Calculation of the molar adsorption enthalpy

Determination of adsorbed amounts by manometry

Before adsorption



At equilibrium



closed system
at constant V and T

V° = dead volume of reactor (known from calibration with helium)

P_i and P = pressures of gas which are measured

V^g = volume of gas at equilibrium (unknown)

$$V^\circ = V^g + V^a$$

$$n_i^g = n^a + n^g$$

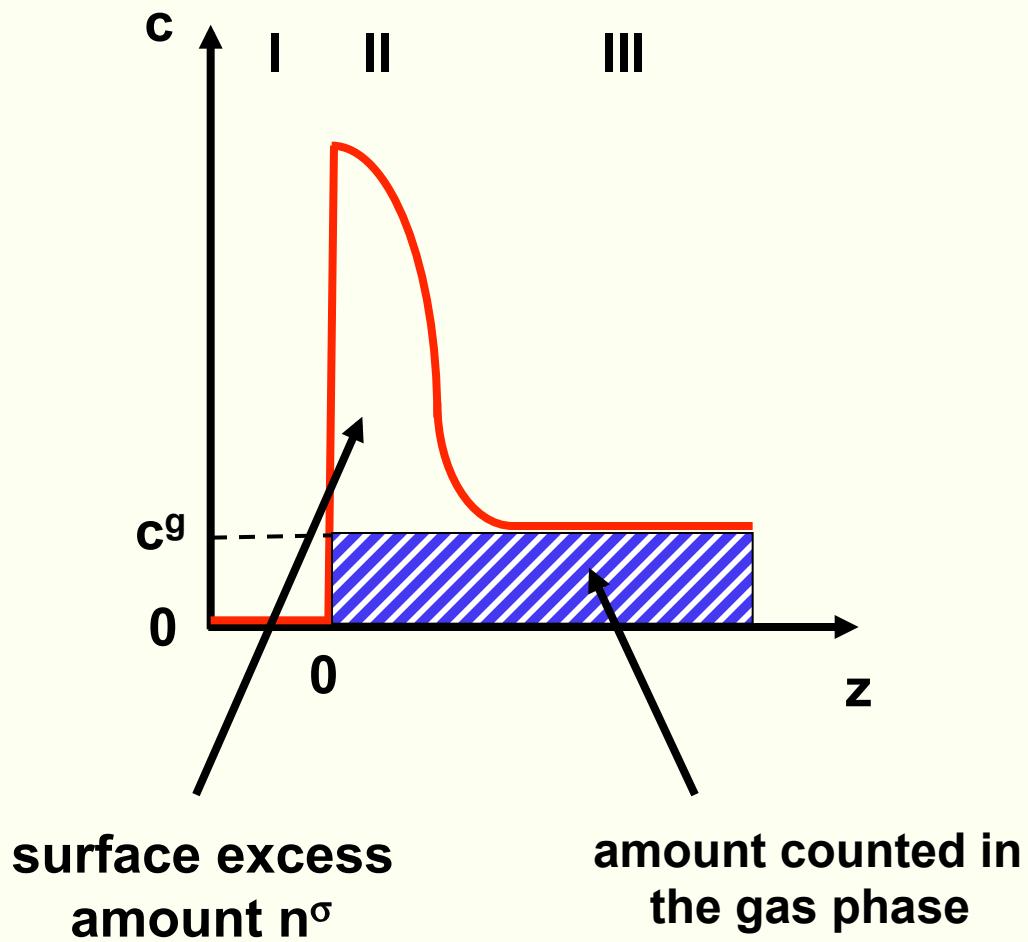
$$V^\circ c_i^g = n^a + V^g c^g$$

with c_i^g and c^g the concentrations of gas (for ideal gas $c_i^g = \frac{P_i}{RT}$ and $c^g = \frac{P}{RT}$)

$$V^\circ c_i^g = n^a + V^\circ c^g - V^a c^g$$

$$V^\circ(c_i^g - c^g) = n^a - V^a c^g = n^\sigma$$

The measurements of P_i and P do not give the adsorbed amount n^a
but the surface excess amount n^σ



$$V^\circ(c_i^g - c^g) = n^a - V^a c^g = n^\sigma$$

$$n^a = V^\circ c_i^g - V^\circ c^g + V^a c^g$$

$$n^a = V^\circ c_i^g - (V^\circ - V^a)c^g$$

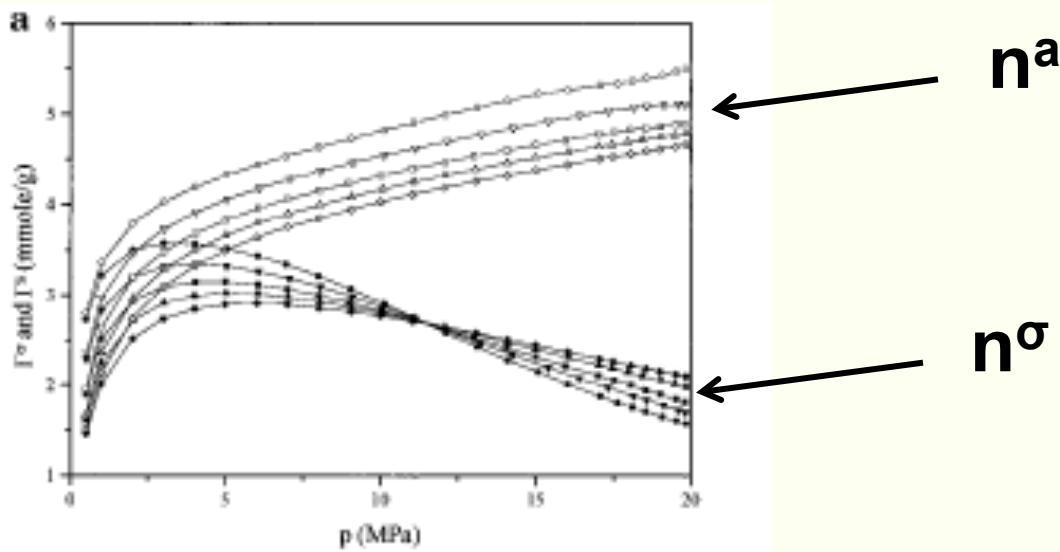
If $V^\circ \gg V^a$ and low pressure of gas then:

$$n^a \approx V^\circ(c_i^g - c^g) = \frac{V^\circ}{RT}(P_i - P)$$

n^a can be directly measured by manometry if the volume of the reactor is large enough and if the pressure of gas is low

Example: Adsorption of methane on 13X zeolite and activated carbon

13X



Activated carbon

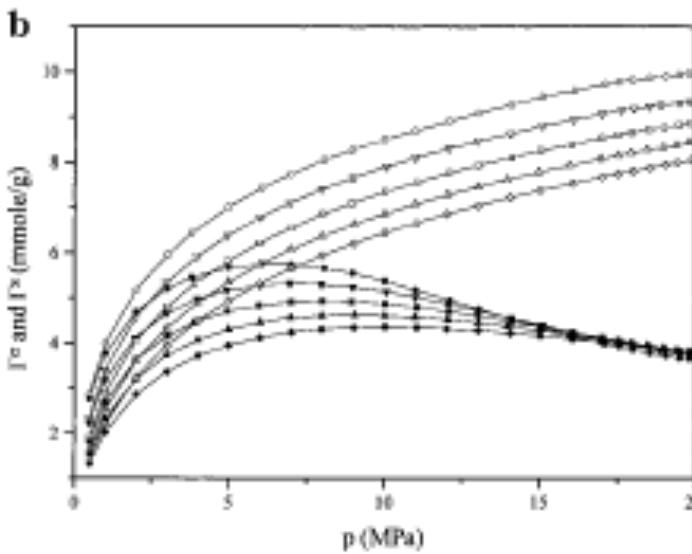
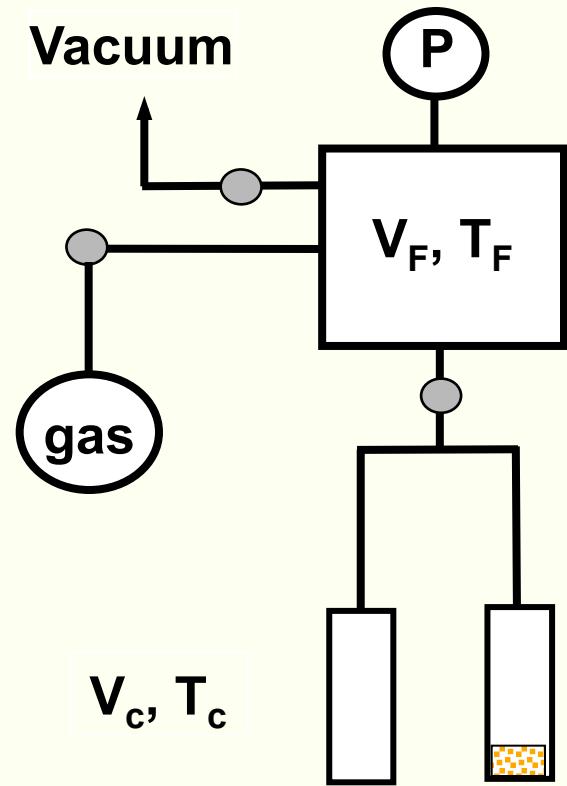
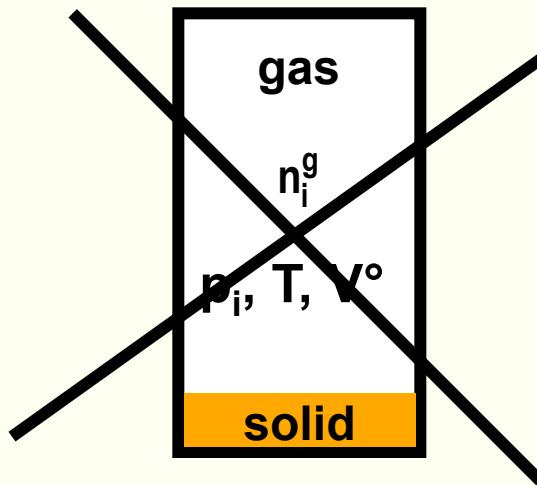


Figure 3. Adsorption excesses (solid symbols) and absolute adsorption isotherms (open symbols) for methane on the 13X molecular sieve (a) and AS active carbon (b) at the temperatures 258.15 K (○, ●), 273.15 K (▽, ▼), 288.15 K (□, ■), 308.15 K (△, ▲), and 318.15 K (◇, ♦).

Practically:

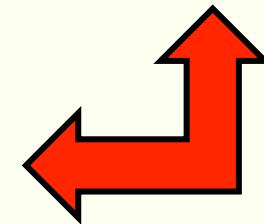


Amount adsorbed at adsorption j:

$$n_j^a = \frac{V_F}{RT_F} (P_{i,j} - P_{f,j}) + \frac{V_c}{RT_c} (P_{f,j-1} - P_{f,j})$$

Total adsorbed at the point j of the isotherm:

$$N_j^a = \sum_j n_j^a$$



Determination of adsorption enthalpy by differential calorimetry

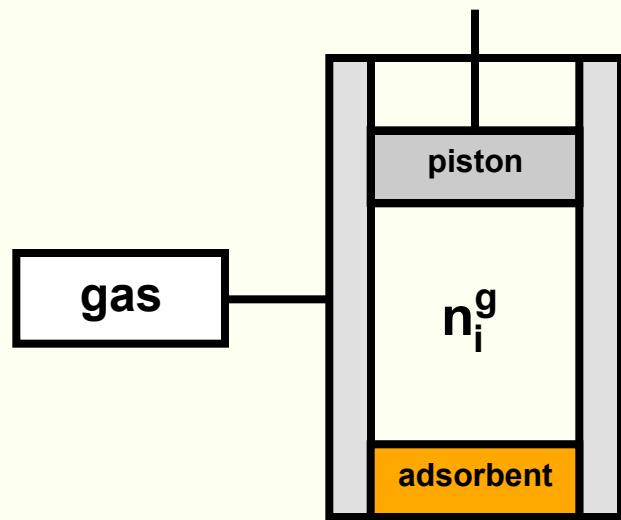
When an amount of gas is introduced in both cells of the calorimeter, two energetic effects must be taken into account:

- in the sample cell: **adsorption of gas in the solid**
 +
**mechanical work exchanged with the outside world due
to the expansion of gas in the sample cell**

- reference cell: **mechanical work exchanged with the outside world
due to the expansion of gas in the reference cell only**

Sample cell:

The sample cell can be considered as the following equivalent thermodynamic system:



	gas	=	adsorbate
$t = 0$	n_i^g , u^g , P_i	0	
t_{equil}	n^g , u^g , P		n^a , u^a

The change in internal energy is: $\Delta U_s = n^a u^a + n^g u^g - n_i^g u^g$

As $n^a + n^g = n_i^g$ it follows: $\Delta U_s = n^a (u^a - u^g)$

This is the integral heat of adsorption (J)

Therefore the differential internal energy is:

$$dU_s = (u^a - u^g)dn^a + n^a du^a = \delta Q_s + \delta W_s$$

The differential mechanical work exchanged with the outside world is defined by:

$$\delta W_s = -PdV_s$$

Let us consider the gas as ideal ($PV_s = n^g RT$), at constant T this relation becomes:

$$\delta W_s = V_s dp - dn^g RT = V_s dp + dn^a RT$$

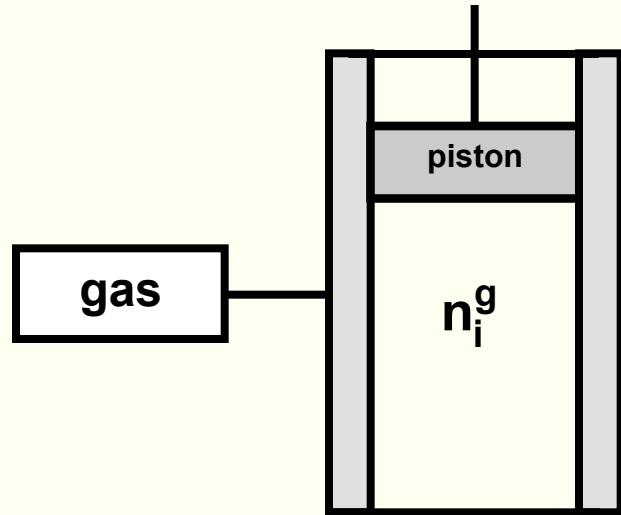
(because $n^a + n^g = n_i^g$ and as the system is closed: $dn^g = -dn^a$)

Thus the differential heat in the sample cell is:

$$\delta Q_s = dU_s - \delta W_s$$

$$\boxed{\delta Q_s = (u^a - u^g)dn^a + n^a du^a - RTdn^a - V_s dp}$$

Reference cell:



Let us consider now that we introduce in the reference cell the same amount of gas as in the sample cell.

If the gas is ideal, at constant temperature the differential internal energy is null :

$$dU_r = \delta Q_r + \delta W_r = 0$$

The differential mechanical work is: $\delta W_r = -P dV_r$

As the gas is ideal: $PV_r = n_i^g RT$ and $PdV_r + V_r dP = 0$

Thus the differential heat in the reference cell is:

$$\boxed{\delta Q_r = -V_r dP}$$

Calorimetric adsorption heat:

The heat measured by differential calorimetry is: $\delta Q^a = \delta Q_s - \delta Q_r$

$$\delta Q^a = (u^a - u^g)dn^a + n^a du^a - RTdn^a + (V_r - V_s)dP$$

Let us define the molar internal energy of the adsorbate at the adsorbed amount n^a by:

$$u^a(n^a) = u^a + n^a \frac{du^a}{dn^a}$$

We obtain: $\delta Q^a = u^a(n^a)dn^a - u^g dn^a - RTdn^a + (V_r - V_s)dP$

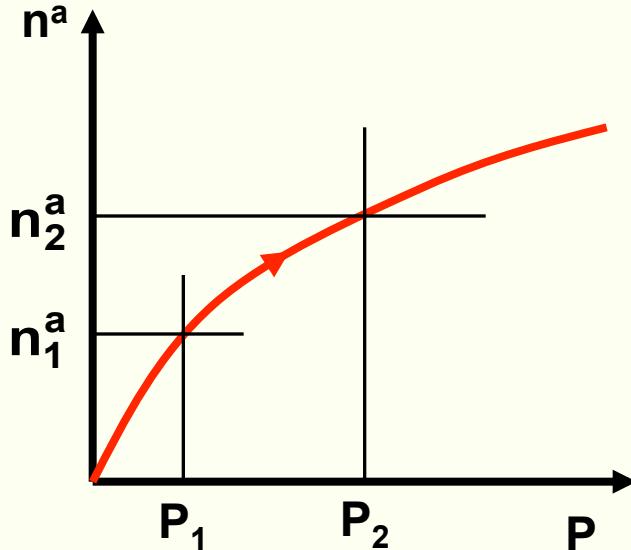
If the volumes of the sample and reference cells are identical and larger than that one of the adsorbent then: $(V_r - V_s)dP \approx 0$

Therefore:

$$\boxed{\delta Q^a = u^a(n^a)dn^a - u^g dn^a - RTdn^a}$$

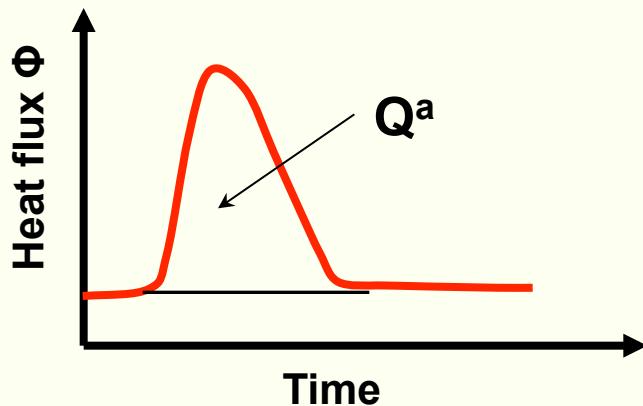
This is the differential heat of adsorption (J)

For a finite adsorption, by integrating between the adsorbed amounts n_1^a and n_2^a and the pressures p_1 and p_2 , we obtain:



$$Q_m^a = \frac{Q^a}{n_2^a - n_1^a} = \frac{n_2^a u(n_2^a) - n_1^a u(n_1^a)}{n_2^a - n_1^a} - u^g - RT$$

$$Q_m^a = \Delta_r U_m^a - RT$$



This is the molar differential heat of adsorption
at the adsorbed amount $\frac{n_1^a + n_2^a}{2}$ (J.mol⁻¹)

Q_m^a corresponds to the differential molar enthalpy of adsorption
at the adsorbed amount $\frac{n_1^a + n_2^a}{2}$:

$$H = U + PV$$

$$\Delta_r H^a = \Delta_r U^a + \Delta_r(PV)$$

$$\Delta_r H^a = \Delta_r U^a + \sum_i v_{i(gas)} RT$$

gas \rightarrow adsorbate

$$\sum_i v_{i(gas)} = -1$$

$$\Delta_r H_m^a = \Delta_r U_m^a - RT$$

$$Q_m^a = \Delta_r H_m^a \left(\frac{n_1^a + n_2^a}{2} \right)$$

(J.mol⁻¹)

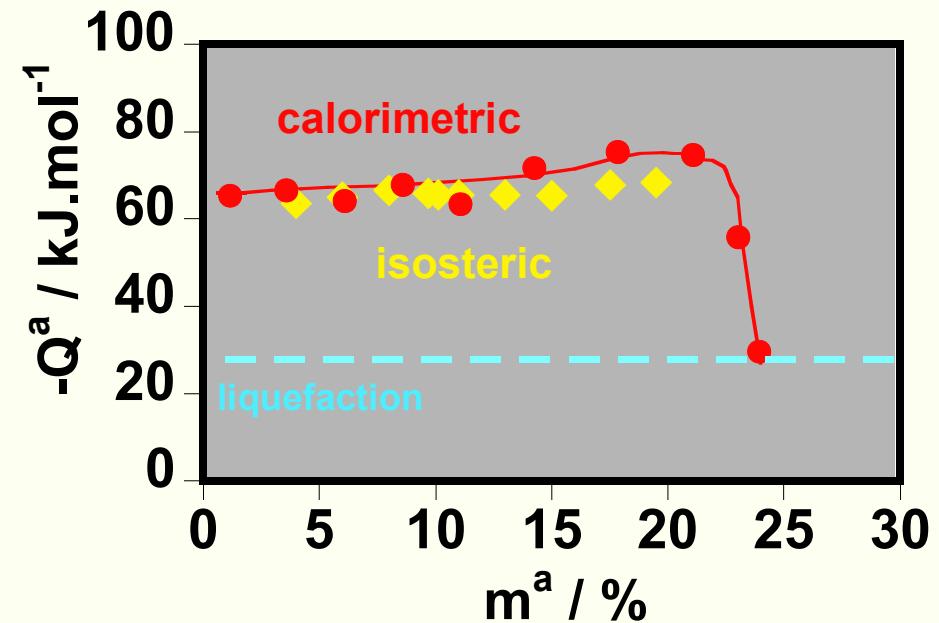
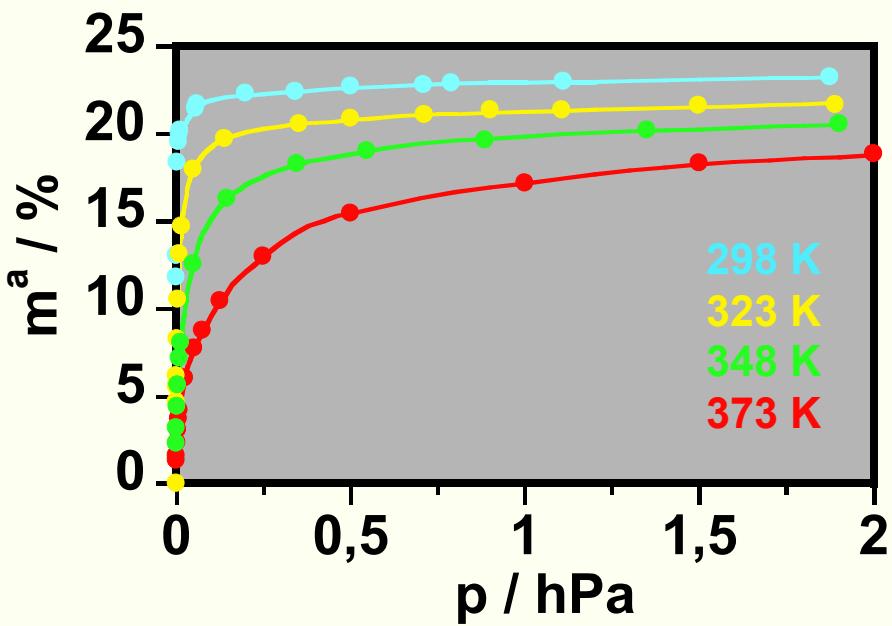
The molar enthalpy of adsorption corresponds also to the isosteric adsorption enthalpy:

$$Q_m^a = \Delta H_{iso}$$

Ex: Agreement between isosteric adsorption enthalpy and calorimetric adsorption heat

$$Q_m^a = \Delta H_m^a \left(\frac{n_1^a + n_2^a}{2} \right) = \Delta H_{\text{iso}}$$

Adsorption of ethylmercaptan on NaX zeolite



Determination of adsorption entropy

As $Q_m^a = \Delta H_{iso}$, the adsorption entropy can be determined by combining the isosteric method and the calorimetric measurements.

At a given adsorbed amount n^a , we can write:

$$\Delta S_m^a(n^a) = \frac{Q_m^a}{R} \times \frac{1}{T} - \ln\left(\frac{P}{P^\circ}\right)_{n^a}$$

calorimetric
measurements

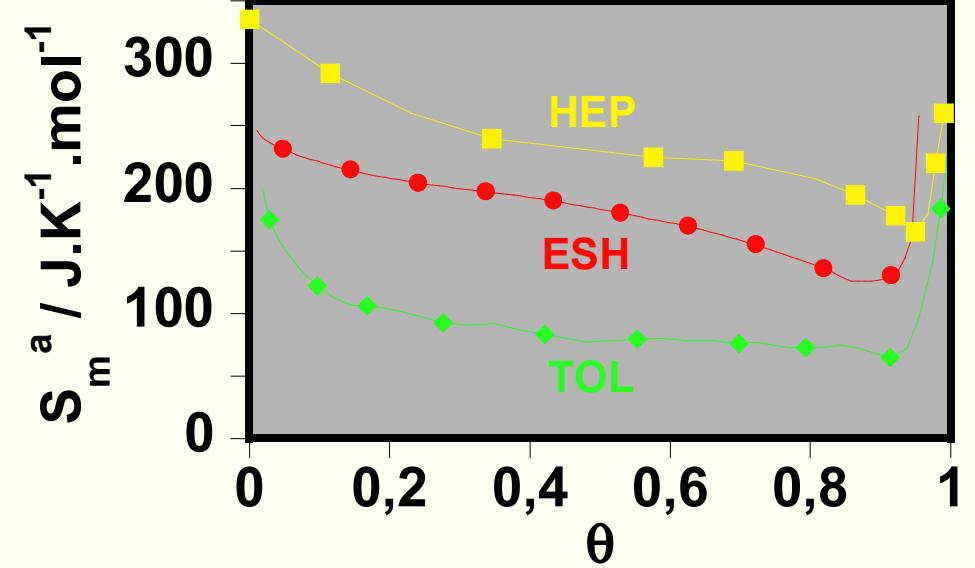
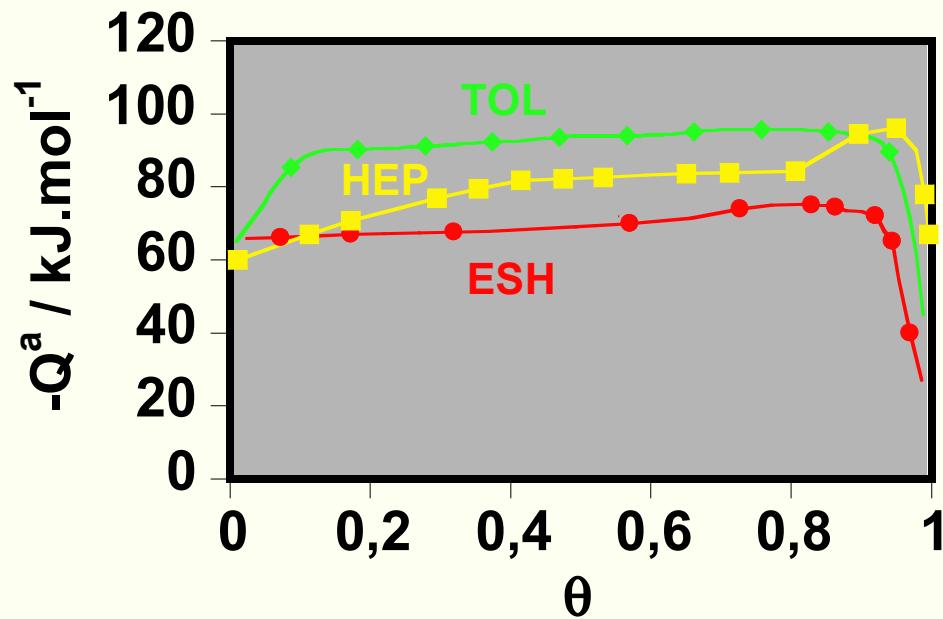
Adsorption
isotherm

Molar entropy of adsorbate: $S_m^a(n^a) = \Delta S_m^a(n^a) + S_m^{g^\circ}$

Ex: Adsorption of single components

Adsorption heat and molar entropy of the adsorbate

Adsorption of ethylmercaptan and hydrocarbons on NaX zeolite



II - Example of application

Characterization of a nanoporous silica material

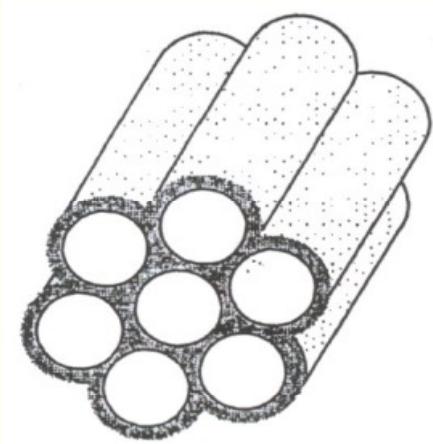
Characterization of Cu-MCM-41 by adsorption of NO and CO

(adsorption of single components)

Aim of this work:

Characterization of copper incorporated in mesoporous MCM-41 materials prepared by original direct synthesis procedure:

- oxydation state of copper ?
- location of copper ?
- dispersion of copper in the material ?



Silice MCM-41

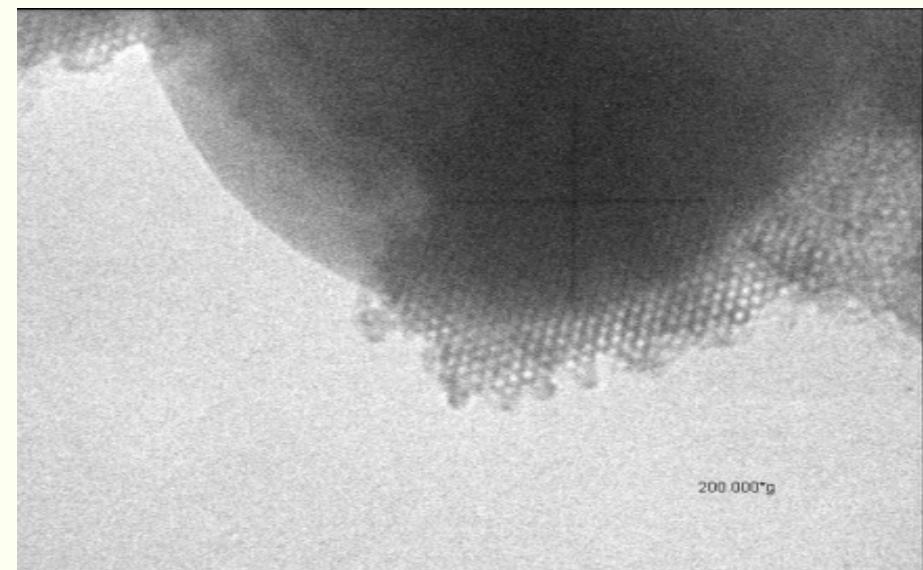
Pore diameter ~ 4 nm

Chemical composition:

Cu : 4.39 wt%

Si : 40.93 wt%

Cu/Si : 0.107



200 000*g

100 nm

ADSORPTION CALORIMETRY

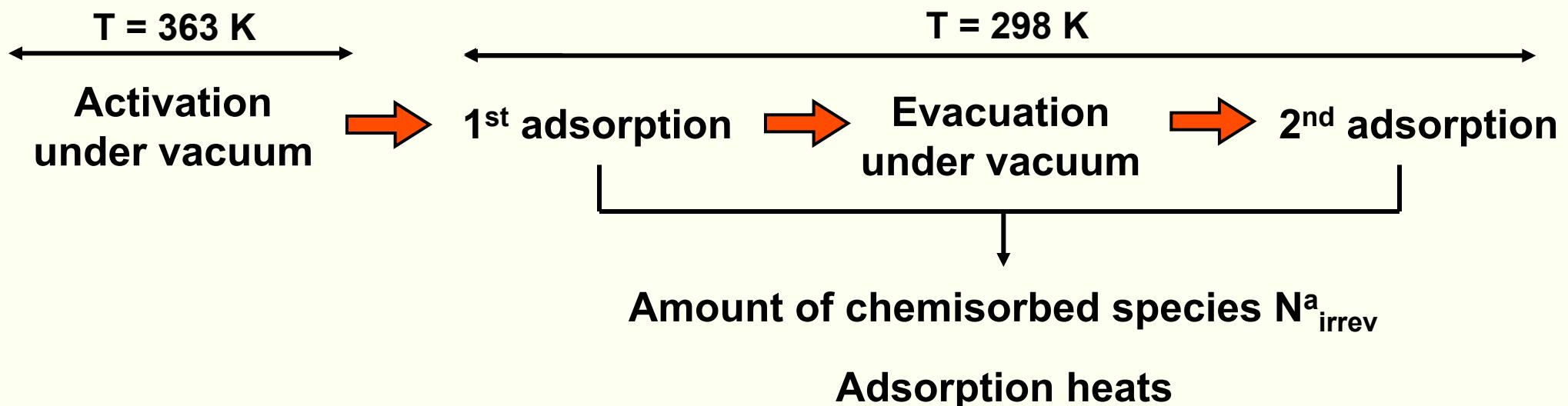
Experimental conditions:

$$m = 300 \text{ mg}$$

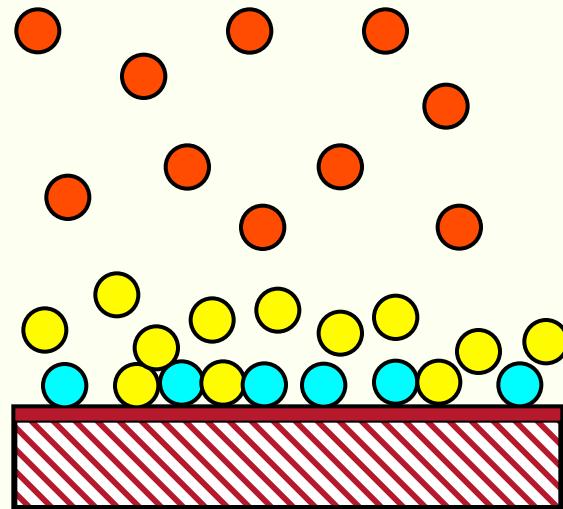
$$T = 298 \text{ K}$$

$$10^{-2} < p < 1000 \text{ hPa}$$

selective molecular probes :

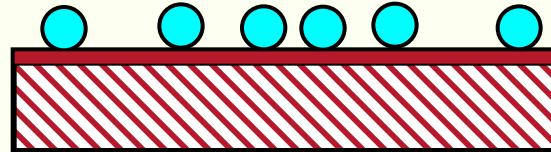


1st adsorption of physisorbed and chemisorbed species



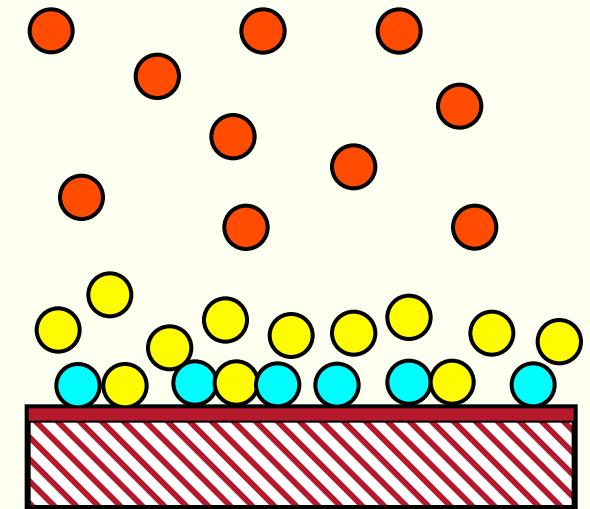
● Chemisorbed

Desorption under vacuum of physisorbed species only



● Physorbed

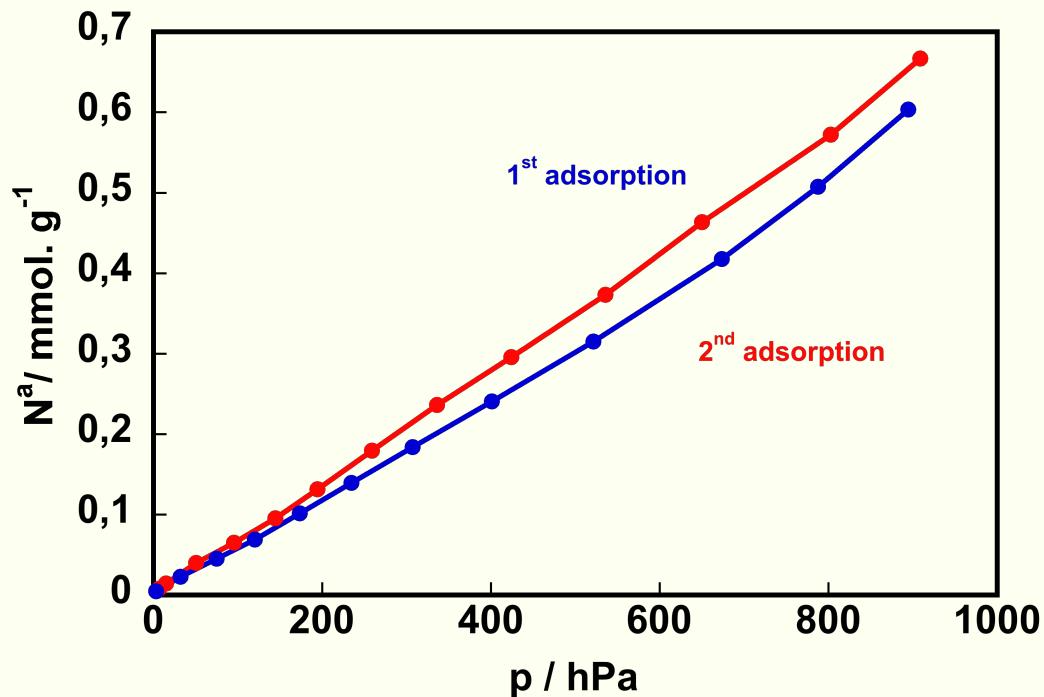
2nd adsorption of physisorbed species only



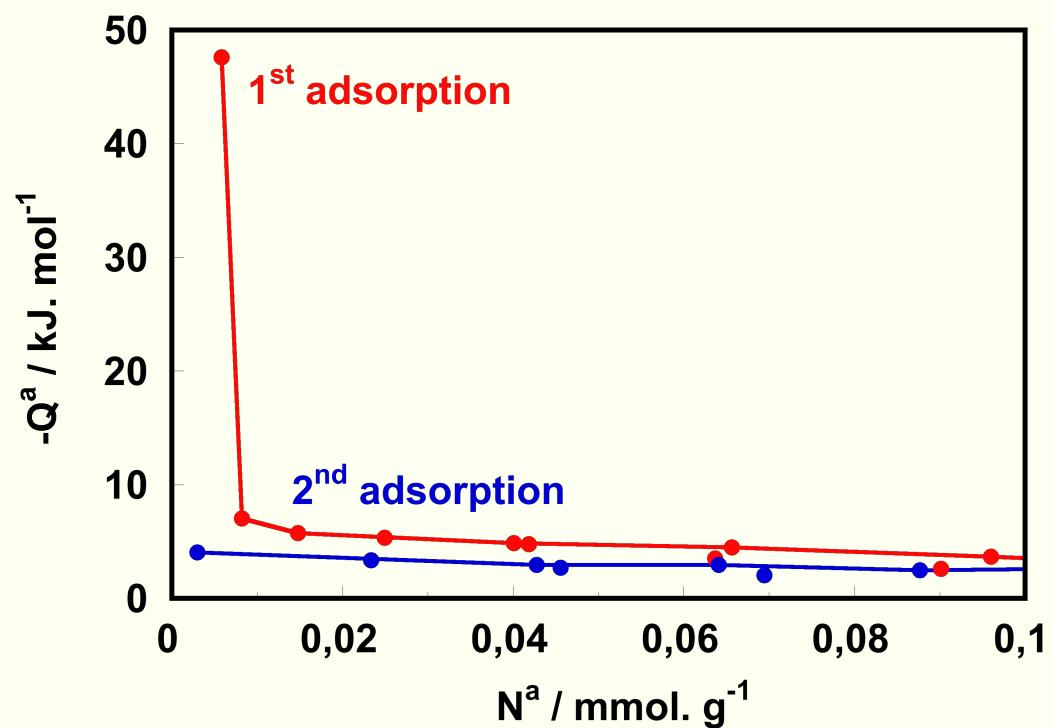
● Gas

ADSORPTION OF CO

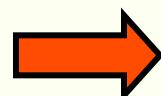
Adsorption isotherm



Adsorption heat



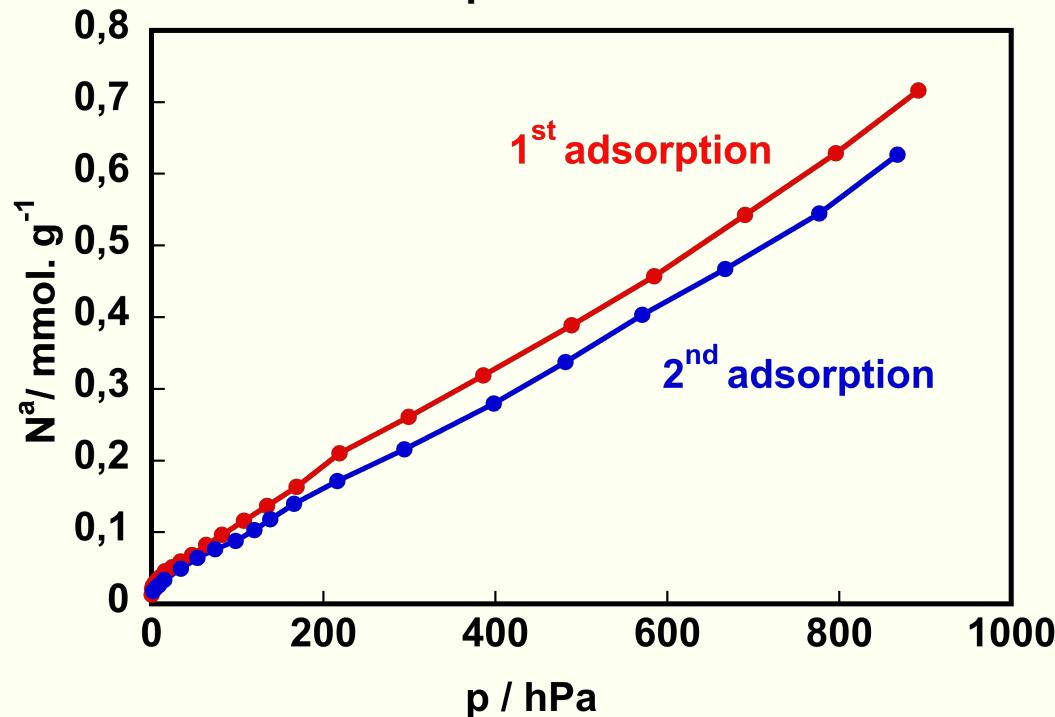
- irreversible adsorption-desorption
- high adsorption heat at zero filling
- no complete evacuation after pumping



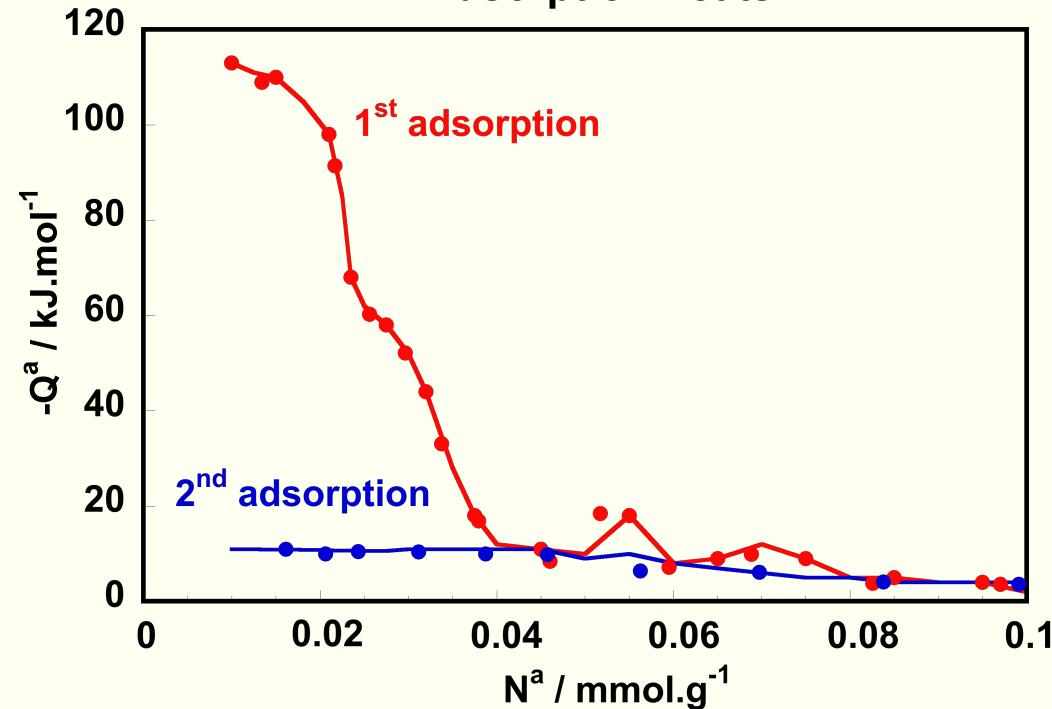
Chemisorption of CO
Presence of a small amount of Cu^+

ADSORPTION OF NO

Adsorption isotherms



Adsorption heats



- irreversible adsorption-desorption
- stronger adsorption affinity than for CO
- very high adsorption heats
- no complete evacuation



Chemisorption of NO
Heterogeneous adsorption
Presence of 2 types of Cu²⁺?

Quantitative estimation of Cu⁺ and Cu²⁺ amounts

→ Single molecular probe – copper ion interaction model

Amount of chemisorbed probe

$$N_{\text{irrev}}^a / \text{mmol.g}^{-1}$$

0.0007 CO

0.0110 NO

→

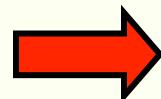
Copper ion content

$$n_{\text{Cu probed}} / n_{\text{Cu total}}$$

~ 0.1 wt% Cu⁺

~ 1.6 wt% Cu²⁺

(initial copper content : 4.39 wt%)

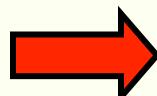


The major part of Cu is inaccessible !

Fraction of copper I and II

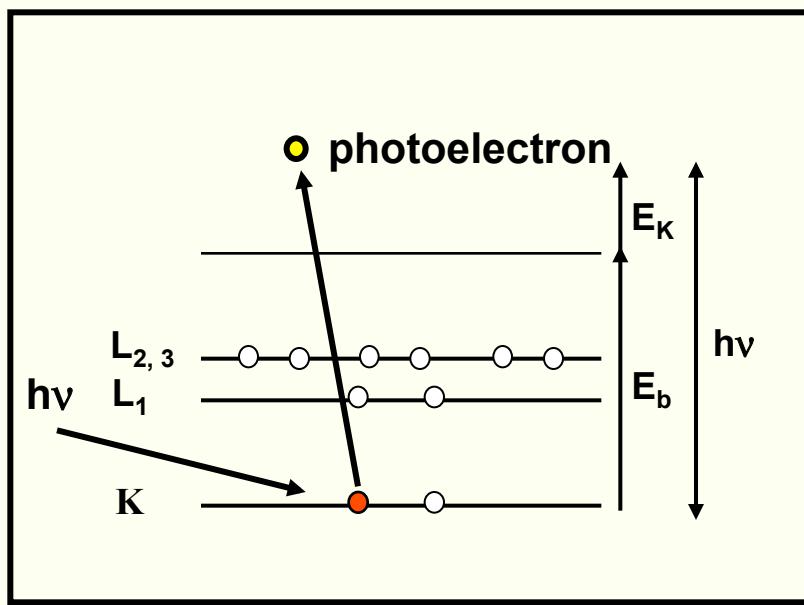
6 % of Cu⁺ and 94 % of Cu²⁺

$$\% \text{Cu}^{2+} = \frac{N_{\text{irrev}}^a(\text{NO})}{N_{\text{irrev}}^a(\text{NO}) + N_{\text{irrev}}^a(\text{CO})} \times 100$$

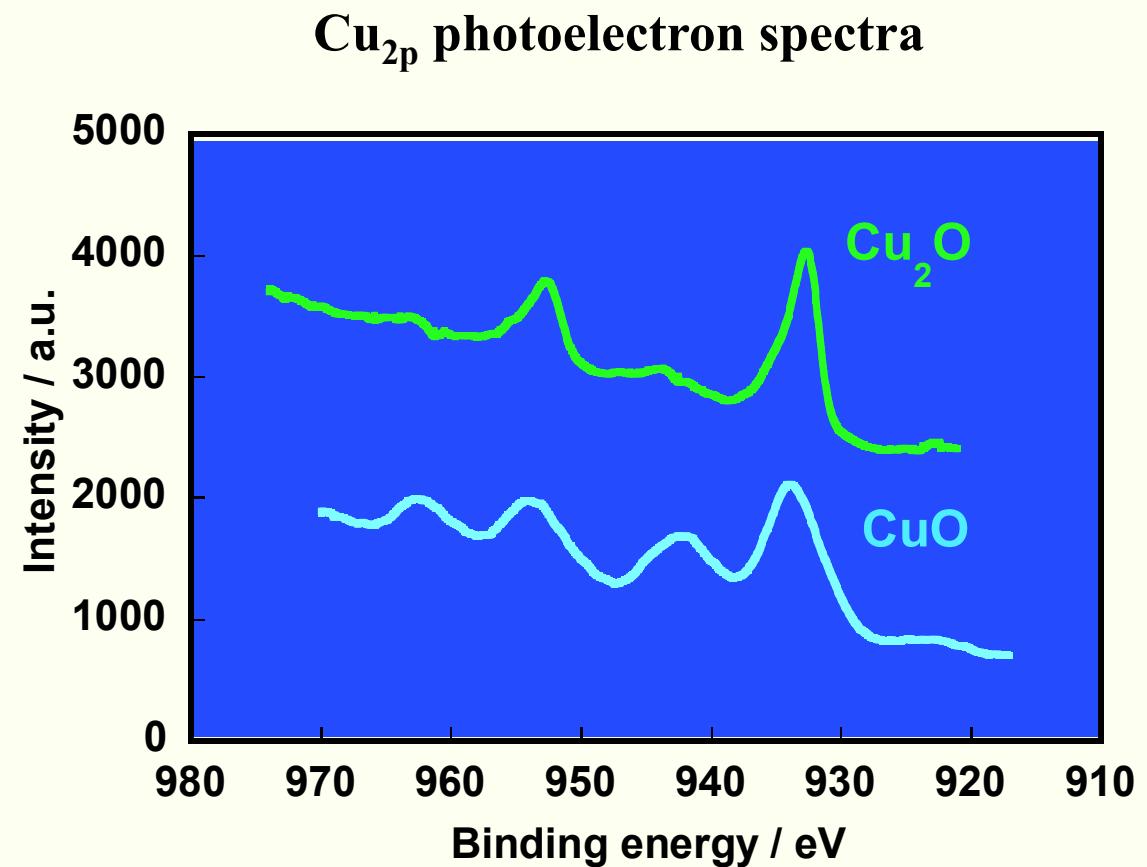


The major part of accessible copper
is at the oxydation state +II

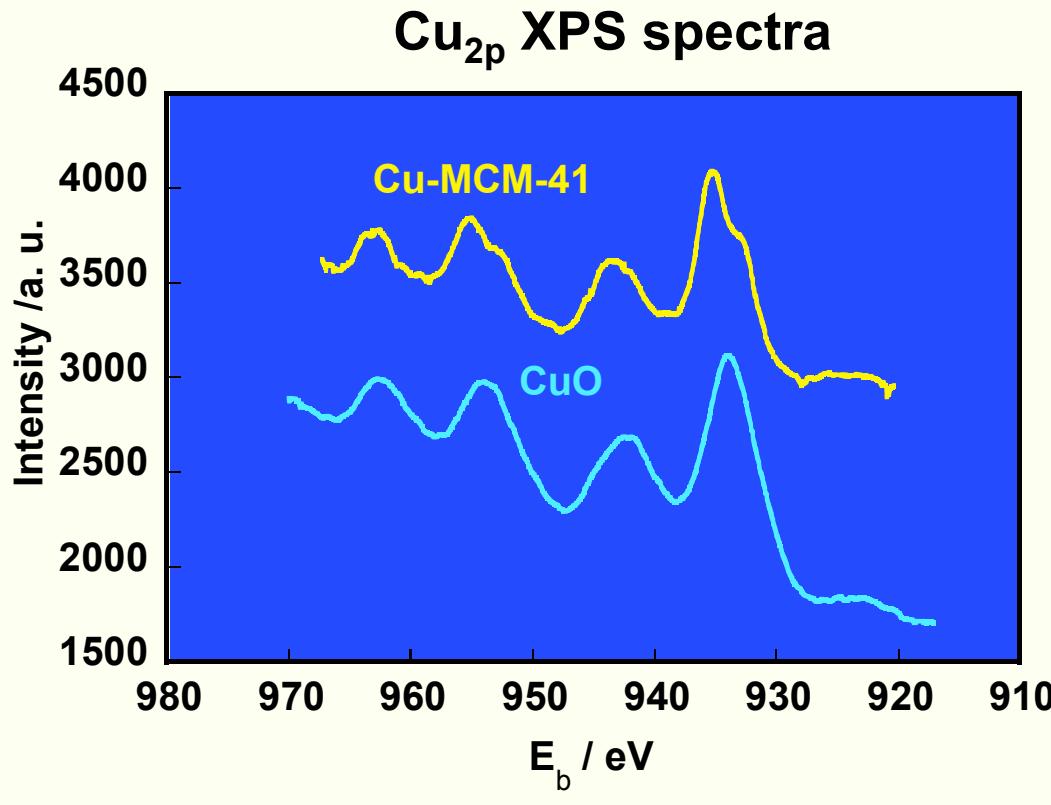
X PHOTOELECTRON SPECTROSCOPY ANALYSIS



Al-K_{a1,2} X-ray source, P = 300 W
T = 298 K



X PHOTOELECTRON SPECTROSCOPY

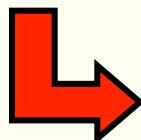


Integrated intensity of Cu_{2p} and Si_{2p}:

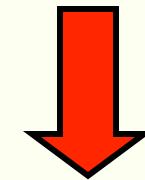
$$\text{Cu/Si} = 0.404$$

Chemical analysis:

$$\text{Cu/Si} = 0.107$$

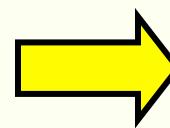
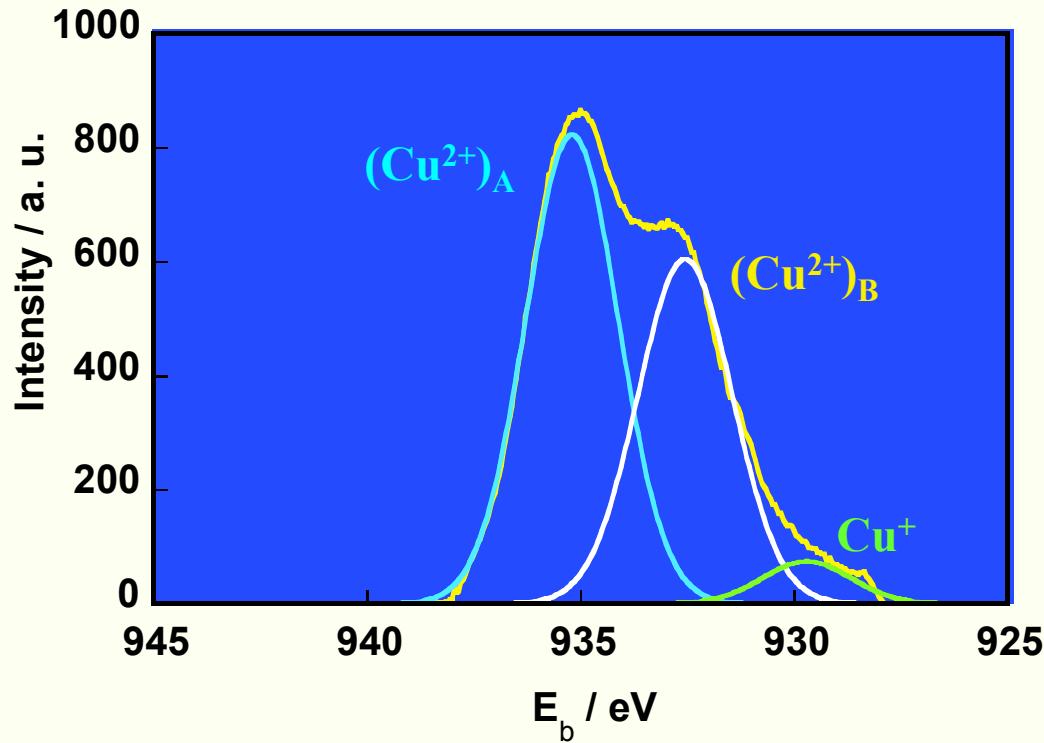


Presence of Cu²⁺



Cu²⁺ is located near
the external surface

Cu 2p_{3/2} peak deconvolution



- ✓ 2 types of Cu²⁺ ions
- ✓ 5% Cu⁺ and 95% Cu²⁺

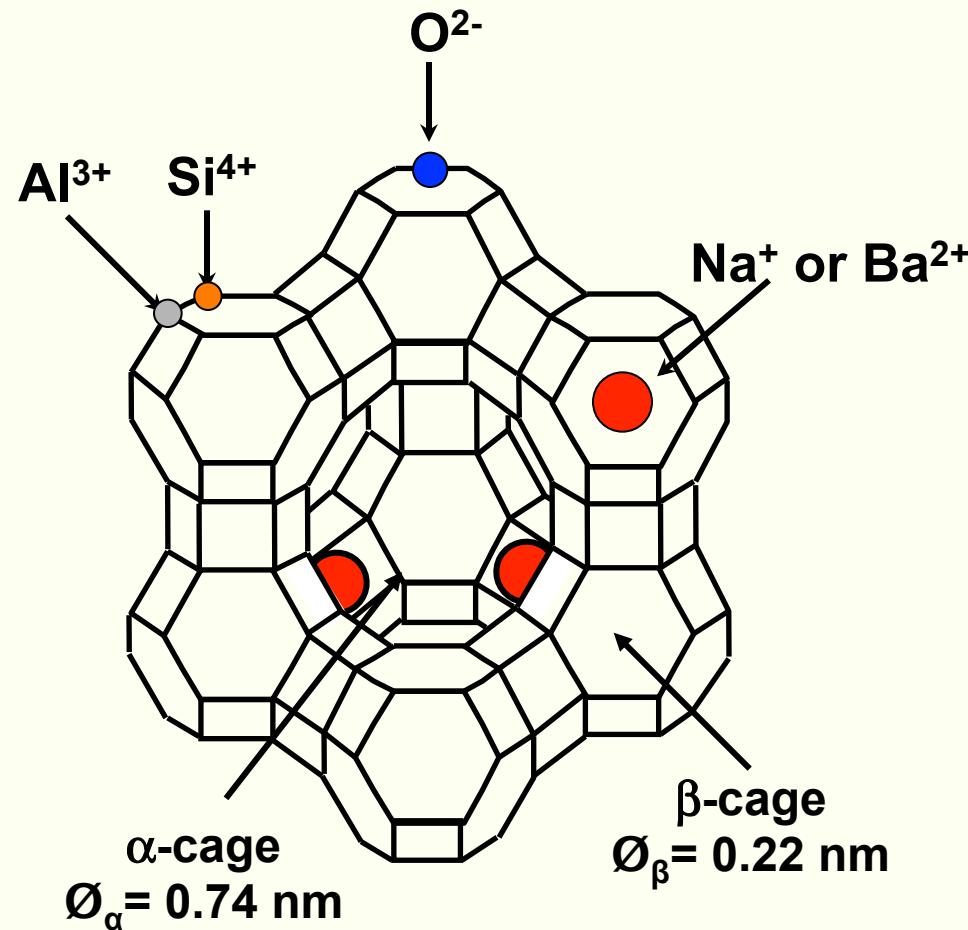
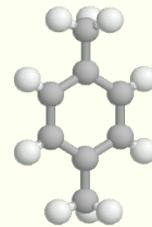
Excellent agreement between calorimetry and XPS analysis !

III - Example of application

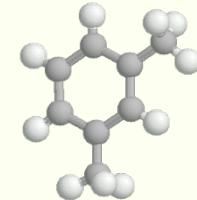
Adsorption of xylene isomers in FAU zeolites

Adsorbate / Adsorbent system

p-Xylene pX

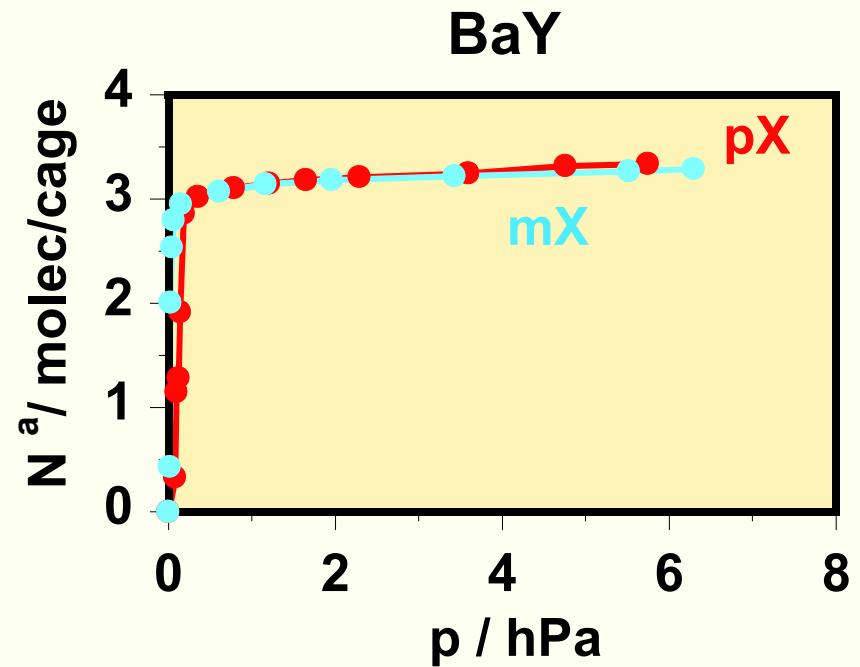
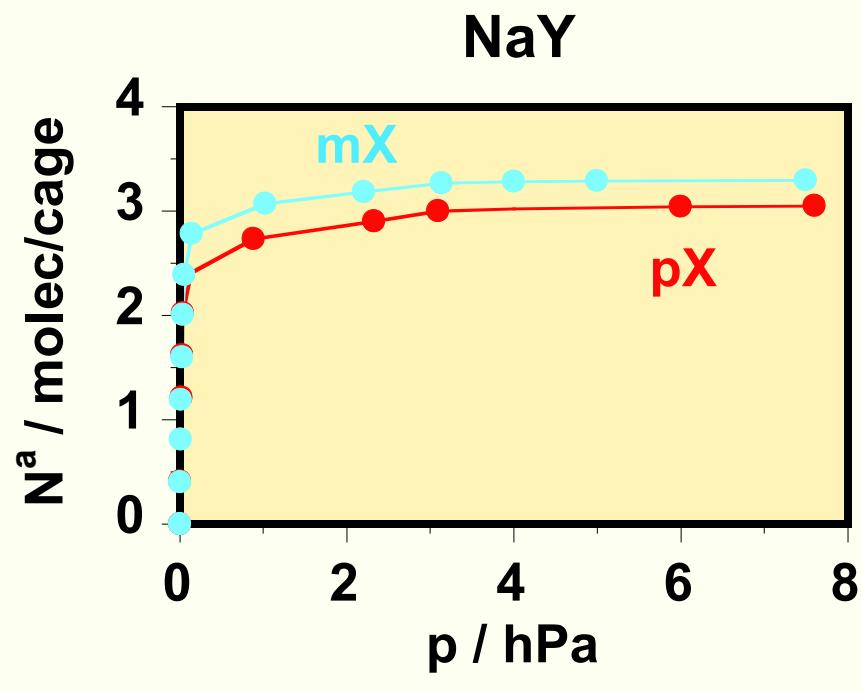


m-Xylene mX



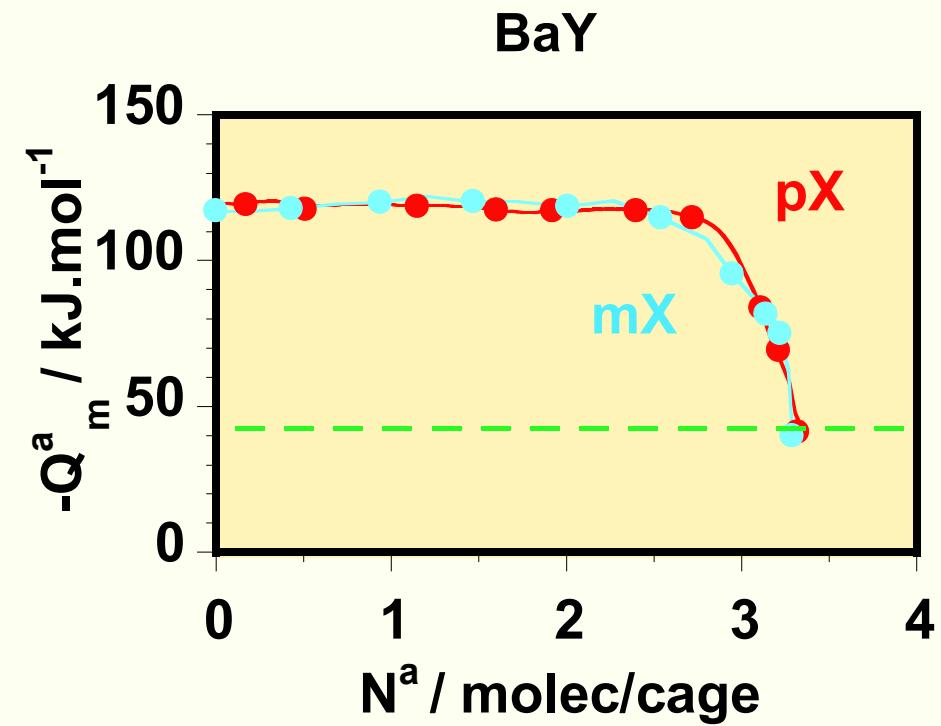
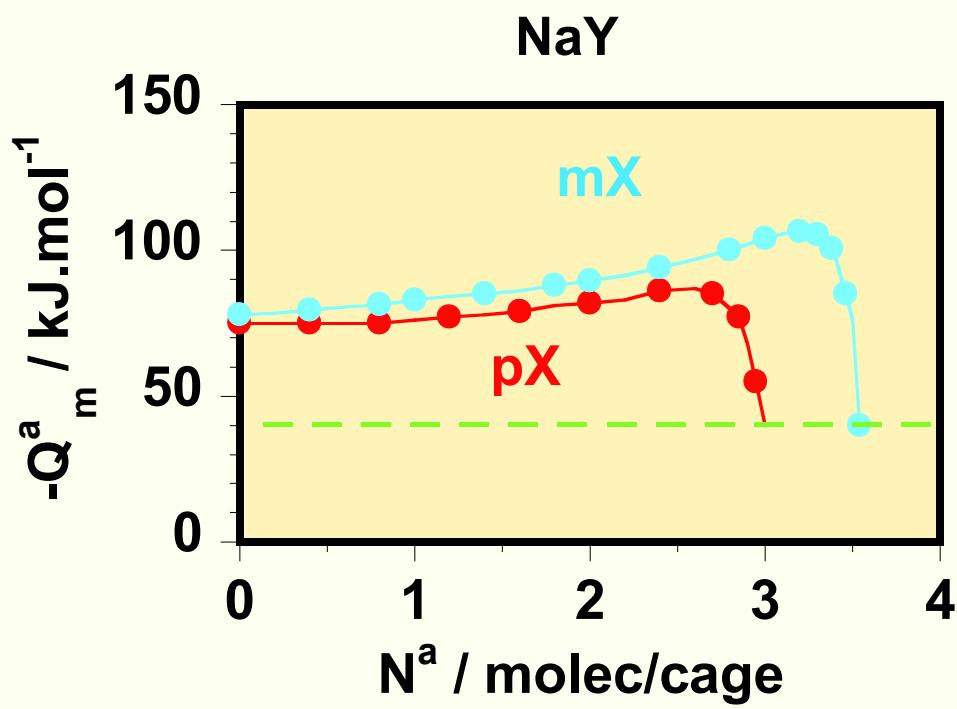
Zeolite FAU Y

Adsorption isotherms of single components determined by manometry at 150°C



Adsorption capacity ~ 3 to 3.5 molec/cage

Adsorption enthalpies of single components at 150°C



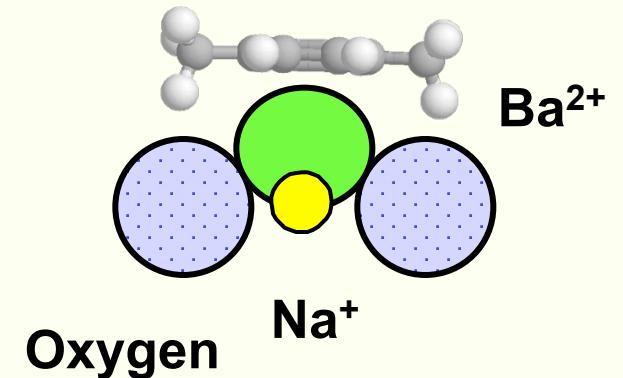
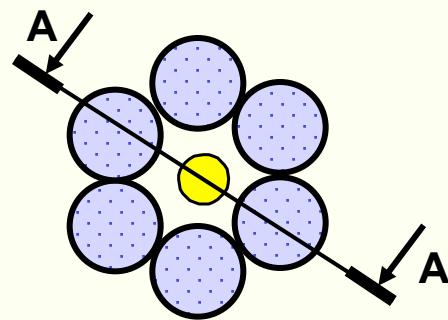
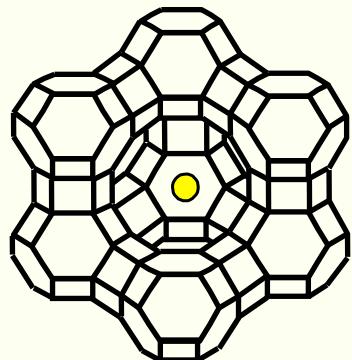
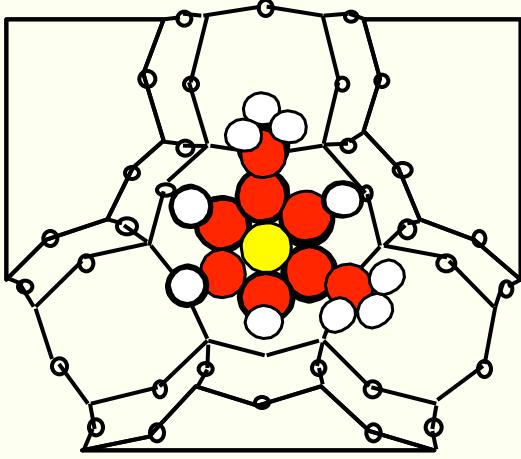
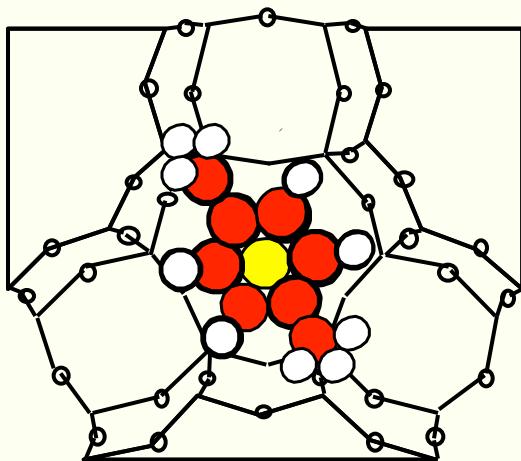
At zero filling:

$$Q_m^a(pX) \approx Q_m^a(mX) \rightarrow \text{similar adsorbate-adsorbent interactions}$$

$$Q_m^a(\text{BaY}) > Q_m^a(\text{NaY}) \rightarrow \text{stronger adsorbate - adsorbent interaction with Ba}^{2+} \text{ than with Na}^+$$

What do these results mean at a molecular level?

Schematic representation of xylene molecules in interaction with the compensation cation on site II in the supercage deduced from neutron diffraction studies



Ba²⁺ out of the plane of hexagonal window
Ba²⁺ more accessible to xylene molecule



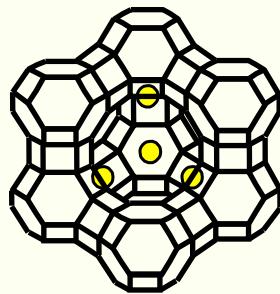
Stronger aromatic ring – cation interaction

**Similar adsorption sites for
pX and mX**

As filling is increasing:

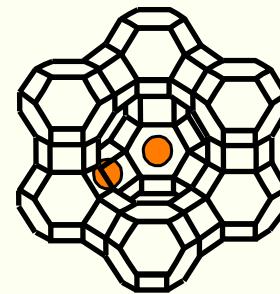
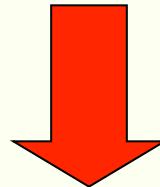
$Q_m^a(\text{NaY})$ increases up to the complete filling of supercages
(effect of adsorbate – adsorbate interactions)

$Q_m^a(\text{BaY})$ is constant up to 2 molec/cage and then decreases



NaY

4 cations per supercage
each molecule interacts with
one cation



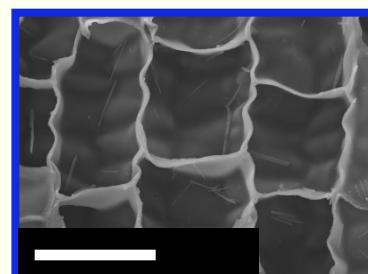
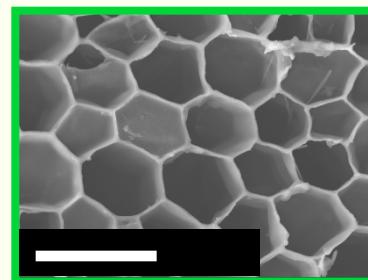
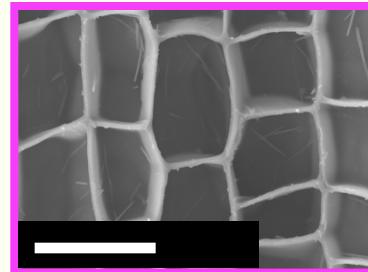
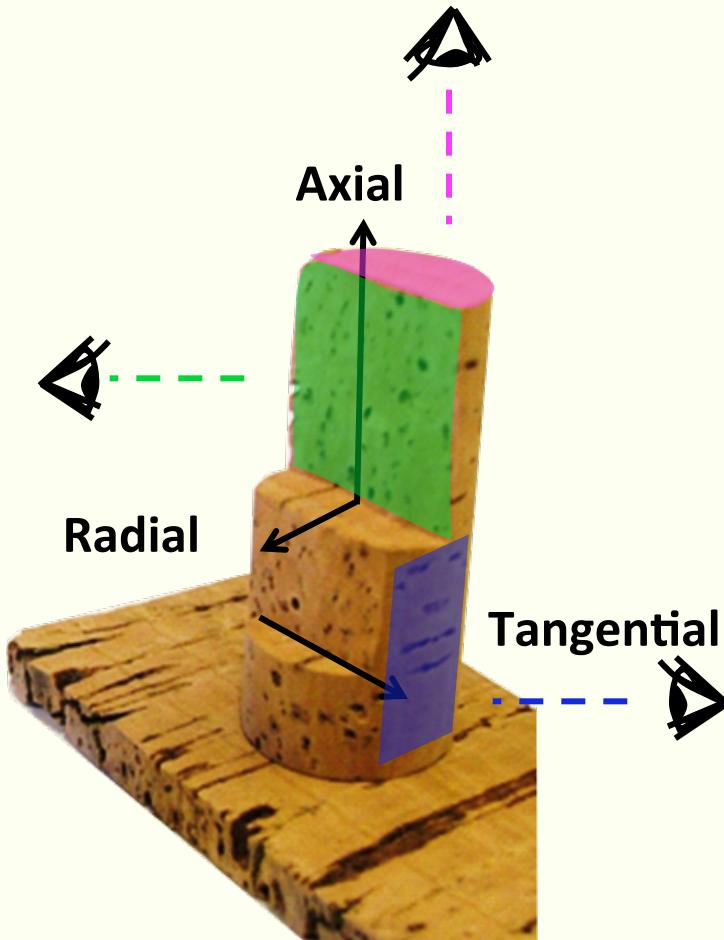
BaY

only 2 cations per supercage
each of the 2 first molecules interact
with one cation while not the third

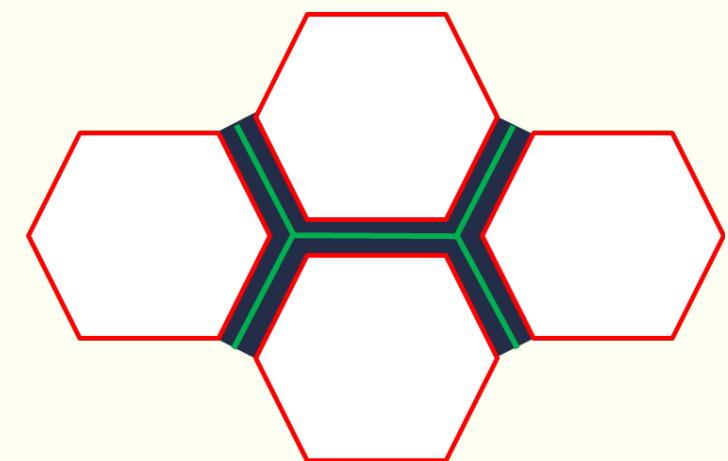
Example of application

**Effect of water on the mechanical
properties of cork**

What is cork?



Chemical Composition:
Suberin : 40 – 45 %
Lignin : 22 – 27 %
Cellulose +
hemicellulose :
9 – 12 %
Waxes : 6 %
Tannins : 6 %

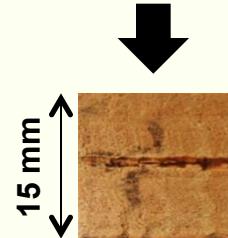


Lagorce-Tachon et al. 2015. J. Food Eng. 149, 214–22111

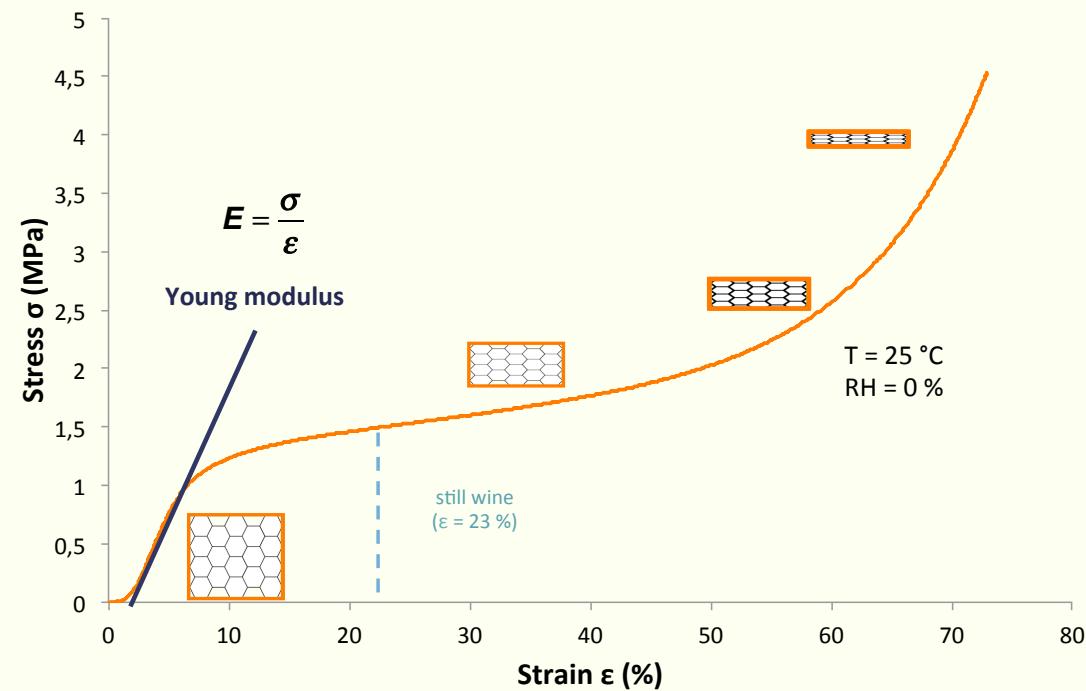
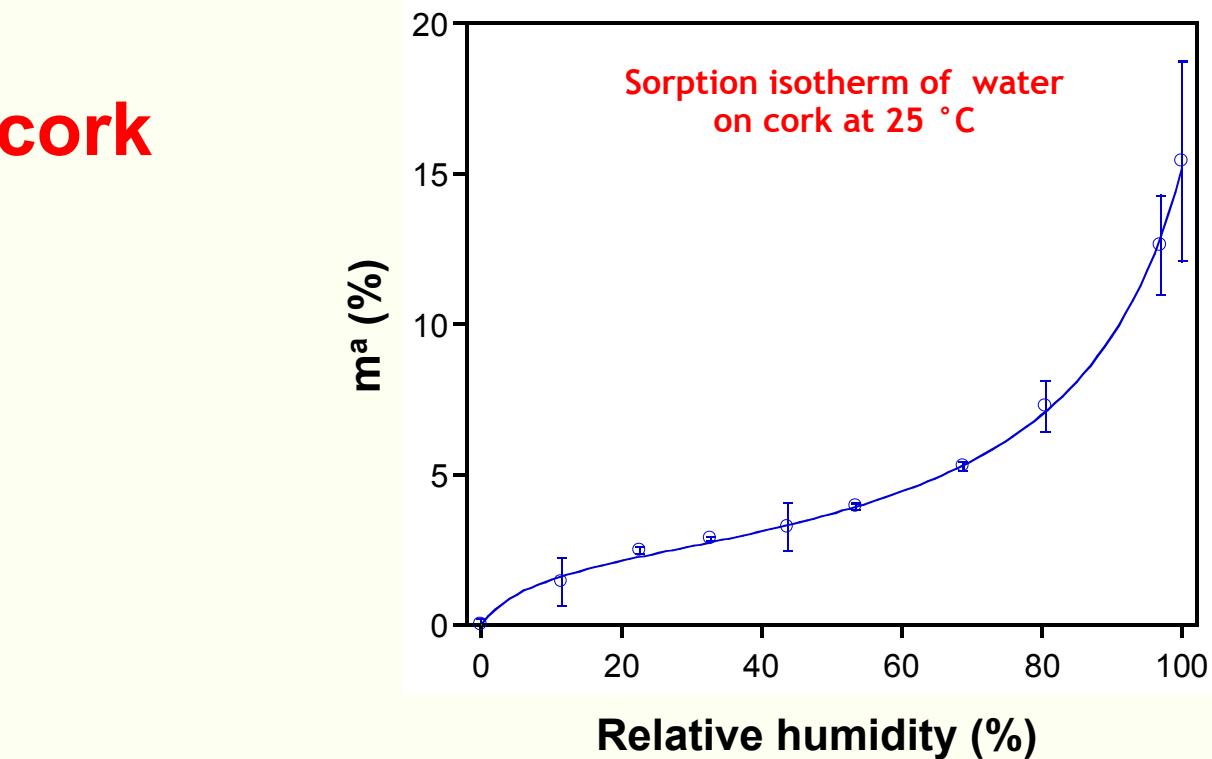
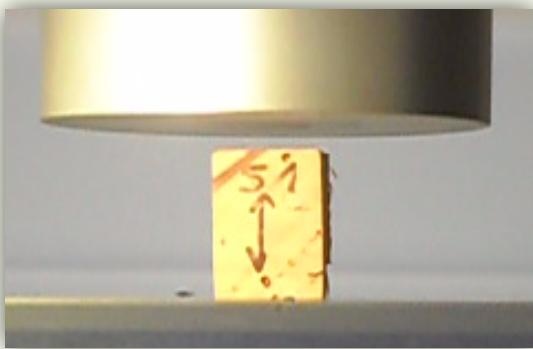
Mechanical properties of cork

Mechanical test of uniaxial compression

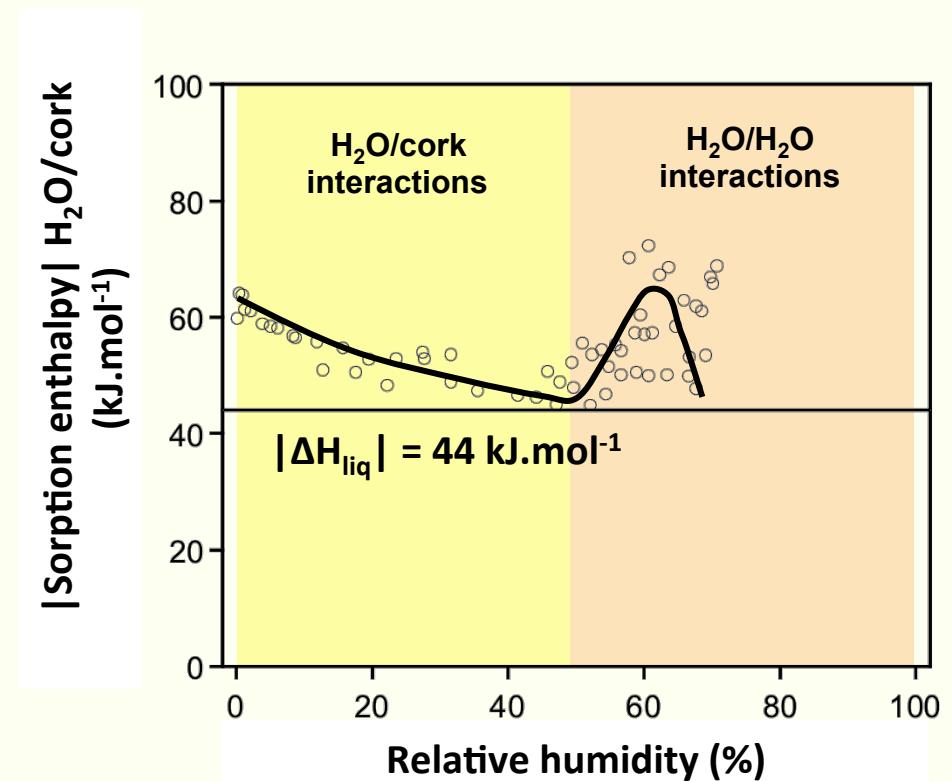
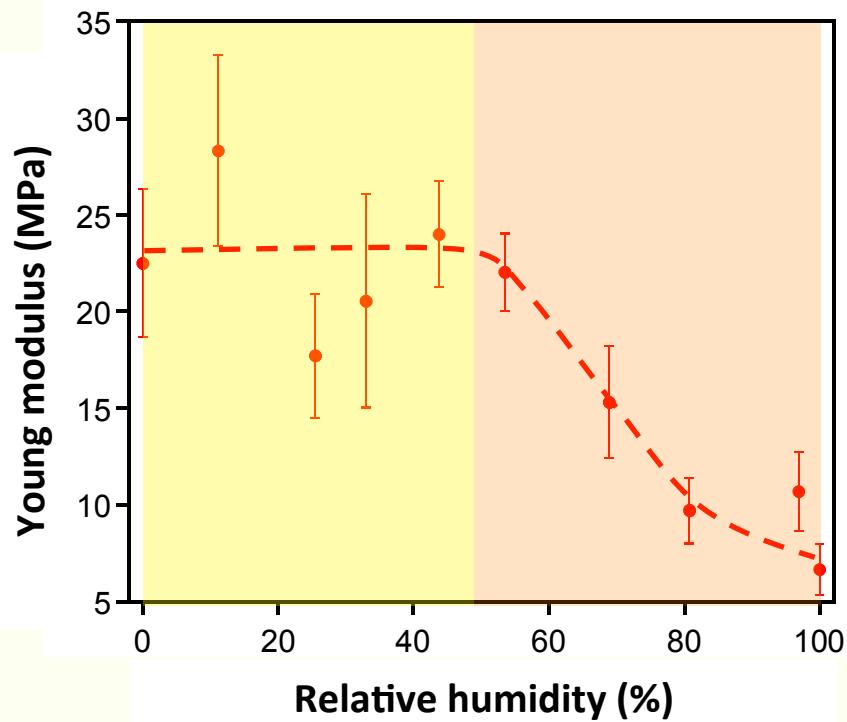
Strain: 80 %



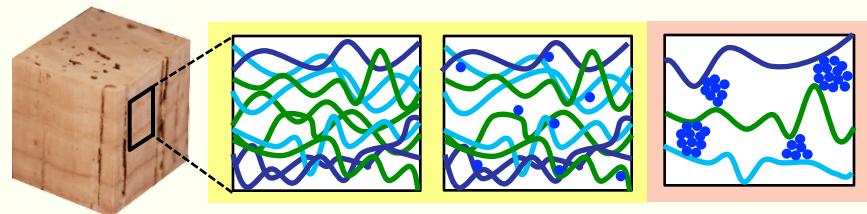
Tangential or radial



Dependence of Young modulus on relative humidity



Formation of water clusters between polymeric chains



Lagorce-Tachon et al. 2015. Mater. Design 82, 148–154
Lequin et al. 2010. 2010. J. Agric. Food Chem. 58, 3438–3445

CONCLUSION

Differential calorimetry coupled with Manometry, GPC and MS:

- is a powerfull tool for studying gas / solid reaction (in particular adsorption)
- is essential to perform a complete thermodynamic study
 - (for single components as well as for mixtures)
 - is a complementary technique useful to obtain information on the reaction mechanism at a molecular level...

But:

- is rather delicate to use (be careful in manipulations!)
- rarely commercialized
- requires a lot of time (be patient!)

REFERENCES

- K.S.W. Sing et al., Pure & Appl. Chem. 57 (4) (1985) 603 – 619.
- On Physical Adsorption, S. Ross and J. P. Olivier, Interscience Publishers (1964).
- Adsorption Analysis: Equilibria and Kinetics, D. D. Do, Imperial College Press (1998).
- Adsorption by powders and Porous Solids, F. Rouquerol, J. Rouquerol and K. Sing, Academic Press (1999).
- Zeolites and Clay Minerals as Sorbents and Molecular Sieves, R. M. Barrer, Academic Press (1978).
- C. Letoquard, F. Rouquerol and J. Rouquerol, J. Chim. Phys. 3 (1973) 559.
- M. Broyer, J.P. Bellat, O. Heintz, C. Paulin, S. Valange and Z. Gabelica, Studies in Surface Science and Catalysis 142b (2002) 1101.
- J.P. Bellat and M.H. Simonot-Grange, Zeolites 15 (1995) 219.
- C. Mellot, M.H. Simonot-Grange, E. Pilverdier, J.P. Bellat and D. Espinat, Langmuir 11 (5) (1995) 1726.
- M.H. Simonot-Grange, O. Bertrand, E. Pilverdier, J.P. Bellat and C. Paulin, J. Thermal Analysis 48 (1997) 741.
- V. Cottier, J.P. Bellat, M.H. Simonot-Grange and A. Méthivier, J. Phys. Chem. B 101 (24) (1997) 4798.
- J.C. Moïse and J.P. Bellat, J. Phys. Chem. B 109 (2005) 17329.
- F. Benoit, G. Weber, J.P. Bellat, C. Paulin, S. Limborg-Noetinger, M. Thomas and P. Mougin, Studies in Surface Science and Catalysis 158 (2005) 1185.
- G. Weber, J.P. Bellat, F. Benoit, C. Paulin, S. Limborg-Noetinger, M. Thomas, Adsorption 11 (2005) 183.
- G. Weber, F. Benoit, J.P. Bellat, C. Paulin, P. Mougin and M. Thomas, Micropor. Mesopor. Mater. 109 (2007) 184.
- M. Thommes et al. Pure Appl. Chem. 87(9-10) (2015) 1051-1069.
- Lagorce-Tachon et al. 2015. J. Food Eng. 149, 214–22111
- Lagorce-Tachon et al. 2015. Mater. Design 82, 148–154
- Lequin et al. 2010. 2010. J. Agric. Food Chem. 58, 3438–3445

Thank You for your attention

Questions?