Adsorption and complementary in situ methods for the characterisation of microporous materials

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CO + ½ O₂ → CO₂ on a Rh catalyst
Animation showing how a gas-phase CO molecule adsorbs, interacts with an O neighbour, and finally desorbs as a CO₂ molecule (C in green, O in red, the catalyst in grey)
What is adsorption
- a short history
- where do we find adsorption

Methodology
- Different adsorption apparatus

What can we characterise using adsorption
- different types of isotherm
- surface area
  - Henry, Langmuir, BET
- Pore volume and external surface area
  - t-plot, as plot
- Micropore size
  - HK
  - ideas behind DFT

Trouble shooting
So what is adsorption?
Adsorption by solids

It is the **increase in concentration** of a gas or dissolved species **in the neighbourhood of a solid**

A **general** phenomenon

To be useful, **needs an extensive surface area**

Active carbon: **100 to 2600 m²** of porous surface per gram of carbon....
The ‘discovery’ of adsorption

- The **ancient Egyptians** already used adsorbents in the form of clay, sand or wood charcoal to desalinate water, clarify fat and oil, or treat diseases; the Greeks and Romans continued; the « sorcerer ‘s black stone» known and used for centuries to suck venom from snake bites is a good adsorbent (around 100 m²/g)

- Around 1775: **first quantitative measurements** of gas adsorption by charcoals (Scheele, Priestley, Fontana)

- 1885: investigation of **decolorizing properties** of charcoal (Lowitz)
The ‘discovery’ of adsorption (cont.)

- 1822: first description of **heat of immersion** (Pouillet)
- 1854: first measurement of **heat of adsorption** (Favre)
- 1881: introduction of word « **adsorption** » (Kayser) and first « **adsorption isotherms** » (Chappuis and Kayser)
- 1909: « **sorption** » combines ad- and absorption (McBain)
- 1916: theory of the **monolayer adsorption** (Langmuir)
- 1938: the **BET** equation (Brunauer, Emmett and Teller)
So what about adsorption in everyday life?
Activated carbons for water treatment
Pressure Swing Adsorption

Gas Mixture A + B → Adsorbent bed → Pure Gas B

http://www.norit.com/?RubriekID=2138
Smaller units for hospital oxygen
‘Hot topics … current and ‘future’ …’

- CO$_2$ recovery
- Hydrogen purification
- Hydrogen storage
- Alkane/alkene separations
- Biodiesel
  - Purification
  - Water from ethanol
- Adsorption of mercaptans

Liquid hydrogen filling station at Munich Airport
However, we can use of adsorption to characterise a solid

☑️ What can we characterise

- surface area
- internal surface area (in the porosity)
- external surface area
- porosity
- pore volume
- pore size
- pore connectivity
So schematically how can we imagine the phenomenon of adsorption?

- Fluid (gas, liquid) or “Adsorptive”
- Adsorbed phase or “Adsorbate”
- Solid or “Adsorbent”
So why do molecules adsorb on a surface?

The resultant of the forces on the surface atoms $A_s$ is not zero.

The internal energy of the surface atoms $A_s$ - with a certain interfacial tension - is greater than the atoms in the bulk $A_B$.
The smaller the particles, the more surface atoms … and the more reactive the surface

Variation of the proportion of surface molecules as a function of the particle size (solid with molar volume $V_m = 30 \text{ cm}^3 \text{ mol}^{-1}$)

Percentage of surface atoms (=%)
Consequences of the presence of a non-negligible quantity of atoms at the surface:
- The atoms can attract other species to the surface: adsorption.
- The atoms can release energy: immersion.

Quantification of the surface atoms by the measurement of the ‘extent of surface’: specific surface area (related to 1 gram of product).
Types of “Texture” found in a Porous Material

a : Surface roughness
b : Bottle-neck shaped pore
c : Opening
d : Interconnection
e : Pores opened at one end
f : Closed porosity
Experimental methods / Pore Width

Micropore filling
Capillary condensation

Adsorption microcalorimetry

Thermoporometry

Mercury porosimetry

Immersion microcalorimetry

micropores mesopores macropores ....

ultra | super

micro capillaries / capillaries / macro capillaries

nanopores

* IUPAC
Definition and Representation of Adsorption Phenomena

The phenomena of adsorption
Gibbs representation of adsorption
Surface excess concentration
So schematically how can we think of adsorption?

Fluid (gas, liquid) or “Adsorptive”

Adsorbed phase or “Adsorbate”

Solid or “Adsorbent”
Adsorption

☑ The phenomenon of adsorption
When a fluid is in the region of solid surface, its concentration increases close the interface.

☑ Definition

☞ The enrichment of one or more components in the region between two bulk phases (gas/solid, liquid/solid)

The word "adsorption" is also used to describe the phase change of a fluid which adsorbs.
Adsorption Definitions

☑ Adsorption

▷ The enrichment of one or more components in the region between two bulk phases (gas/solid, liquid/solid)

☑ Gas/Solid Adsorption :

▷ The accumulation is due to the *solid attractive forces* on the gas molecules
▷ The solid material on which adsorption occurs is called the *adsorbent*
▷ The gas is called adsorptive and when it’s in the adsorbed state, the *adsorbate*
▷ Physisorption or chemisorption

☑ Adsorption Liquid/Solid : it always involves a competition between the solvent and solute
Physisorption or Chemisorption

Adsorption is brought about by the interactions between the solid and the molecules in the fluid phase

ียว Two kinds of forces are involved, which give rise to either physical adsorption or chemisorption

☑️ **Physisorption**

→ General phenomenon

→ A physisorbed molecule keeps its identity and on desorption returns to the fluid phase in its original form

→ Gas adsorption is exothermic and the amount adsorbed decreases with the temperature at a given pressure

→ Multi-layer adsorption

☑️ **Chemisorption**

→ Specific: depends on the reactivity on the adsorbent and adsorptive

→ A chemisorbed molecule undergoes reaction or dissociation, loses its identity and cannot be recovered by desorption

→ Adsorption can be exothermic, endothermic or athermic

→ Chemisorption occurs only as a monolayer
So schematically how can we think of adsorption?

- Fluid (gas, liquid) or “Adsorptive”
- Adsorbed phase or “Adsorbate”
- Solid or “Adsorbent”
Schematically, What is adsorption?

Concentration of the adsorbed phase

Concentration of the gas phase

[c]

Z
Surface excess concentration: $\Gamma$

$$\Gamma = \frac{n \sigma}{A}$$

$n \sigma$ is the surface excess quantity
$A$ is the extent of surface
$a$ is the specific surface area ($= A / m^s$)

$$\frac{n \sigma}{m^s} = \Gamma \cdot a$$
Adsorption equilibrium

One equilibrium adsorption state, at one temperature $T$, is characterised by one value of the surface excess concentration $\Gamma$ which depends on the gas pressure $p$:

$$\Gamma.a = \frac{n^\sigma}{m^s} = f(p).g(T)$$
Adsorption isobar: \( p = \text{cte} \)

\[ \Gamma \cdot a = \frac{n^\sigma}{m^s} = f(T) \]
Argon isotherm at 77.4 K

\[ \Gamma. a = \frac{n^\sigma}{m^s} = f(p) \]
Definition of the Adsorption Isotherm

An adsorption isotherm is the set of equilibrium states, for one temperature \( T \) given, for values of pressure between 0 and \( p^\circ \) (the saturation vapour pressure of the adsorptive at \( T \)).

\[
p/p^\circ \text{ is known as the "equilibrium relative pressure".}
\]
Physisorption Isotherms

Adsorption is an exothermic phenomena

Isosteric Enthalpies

\[ \Delta_{ads} h = -R \frac{T_1 T_2}{T_2 - T_1} \ln \left( \frac{p_2}{p_1} \right) n^\sigma / m^s \]
Argon isotherm at 77.4 K:
Indicative points

\[ \Gamma.a = \frac{n^\sigma}{m^s} = f(p) \]
Measurement of Adsorption Isotherms

Adsorption manometry
Adsorption gravimetry
Procedure of an adsorption experiment
Commercial Apparatus (Manometry)
Adsorption Volumetry : “Brunauer” apparatus

Adsorption Manometry: Simplified Schema

- Pressure gauge
- Constriction
- Adsorptive
- Manifold
- Vacuum
- Stopcock
- Adsorption Cell
- Adsorbent
Adsorption Gravimetry: McBain Balance

Diagram:

- Adsorptive
- Vacuum
- Bucket

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FEZA School
2nd Sept. 2008
Adsorption Gravimetry:
magnetic compensation symmetrical balance

Diagram:
- Pressure gauge
- Adsorptive
- Vacuum
- Flag
- Sample
- Reference
Magnetic Suspension Balance

3 different positions
- Position 0: tare and calibration
- Position 1: measurement of the mass adsorbed
- Position 2: measurement of the gas density
Procedure of an adsorption experiment

- Outgassing
  - under vacuum
  - temperature

Obtain a well-defined state of the sample prior to adsorption

Elimination of species adsorbed during storage (e.g. H$_2$O) without degradation
Procedure of an adsorption experiment

- Outgassing
  - under vacuum
  - temperature

- Determination of the dead space volume \( (v_{g,0}) \)
  - gas that one considers non-adsorbed (He)
Procedure of an adsorption experiment

- **Outgassing**
  - under vacuum
  - temperature

- **Determination of the dead space volume** ($v^g,0$)
  - gas that one considers non-adsorbed (He)

- **Adsorption**
  - continuous method
    - $D_n^s = D_n^e - D_n^r$
  - point by point method
    - $n^i$ in $v_{ref} + v^g,0$
    - $n^f$ in $v_{ref} + v^g,0$
    - $n^s = n^i - n^f$
Calculation of the amount adsorbed

☑ Amount of adsorptive gas introduced into the system
   \[ n_i = \frac{P_{\text{ref}} \cdot V_{\text{ref}}}{R \cdot T_{\text{ref}}} \]

☑ Amount adsorbed: \( n^\sigma = n_i - n_f \)
   where \( n_f \) is the amount left in the gas phase

☑ \( n_f \) is determined using a gas that is not adsorbed (e.g. He) or via a prior blank experiment on an empty cell
   - Determination of a reference curve \( n_f = f(P) \)

☑ At equilibrium: \( n^\sigma = n_i - f(P_{\text{equilibrium}}) \)
Where can the measurement go wrong
Low pressure

Problem of equilibrium

\[ \frac{n^\circ}{m^s} \] vs \[ \log{\frac{p}{p^\circ}} \]
Hysteresis: the desorption branch does not rejoin the adsorption branch (1)

Problems?

• Simple experimental error

• Increase in temperature (due to excess loss in liquid nitrogen from the cryostat)
Hysteresis: the desorption branch does not rejoin the adsorption branch (2)

Problems?

- Simple experimental error
- Leaks
- Equilibrium
- Adsorbate retained
  - ultramicropores
  - organic chains
Interpretation and Classification of Adsorption Isotherms
Interpretation of Adsorption Isotherms

Mechanisms of adsorption
- localised adsorption
- micropore filling
- monomolecular adsorption
- multimolecular adsorption
- capillary condensation

Classification of physisorption isotherms: BDDT, IUPAC, Sing
IUPAC Classification of physisorption isotherms

\[ \frac{n^\sigma}{m^s} \]

\[ \frac{p}{p^0} \]

\[ T < T_c \]
Type II Isotherm: Adsorption on a purely non-porous sample

Formation of a statistical monolayer

Multimolecular adsorption
Type IV Isotherm: Adsorption on a purely mesoporous sample: \( d \approx 2 \text{ à } 50 \text{ nm} \)

Formation of a statistical monolayer
Multimolecular adsorption
Capillary condensation
Hysteresis

\[ \frac{d(\text{pore})}{d(\text{gas})} = 5 \text{ à } 125 \]
Type III and V isotherms

- **Type III**:  
  - weak adsorbent-adsorbate interactions
  - indicative of weak adsorbent-adsorbate interactions
  - hysteresis loop associated with the mechanism of pore filling and emptying

- **Type V**:  
  - indicative of weak adsorbent-adsorbate interactions
  - hysteresis loop associated with the mechanism of pore filling and emptying
Type VI Isotherm

- Type VI: stepped isotherm
  - relatively rare
  - associated with layer-by-layer adsorption on a highly uniform surface
Adsorption on a purely microporous sample: $d \approx 0.4 \text{ à } 2 \text{ nm}$

$d(pore) / d(gas) = 1 \text{ à } 5$

Micropore filling
ultramicropores
supermicropores
\(\triangleright\) co-operative mechanism
Exploitation of the adsorption isotherm

- Capillary Condensation
- Formation of a monolayer
- Multimolecular Adsorption
- Localised Adsorption
- Micropore filling

\[ n^s/m^s \]
Confrontation results vs. Calculations

☑️ It is quite possible to get good experimental data
   - outgassing
   - equilibrium
   - enough adsorption points

☑️ It is more difficult to be really sure of the results from the calculations
   - are the assumptions valid
   - are they general to all pore sizes
   - what about the chemical nature of the solid surface?
Exploitation of the adsorption isotherm

- Capillary Condensation
  - Kelvin equation (BJH)
  - Broekhoff de Boer
  - DFT

- Monolayer formation
  - BET
  - Multimolecular Adsorption
    - t-plot
    - \( \alpha_S \) method

- Localised Adsorption
  - Adsorption Energies
  - Micropore filling
    - HK
    - DFT
    - Dubinin, MP .... Monte Carlo

\( n^\sigma/m^s \) vs. \( p/p^\circ \)
Characterisation of solids by adsorption → Surface area

Methods available:
- Langmuir (Single layer coverage)
- BET (Multilayer coverage)
- ‘t’-plot
The Langmuir theory
Condensation / Evaporation Mechanisms

• All sites are energetically identical
• Gas sticks to the surface: 1 layer only possible
• No lateral interactions
• Gas bounces off a species already adsorbed
Langmuir Theory (Chimisorption)

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

$N^s = \text{number of adsorption sites}$
$N^a = \text{number of molecules adsorbed}$

Degree of coverage:

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

- Chemisorption Isotherm
- Often used in Chem. Eng. for adsorption at $T_{\text{amb}}$

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

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

  - Henry’s Law \[ n^\sigma = n_m^\sigma bp \]

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

  - $n^\sigma = n_m^\sigma$

\[
b = K \exp^{E/RT}
\]
Langmuir Isotherm: influence of the adsorption co-efficient ‘b’
In the linear form:

\[ \frac{p}{n} = \frac{1}{n_m b} + \frac{p}{n_m} \]

- \( n \) is the specific amount of gas adsorbed at the equilibrium pressure \( p \)
- \( n_m \) is the monolayer capacity (\( \theta = n/n_m \))
- \( b \) the adsorption coefficient, exponentially ‘related’ to the positive value of the energy of adsorption \( E \)
Calculation of the surface area using the Langmuir equation
Ar at 87.28 K on zeolite 13X

\[
\frac{n}{\mu \text{mol g}^{-1}}
\]

\[
\frac{p}{p^0}
\]

\[
\frac{p}{n}
\]

\[
R^2 = 0.9987 \quad a = 637.8 \text{ m}^2 \text{g}^{-1}
\]
BET theory
BET equation: one of the 10 most significant papers in science


Stephen Brunauer 1903-1986

Paul H Emmett 1899-1985

Edward Teller 1908-1957
Brunauer Emmett et Teller (BET) Theory

✓ Hypotheses

✓ 1 type of “adsorption site”

✓ no lateral interactions

✓ from the second layer $E_1 \approx E_L$ molar liquefaction energy of the adsorptive
Basic assumptions used in BET theory

surface $s_o$ covered by 0 adsorbed layer

... $s_1$ ... 1

... ... ...

... $s_i$ ... i

total surface $A = s_o + s_1 + ... + s_i + ...$
Brunauer Emmett et Teller (BET) Theory

☑ Even more equations

✦ $N = \text{number of layers}$

$x = \frac{p}{p^0} = \text{equilibrium relative pressure}$

✦ If $N \to \infty$

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

✦ Transformed BET equation

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

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

$$\frac{n}{n^a_m} = Cx \cdot \frac{1 - (N + 1)x^N + N_{x+1}^N}{1 - x \cdot 1 + (C - 1)x - Cx^{N+1}}$$
Influence of the number of layers $N$ on the shape of a theoretical BET adsorption isotherm

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

Curve with general shape of type II isotherm

$N = 25 \text{ à } \infty$

$N = 7$

$N = 6$

$N = 5$

$N = 4$
Influence of the Energetic Constant “C” on the shape of a theoretical BET adsorption isotherm

C < 10: the shape changes, the point of inflection is lost (type III isotherm)

\[
\frac{n}{n^a_m} = \frac{Cx}{(1-x)[1+x(C-1)]}
\]
Treatment of the isotherm by the BET method
exempla: alumina NPL / N\textsubscript{2} / 77 K

\[ y = 89.95x + 1.31 \]

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

Slope: \[ n_m^a = \frac{1}{S + I} \approx 0.011 \]

Intercept: \[ C = \frac{S}{I} + 1 \approx 70 \]
Application of the BET equation

- Graph
  \[
  \frac{p/p^o}{n^a(1 - p/p^o)} = f(P/P_0)
  \]

- 0.05 < P/P_0 < 0.30: find a linear variation
- In this linear part, the slope and the intercept allow to calculate \( n^a \) and \( C \)
- With \( n^a \rightarrow \) Specific surface area.

- \( C \sim \exp \{(E_1 - E_L)/RT\} \) energetic parameter which gives information to the interaction between the adsorbate and the adsorbent

- 1 point method: when \( C \) is large \( n^a_m = n^a(1 - p/p^o) \)
Checking results obtained using the BET method

example: alumina NPL / N₂ / 77 K

\[ n_m^a \approx 0.011 \]

\[ C \approx 70 \]

\[ \frac{p}{p^0} \] at \[ n_m^a \]

\[ \approx \frac{1}{\sqrt{C} + 1} = 0.107 \]
Hypothesis of the measurement of specific surface area

\[ n_m^a = \text{quantity of substance required to cover the surface with a monomolecular layer} \]

\[ \sigma_m = \text{area occupied by a single molecule in the monolayer} \]

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

For \( N_2 \) at 77,35 K \( \sigma_m = 0,162 \text{ nm}^2 \frac{a}{m^2 g^{-1}} = \frac{0,097 n_m^a}{\text{mol} g^{-1}} = \frac{4,35 \nu_m^a}{\text{cm}^3 g^{-1}} \)

where \( \nu_m^a \) is the volume of adsorbed gas (STP) necessary to cover the surface of one gram of adsorbent with a monolayer
Cross sectional area of adsorbate molecules ‘$\sigma_m$’

Hypotheses
* adsorbed molecules treated as spheres of radius $r$ occupying an area $\sigma_m$ on the surface of a solid completely covered by a monolayer
* monolayer supposed to be
  - compact (hexagonal compact arrangement)
  - liquid (density $\rho$ at the temperature of adsorption)

Calculations

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

$N_A$ Avogadro constant
$M$ Molar mass of substance adsorbed

Examples: $N_2$ à 77,35 K $\sigma_m = 0,162$ nm$^2$
$H_2O$ à 300 K $\sigma_m = 0,105$ nm$^2$
Assessement of specific surface area by gas adsorption

☑ General idea :

☞ Determination of $n_a m$ → Estimation of the amount of adsorbate required to cover the unit mass of solid surface with a complete monomolecular layer.

☞ The specific surface area of the adsorbent is :

$$a_{BET} = n_a m . N_A . \sigma_m / m$$

with $m$ the adsorbent mass, $N_A$ the Avogadro constant and $\sigma_m$ area occupied by one molecule
Calculating the specific surface area using BET example: alumina NPL / N\(_2\) / 77 K

\[ n^a_m \approx 0.011 \]
\[ C \approx 70 \]

\[ a_{BET} = n^a_m \times N_A \times \sigma_{N_2} \]

\[ a_{BET} = 0.011 \times 10^{-3} \times 6.02 \times 10^{23} \times 0.162 \times 10^{-18} \]

\[ a_{BET} = 1.07 \text{ m}^2 \text{ g}^{-1} \]

\[ a_{BET} \approx n^a_m \times 100 \]
‘t’ & ’α_s’ - methods
t or $\alpha_s$ method: background

- **Kiselev 1957**
  - search for the standard isotherm - non-porous
  - $\Gamma = n/A_{BET} \implies n/n_m$

- **Lippens-de Boer 1965**
  - thickness of the layer, $t$
  - $t = (n/n_m)d' \implies d' = M / (\sigma L \rho_{liq}) = 0.354$
  - $t = 0.354 \, n/n_m$

- **Sing 1968**
  - $n_m$ implies $A_{BET}$
  - chemical effects of the surface, at low coverage, are not taken into account
    - reference sample of *same chemical nature*
  - replace $n_m$ by $n_{0.4}$ ($n$ at $p/p^0 = 0.4$)

\[ \alpha_s = \frac{n}{n_{0.4}} \]
"t" method (de Boer) \[1\]

Non-porous solids $\rightarrow$ multimolecular adsorption

- $t$ (thickness of the adsorbed layer) *increases with* \( p/p^o \) *according to a*
  "universal t curve" \([= 0,354 \, n^a/n_m = f(p/p^o)]\)

- the layer covering the surface (supposed liquid)
  $A$ occupies a volume $V^l$: $V^l = A \cdot t$
Fitting the ‘t’ curve

Data from «de Boer»

‘Physical and Chemical Aspects of Adsorbents and Catalysts’
p.33.

Harkins et Jura

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

Halsey

\[ t = 0.354 \times \left( \frac{-5}{\ln\left( \frac{p}{p^\circ} \right)} \right)^{1/3} \]
Construction of the t-plot

$n^a/m^s$

Unknown Isotherm

$p/p^o$

\[ t \]

't' curve
Isotherms and corresponding ‘t’ plots

Type II

Type IV

Capillary condensation

Type I

Micropore filling

Non porous adsorbent
"t" Method (de Boer) [2]

Solid under investigation → adsorption isotherm which can be transformed using the universal "t" curve

→ "transformed t curve" with co-ordinates: \( n^a/m^s, t \)

→ if there is a linear region, one can calculate \( a(t) \) from the slope \( s_t \):

for \( \text{N}_2 \) adsorbed at 77.35 K (\( v_l = 34.61 \text{ cm}^3 \text{ mol}^{-1} \))

\[
a(t) = 34.6 \times \left( \frac{s_t}{\text{mmol g}^{-1} \text{ nm}^{-1}} \right)
\]

\[
s_t = \left( \frac{n^a}{m^s} \right)/t \quad \text{where } m^s = \text{sample mass}
\]
Treatment of the isotherm using the ‘t’ method
example: alumina NPL / N$_2$ / 77 K

\[ y = 0.0203x + 0.0046 \]

\[ a(t) = 34.6 \times \left( s_t / \text{mmol g}^{-1} \text{ nm}^{-1} \right) \]
\[ a(t) = 34.6 \times 0.0203 \text{ m}^2 \text{ g}^{-1} \]
\[ a(t) = 0.70 \text{ m}^2 \text{ g}^{-1} \]
Comparison of specific surface areas obtained: alumina NPL / N$_2$ / 77 K

\[ n^a / \text{mmol g}^{-1} \]

\[ a_{\text{BET}} = 1.07 \text{ m}^2\text{.g}^{-1} \]

\[ a_t = 0.7 \text{ m}^2\text{.g}^{-1} \]
Microporous Materials

‘very special isotherms’
Adsorption on a purely microporous sample: \( d \approx 0.4 \text{ à } 2 \text{ nm} \)

\[ \frac{d(\text{pore})}{d(\text{gas})} = 1 \text{ à } 5 \]

Micropore filling:
- ultramicropores
- supermicropores
- co-operative mechanism
Potential energy in a slit-shaped pore

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

\( \sigma = 1 \text{ nm} \)

\( \varepsilon/k = 124 \text{ K} \)

\( w = 14 \sigma \)
\( w = 8 \sigma \)
\( w = 4 \sigma \)
\( w = 3 \sigma \)
\( w = 2.5 \sigma \)
\( w = 2 \sigma \)

\( \sigma \approx r_{gas} \)
Adsorption isotherms with microporous samples: use of semi-log plots

DAY / N₂ / 77K

AIPO₄-11 / N₂ / 77K

VPI-5 / Ar / 87K
Microporous Materials

what about using the BET method to characterise the ‘surface area’?
Effective molecular area ‘\( \sigma \)’ adsorbed in micropores

- Slits: \( \sigma = 1 \)
- Cylinders: \( \sigma = 1 \) vs. \( \sigma = 2 \) vs. \( \sigma = 4 \)

Ultramicropores: \( a_{\text{BET}} \) underestimated
The concept of “Equivalent BET Surface Area”

✓ In the case of microporous samples, the BET equation can still be applied (for very low equilibrium relative pressures)

✓ Here, one talks of an \textit{equivalent} BET surface area obtained on supposing that the quantity $n_m$ (determined via the BET law) is adsorbed in a single monomolecular layer
Nitrogen adsorption at 77 K on a microporous alumina
“BET” treatment in the case of a microporous solid:

microporous alumina / N₂ / 77K

\[ y = 0.476x + 0.0005 \]

\[ n^a_m = \frac{1}{S + I} \approx 2.10 \]

\[ C = \frac{S}{I} + 1 \approx 953 \]

\[ a_{BET} = n^a_m \times N_A \times \sigma_{N_2} \]

\[ a_{BET} = 2.1 \times 10^{-3} \times 6.02 \times 10^{23} \times 0.162 \times 10^{-18} \]

\[ a_{BET} = 205 \, m^2 \, g^{-1} \]
The concept of “Equivalent BET Surface Area”

☑ In the case of microporous samples, the BET equation can still be applied (for very low equilibrium relative pressures)

☑ Here, one talks of an equivalent BET surface area obtained on supposing that the quantity $n_m$ (determined via the BET law) is adsorbed in a single monomolecular layer
Characterisation of solids by adsorption → Microporosity

Methods available:

- ‘t’-plot → total pore volume
- HK method → pore size
- DFT → pore size
- ‘α_s’-plot’ → surface area and pore volume
- MP method → pore size
- Dubinin methods → ???
‘t’ & ‘αs’ – methods (cont)
Isotherms and corresponding ’t’ plots

Type I
Non porous adsorbent

Type II
Capillary condensation

Type IV
Micropore filling
Nitrogen adsorption at 77 K on a microporous alumina
‘t’ and $\alpha_S$ calculation : $N_2 / 77K /$ microporous alumina

$\alpha_S$ calculation with ref. Alumina NPL

\[ y = 4.3472x \]
\[ R^2 = 0.973 \]

\[ a_x = \left( \frac{a_{BET}(\text{ref})}{n_{0.4}^a(\text{ref})} \right) \times \text{slope} \]

\[ a_{BET}(\text{ref}) = 1.07 \text{ m}^2 \text{ g}^{-1} \]
\[ n_{0.4}^a(\text{ref}) = 0.016 \text{ mmol.g}^{-1} \]

\[ a_{\alpha_s} = 290 \text{ m}^2 \text{ g}^{-1} \]
\[ a_{BET} = 205 \text{ m}^2 \text{ g}^{-1} \]

Ultramicropores $a_{BET}$ underestimated
Summary : ‘t’ / $\alpha_S$ methods for the characterisation of microporous solids

☑ Need a good expression of the ‘t’ curve $\Rightarrow$ HJ, FHH...
☑ The 't' method does not work for $t < 1$nm in the programs supplied commercially
☑ $\alpha_S$ requires a good reference isotherm for each sample type
   $\Rightarrow$ It is then possible to extract ultra- and super- micropore volumes / surfaces
☑ Neither method gives any information on pore size distribution
   $\Rightarrow$ MP method
   $\Rightarrow$ HK
   $\Rightarrow$ DFT
HK – method
Horwath-Kawazoe Method: background

☑ Horwath-Kawazoe - 1983
  ✶ expression for slit shaped pores (carbons)
  ✶ N-C interactions at 77 K

☑ Saito-Foley - 1991
  ✶ expression for cylindrical pores
  ✶ Ar-O (87 K)

☑ Cheng-Yang - 1994
  ✶ expression for spherical pores
  ✶ correction for isotherm non-linearity
Horwath-Kawazoe method: calculations

- Pore filling pressure $\propto$ gas-solid interaction
- Set-up for slit shaped carbon micropores

\[ \Phi(z)_{\text{pore}} = \Phi_{g-s}(z) + \Phi_{g-s}(H - z) \]

Interaction of a molecule with the each wall of a slit shaped pore

Gas-solid Interactions `first plane`

Gas-solid Interactions `second plane`
**Horvath-Kawazoe Method (HK)**

**Assumptions**
- Pores of width $= H$
- Pressure of micropore filling related to the energy of adsorbate-adsorbent interaction

**Calculations** : $N_2, 77 K / Carbon$ molecular sieve

\[
\ln \left( \frac{p}{p^o} \right) = \frac{61,23}{(H - 0,64)} \left[ \frac{1,895 \times 10^{-3}}{(H - 0,32)^3} - \frac{2,709 \times 10^{-7}}{(H - 0,32)^9} - 0,05014 \right]
\]
Horwath-Kawazoe and Saito-Foley: formulas!

- **H-K**
  - 10-4 potential function to describe the interactions:

  \[
  \Phi(z)_{pore} = k \int \left[ \left( \frac{\sigma}{z} \right)^{10} - \left( \frac{\sigma}{z} \right)^{4} + \left( \frac{\sigma}{H-z} \right)^{10} - \left( \frac{\sigma}{H-z} \right)^{4} \right] dz
  \]

- **S-F**
  - \[ \ln \left( \frac{p}{p^0} \right) = \frac{62.38}{H-0.64} \cdot \left[ \frac{1.895 \cdot 10^{-3}}{(H-0.32)^3} - \frac{2.7087 \cdot 10^{-7}}{(H-0.32)^9} - 0.05014 \right] \]

  \[ \ln \left( \frac{p}{p^0} \right) = \frac{28.57}{H-0.612} \cdot \left[ \frac{1.584 \cdot 10^{-3}}{(H-0.306)^3} - \frac{1.729 \cdot 10^{-7}}{(H-0.306)^9} - 4.793 \cdot 10^{-2} \right] \]
Horwath-Kawazoe (S-F) Method

« DAY »
Horwath-Kawazoe (S-F) method obtained with AlPO$_4$-11

\[ \text{Differential Pore Volume / cm}^3 \cdot \text{g}^{-1} \]

Pore width / nm

\(0.39 \times 0.63\) nm

\[ \text{can be mislead by an unusual two step pore filling process} \]
Horwath-Kawazoe method : summary

☑ Require good points at very low pressure
  ➤ < $10^{-5}$ p/p$_0$
  ➤ equilibrium pressure gauge stability !!!!

☑ H-K
  ➤ aimed for carbons and nitrogen at 77K

☑ Saito-Foley
  ➤ aimed at zeolite cylinders and argon at 87K

☑ Attention first peak : artefact in calculation
DFT
Type I isotherm: DFT
1. Construction of reference isotherms

2. Reconstruction of the experimental isotherm using the reference isotherms
DFT results obtained with carbon fibre’s

![Graph showing DFT results](image-url)
Overall Summary for Microporous Solids

☑ Microporous samples usually give rise to Type I isotherms

☑ An estimation of the specific surface area of microporous samples can be done using the following approaches:
   - BET method → “equivalent surface area”
   - ‘t’ method → external surface area
     - not adapted for the total surface area

☑ Pore size distribution of micropores
   - Horwath-Kawazoe
   - DFT
Exploitation of the adsorption isotherm

- Capillary Condensation
  - Kelvin equation (BJH)
  - Broekhoff de Boer
  - DFT

- Monolayer formation
  - BET
  - Multimolecular Adsorption
    - t-plot
    - $\alpha_S$ method

- Localised Adsorption
  - Adsorption Energies
  - Micropore filling
    - HK
    - DFT
    - .... Monte Carlo

$p/p^\circ$ $n^\sigma/m^s$
Physisorption Isotherms

Adsorption is an exothermic phenomena

Isosteric Enthalpies

\[ \Delta_{ads}h = -R \left( \frac{T_1T_2}{T_2 - T_1} \right) \ln \left( \frac{p_2}{p_1} \right) \frac{n^{\sigma}}{m^{s}} \]
Calorimetry @ 77K

Hydrogen / MIL91 @ 77K

Calorimetry @ LT
- T : 77K (87K)
- $P_{\text{max}}$ : 1bar
- QS : 200-300mg
Adsorption coupled with XRPD
AIPO₄-11 / N₂ / 77K
Adsorption Microcalorimetry

Methane on AlPO$_4$-11

- $\Delta_{ads} h / \text{kJ.mol}^{-1}$
- $n^a / \text{mmol.g}^{-1}$
- $p / p_0$

- $|\Delta_{vap}H_{CH_4}|$

Neutron diffraction:
- methane translational mobility increases!!

A: $D_t = 0.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

B: $D_t = 2.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$
Adsorption-desorption isotherm:
microporous model $\mathcal{O}$ Silicalite-1 / $N_2$ at 77K

hysteresis $\mathcal{O}$ cracks

Sub-step at low $p/p^0$!!
Adsorption Microcalorimetry

Methane at 77 K / Silicalite

- Energetically homogeneous micropore structure
Adsorption Microcalorimetry

Argon at 77 K / Silicalite

\[ \Delta_{\text{ads}} h / \text{kJ.mol}^{-1} \]

\[ n^a / \text{mmol.g}^{-1} \]

\[ \frac{\rho}{\rho^0} \]

\[ Q / \text{Å}^{-1} \]

\[ |\Delta_{\text{vap}} H_{\text{Ar}}| \]

Neutron scattering

Disordered fluid \[ \leftrightarrow \beta \rightarrow \text{ordered “solid”} \]
Adsorption Microcalorimetry

Nitrogen at 77 K / Silicalite

- $\Delta_{ads} h / \text{kJ.mol}^{-1}$

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

- $p / p^0$

- $Q / \text{Å}^{-1}$

Disordered fluid $\leftrightarrow \alpha \Rightarrow$ Ordered fluid $\leftrightarrow \beta \Rightarrow$ Ordered "solid"

Neutron scattering

$\Delta_{vap} H_{N_2}$

5.4 mmol.g$^{-1}$

4.1 mmol.g$^{-1}$

2.5 mmol.g$^{-1}$

0 mmol.g$^{-1}$

Philip LLEWELLYN

FEZA School

2nd Sept. 2008
Exploitation of the adsorption isotherm

- Capillary Condensation
  - Kelvin equation (BJH)
  - Broekhoff de Boer
  - DFT
- Monolayer formation
  - BET
  - Multimolecular Adsorption
- Localised Adsorption
  - Adsorption Energies
  - Micropore filling
  - HK
  - DFT
  - $\alpha_S$ method
  - Monte Carlo

$p/p_0 n^\sigma/m_s$
Differences in properties of adsorptive molecules

<table>
<thead>
<tr>
<th>Adsorptive</th>
<th>CH₄</th>
<th>Ar</th>
<th>Kr</th>
<th>O₂</th>
<th>N₂</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular dimensions / nm</td>
<td>0.42</td>
<td>0.38</td>
<td>0.40</td>
<td>0.39 x 0.28</td>
<td>0.41 x 0.30</td>
<td>0.37 x 0.42</td>
</tr>
<tr>
<td>Kinetic diameter / nm</td>
<td>0.38</td>
<td>0.34</td>
<td>0.36</td>
<td>0.35</td>
<td>0.36</td>
<td>0.39</td>
</tr>
<tr>
<td>Cross-sectional area $\sigma$ / nm²</td>
<td>0.158</td>
<td>0.138</td>
<td>0.195</td>
<td>0.141</td>
<td>0.162</td>
<td>0.168</td>
</tr>
<tr>
<td>Polarizability $\alpha$ $10^{-3}$ nm³</td>
<td>2.60</td>
<td>1.63</td>
<td>2.48</td>
<td>1.59</td>
<td>1.76</td>
<td>1.95</td>
</tr>
<tr>
<td>Dipole moment m / $10^{-30}$ Cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td>Quadrupole moment Q / $10^{-40}$ Cm²</td>
<td></td>
<td></td>
<td></td>
<td>-1.3</td>
<td>-5.0</td>
<td>-12.3</td>
</tr>
<tr>
<td>Enthalpy of Liq. $-\Delta_{vap}H$ / kJ.mol⁻¹</td>
<td>8.18</td>
<td>6.49</td>
<td>10.50</td>
<td>6.92</td>
<td>5.57</td>
<td>6.03</td>
</tr>
<tr>
<td>Liquid density at 77 K $\rho_l$ / g.cm⁻³</td>
<td>0.424</td>
<td>1.394</td>
<td>2.415</td>
<td>1.141</td>
<td>0.809</td>
<td>0.789</td>
</tr>
<tr>
<td>Solid density at 77 K $\rho_s$ / g.cm⁻³</td>
<td>0.489</td>
<td>1.623</td>
<td>2.826</td>
<td>1.300</td>
<td>0.945</td>
<td>0.924</td>
</tr>
</tbody>
</table>
Nitrogen isotherms taken at different points during the calcination of MCM-41

Problems?

• Adsorbate retained inside organic chains
Getting more points during the vertical regions of the isotherm (for ASAP)

I’ve added this after our discussions on Friday!

To add more points on adsorption at low pressure

Analysis Conditions

Low Pressure

- Incremental dose mode
- Dose amount ____ cm³/g
- Min (0.3 to 1) hours
- Max 4 hours

To add more points later on adsorption / desorption (eg more MCM type materials)

Analysis Conditions

- Maximum volume increment ____ cm³/g
Krypton vs. Nitrogen vs. Argon

Krypton is often recommended for the estimation of very low surface areas.

**Why ?** The \( p^o = 1.8 \text{ mmHg} \) : thus error on the estimation of the amount not adsorbed in the sample cell is very low w.r.t. nitrogen.

**But !** Krypton does not wet solids well: thus \( \sigma \) varies (1.8 to 2.1 nm\(^2\)).

Nitrogen is the standard adsorptive for experiments at 77K.

**Why ?** Cover the real \( p/p^o \) range up to liquid saturation, good wetting.

**But !** \( \sigma \) can vary w.r.t. surface chemistry, std 0.162 nm\(^2\) can be 0.13 nm\(^2\).

Argon can be a compromise.

**Why ?** Good wetting for a non-polar adsorptive, \( \sigma \) does not seem to vary (0.138 nm\(^2\)), but between vapor 8 (297 mmHg) corresponds to solid Ar at...
Schematics of the Solid “Argon” Effect

Nitrogen adsorption

The argon adsorption is thus truncated at 77 K due to solidification.
Argon can show hysteresis at 77 K when Nitrogen does not.

Argon
Closure point: $p/p^° = 0.2$

Nitrogen
Closure point: $p/p^° = 0.4$

Pore diameter of 3.8 nm corresponds to a nitrogen desorption at $p/p^° = 0.42$ -> catastrophic desorption.
To what branch do we apply mesopore size calculations

- DFT suggests that for pores larger than 6nm both the experimental adsorption and desorption branches follow the theoretical spinoidal condensation and equilibrium evaporation phenomena.

- For pores smaller than 4 nm, the experimental adsorption and desorption branches follow the same path (no hysteresis). Theory suggests that this occurs at equilibrium evaporation pressures.

- Intermediate pores (4-6 nm), the desorption is fine (experiment and theoretical equilibrium coincide), the experimental adsorption branch is not able to be described.

- Theory would suggest that the closing point for hysteresis occurs at lower pressures than those observed experimentally.
Adsorption in a nanoporous material

Adsorption on specific sites
Adsorption coupled with XRPD

Christian, Thomas & Patricia @ ESRF

MIL53 Fe / CO$_2$

Adsorption

Desorption

Vacuum

$P_{\text{CO}_2} 80 \rightarrow 10$ mbar

$P_{\text{CO}_2} 1.5 \rightarrow 0.4$ bar

$P_{\text{CO}_2} 8.8 \rightarrow 1.7$ bar

$P_{\text{CO}_2} 3.7 \rightarrow 8.8$ bar

$P_{\text{CO}_2} 0.6 \rightarrow 2.1$ bar

$P_{\text{CO}_2} 50 \rightarrow 400$ mbar

Vacuum
Understanding the sorption phenomena through collaborative research e.g. CO₂ / MIL53(Cr)

What do we define as an **Interface**?

☑ An **interface** is the separation between two volumic phases.

Although one often uses either the terms surface or interface, the word “interface” is often used when one considers two condensed phases which are often explicitly named.

E.g.: solid/liquid interface; solid/gas interface.

☑ The term "**surface**" is used to describe the solids interface whether it be in contact with another phase (gas or liquid) or not (under vacuum).
Several definitions concerning powders

- **Agglomerate**: rigid assembly of particles
- **Aggregate**: lose assembly of particles
- **External surface area**: that excluding the pores, but including any surface roughness
- **Internal surface area**: in the pore volume
- **Specific surface area**: surface area per gram of solid
- **Roughness**: resulting from cavities that are more large than deep
Definitions used for Powders and Porous Materials

- Texture: geometric arrangement of particles and pores in a grain
- Geometric surface (with respect to 1g of material)
- External Surface: includes all irregularities (more large than deep)
- Internal Surface: includes all the accessible pores (to a given probe molecule)
- Porosity
- Pore size distribution: surface (or pore volume) distribution of the as a function of the pore width.

$$a = \frac{6}{m^2 \text{g}^{-1}} \left( \frac{\rho}{g \cdot \text{cm}^{-3}} \right) (\text{dUM})$$

$$\varepsilon = \frac{V_p}{V_r + V^s}$$

$$V_p = \text{pore volume (accessible ?)}$$

$$V^s = \text{volume occupied by the non porous bulk material}$$
Geometrical Surface

✓ Area of the interface which can be calculated directly from the particle geometry
✓ This area is related to a gram of solid supposed to be non-porous and is noted $a$
✓ For spherical particles of diameter $d$ and density $\rho$:

$$a = \frac{6}{\rho \ d}$$

✓ $a$ in $\text{m}^2\text{g}^{-1}$, $\rho$ in $\text{cm}^3\text{g}^{-1}$, $d$ in $\mu\text{m}$
Definitions

- Internal surface area: area of pore walls
- External surface area: area of surface outside pores
- Total surface area = Internal surface area + External surface area

The properties of a porous solid depend on the pore geometry, the pore size and the pore size distribution

- Micropore: pore of internal width less than 2 nm
- Mesopore: pore of internal width between 2 and 50 nm
- Macropore: pore of internal width greater than 50 nm

* Pore width = pore size: the available distance between the two opposite walls
Porosity is usually defined as the ratio of the volumes of voids and pores (open and closed) to the volume occupied by the solid:

\[ \varepsilon = \frac{V_p}{V_p + V_s} \]

- \( \varepsilon \): porosity
- \( V_p \): volume of voids and pores
- \( V_s \): \( V_{\text{total}} - V_p \)

Pore size distribution: the pore distribution according to their width.
More definitions for Porous Materials

- Pore: open or closed cavity; in the latter case, more deep than wide
- Pore Width: more general than diameter
- Micropores: pore width below 2 nm
- Mesopores: pore width between 2 and 50 nm
- Macropores: pore width above 50 nm

\[ \frac{d(\text{pore})}{d(\text{gas})} = 1 \text{ to } 5 \]

\[ \frac{d(\text{pore})}{d(\text{gas})} = 5 \text{ to } 125 \]
How can we calculate the quantity adsorbed?

(a) Interfacial layer

Quantity adsorbed: \( V^a \)

Surface: \( A \)

Solid: \( V^s \)

Residual gas: \( V^g \)

Quantity adsorbed: \( n^a \)

\[
n^a = A \int_0^\tau c \, dz
\]
How can we calculate the quantity adsorbed?

(b) Representation of GIBBS

- Gibbs dividing surface “GDS” : \( A \)
- Solid : \( V^s \)
- Excess quantity adsorbed : \( n^\sigma \)
- Total volume : \( V^{g,0} \)

Surface excess concentration \( \Gamma \)

\[
\Gamma = \frac{n^\sigma}{A}
\]

Excess quantity adsorbed \( n^\sigma \)

\[
n^\sigma = n^g_i - n^g_f
\]

\( n^a = n^s + c^g \cdot V^a \)

\( T \downarrow : n^a \approx n^\sigma \)
Argon adsorption in the nanopores of VPI-5 (d: 1.2 nm)
So schematically how can we think of adsorption?

Solid or “Adsorbent”

Fluid (gas, liquid) or “Adsorptive”

Adsorbed phase or “Adsorbate”

Solid or “Adsorbent”