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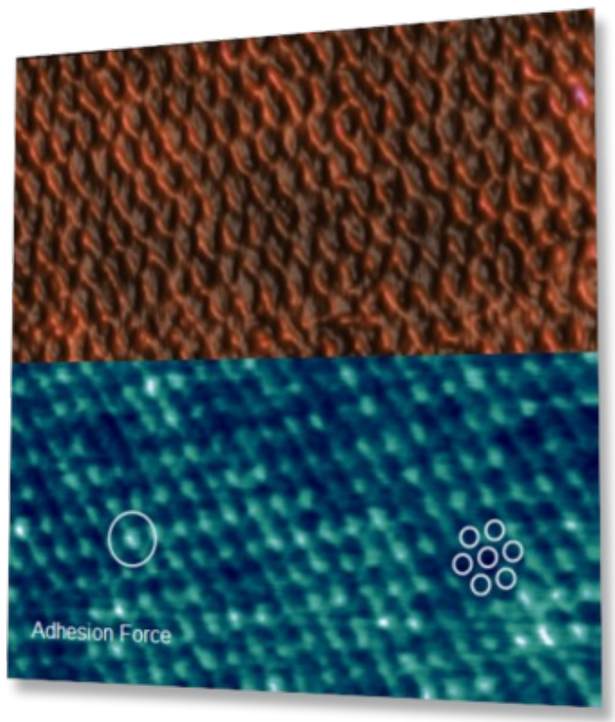
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Adsorption onto Solid Surfaces

Lecture 34

Adhesion and Friction

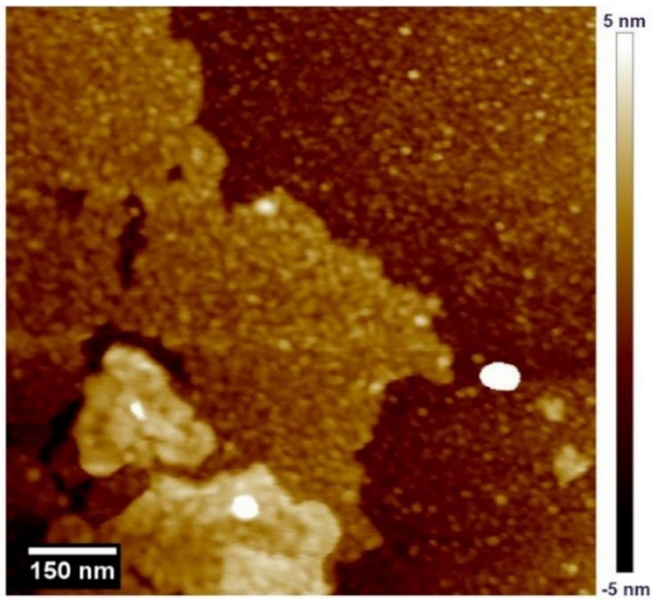


Lecture 36

Adsorption at Fluid-Fluid Interfaces

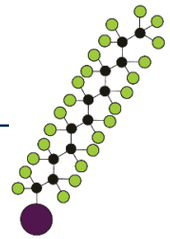
Surface adsorption (recap)

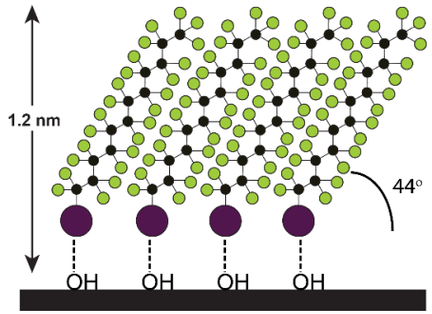
- High-energy surfaces will readily adsorb molecules from the air or from solution to reduce their surface energy (γ_{SV}).
- Adsorption can be chemical or physical.
- The adsorption of even a single layer (i.e. monolayer) can dramatically alter the properties of a surface, especially:
  - Wettability
  - Conductivity
  - Friction
  - Reactivity



AFM image of a monolayer adsorbed on a carbon film. (Neto, unpublished, 2019)

Thin organic films



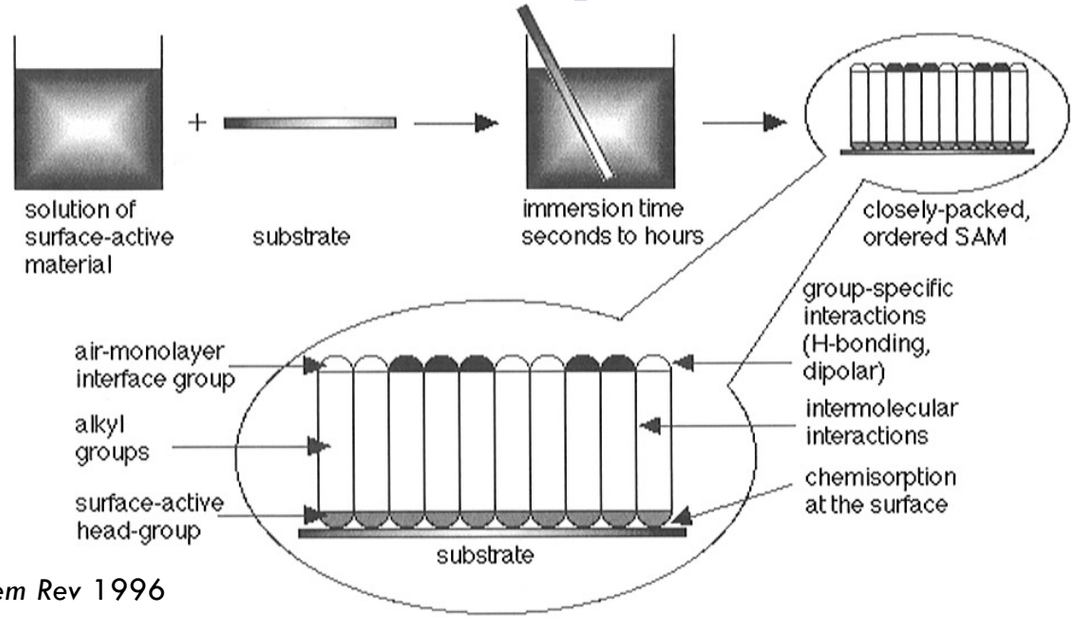


- Thin organic films of a few nanometers thickness (a monolayer) have many practical applications:
  - sensors
  - detectors
  - displays
  - electronic circuit components

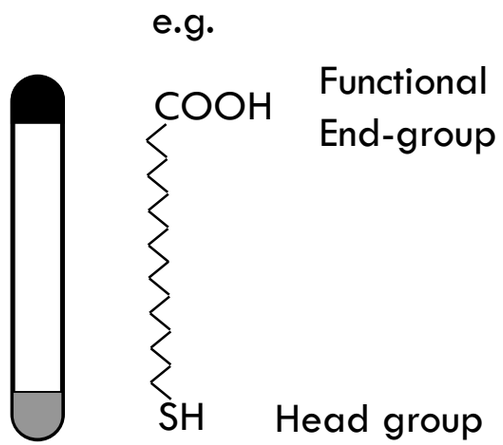
- Organic molecules can be synthesised with desired structure and functionality. This step, in conjunction with a sophisticated thin-film deposition technology, enables the production of electrically, optically and biologically active components on a nanometer scale.

- Various organic thin film can be deposited on a solid substrate, such as
  - Self-Assembled Monolayers (SAMs)
  - Langmuir-Blodgett films (not described here)

Self-assembled monolayers (SAMs)



Ulman, *Chem Rev* 1996



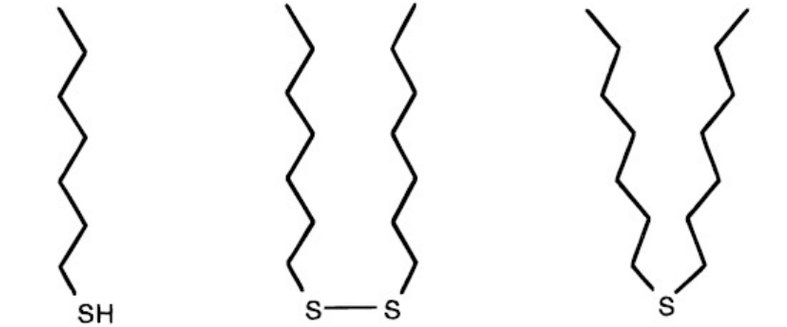
SAMs are ordered molecular assemblies formed by the adsorption of surface-active molecules on a surface.

They can be formed by a variety of molecules and on several substrates. Most commonly:

- by adsorption of alkyl sulphides on gold
- alkylchlorosilanes on hydroxylated surfaces (silicon oxide, quartz, mica);
- long chain n-alkanoic acids on metal surfaces (aluminium oxide, copper oxide and silver).

SAMs of thiols on gold

Example of surface-active organosulfur compounds that form ordered SAMs on gold substrates.



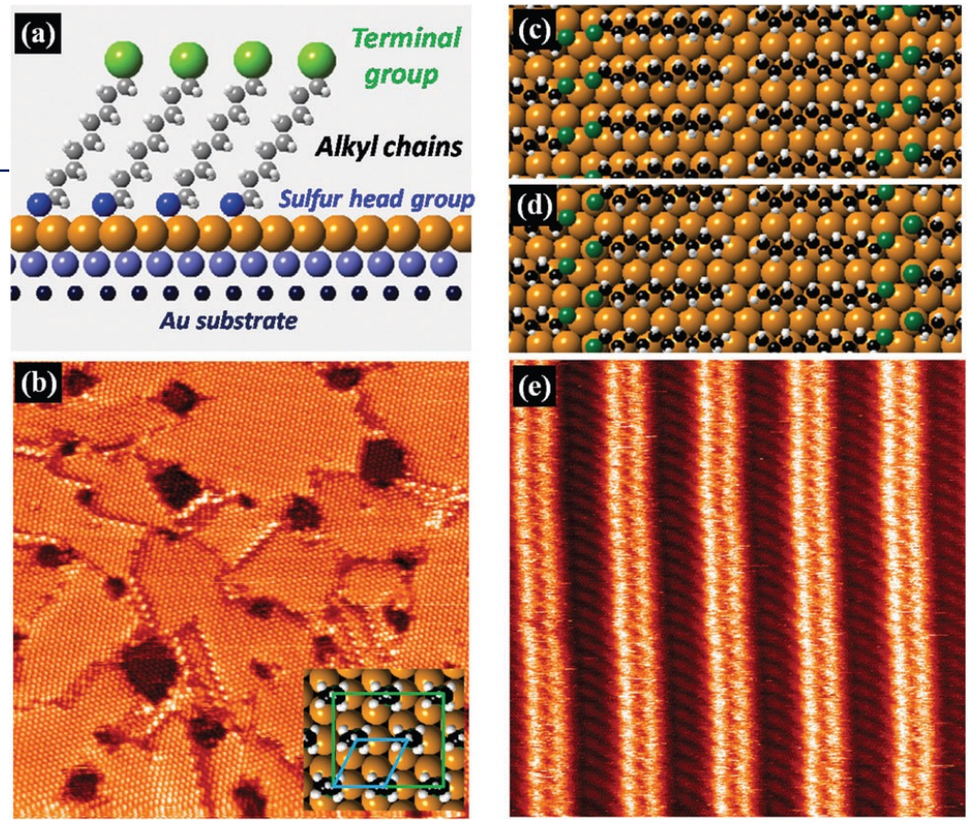
Alkanethiol dialkyl disulfide dialkyl sulfide

Chemisorption of alkanethiols and di-*n*-alkyl disulfides on clean gold gives monolayers, probably forming the Au(I) thiolate (RS-) species.

The mechanism of formation of SAMs from thiols and disulfides is probably an oxidative addition of the S-S bond to the gold surface

$$RS\text{-}SR + Au_n^0 \longrightarrow RS^- Au^+ \cdot Au_n^0$$

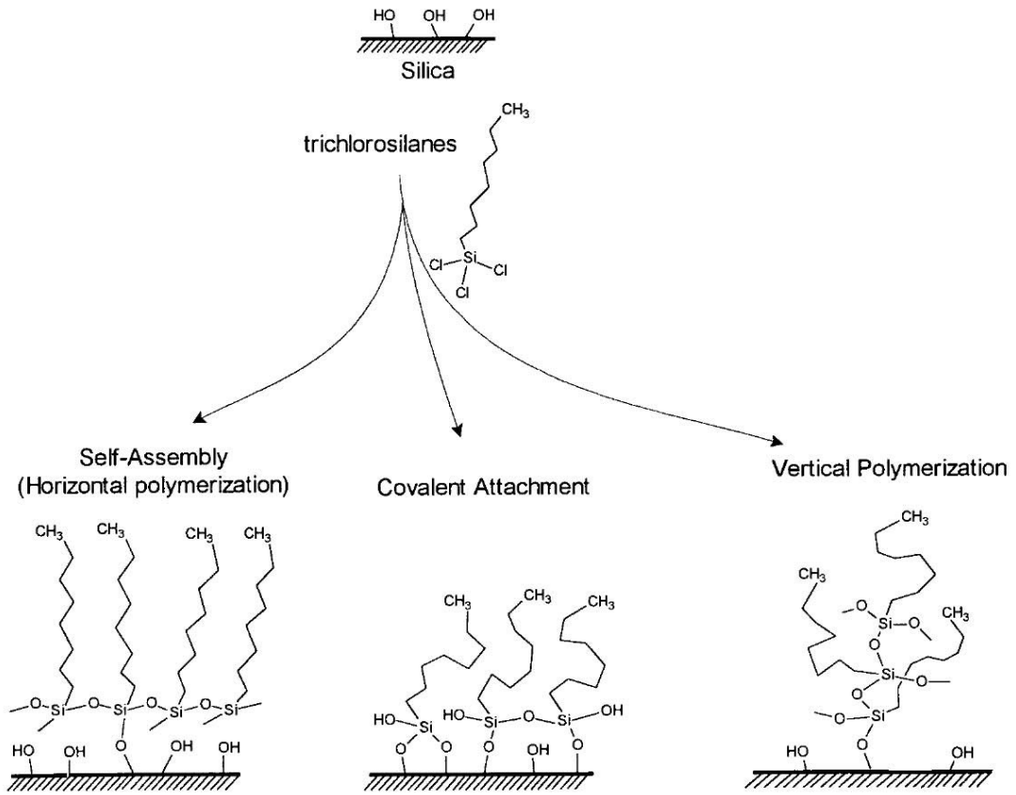
$$R\text{-}S\text{-}H + Au_n^0 \longrightarrow R\text{-}S^- Au^+ \cdot Au_n^0 + 1/2H_2$$

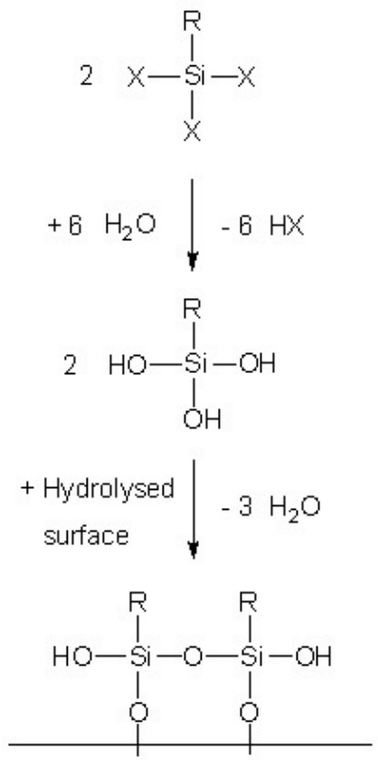


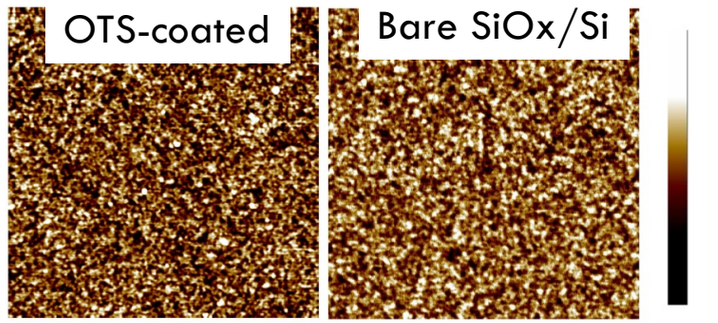
a) Oversimplified model which assumes that –SR is directly attached to a perfect Au(111) surface. (b) STM image of an octanethiol monolayer at saturation coverage. 40 nm × 40 nm. (c) and (d) Structural models of the striped phase consisting of lying down thiolate. (e) STM image from a striped phase of octanethiol monolayer. Image size 15 nm × 15 nm. Guo & Li, *PCCP 16, 19074-19090, (2014)*.

Silanisation

Most commonly used: octadecyltrichlorosilane (OTS) Cl_3-Si-$(CH_2)_{17}$-CH_3 on silica. It is rarely a simple monolayer! The trichlorosilane group reacts chemically with the silanols on the surface and grafts the hydrophobic chain onto the substrate. However, it also react with other silane groups and polymerises.



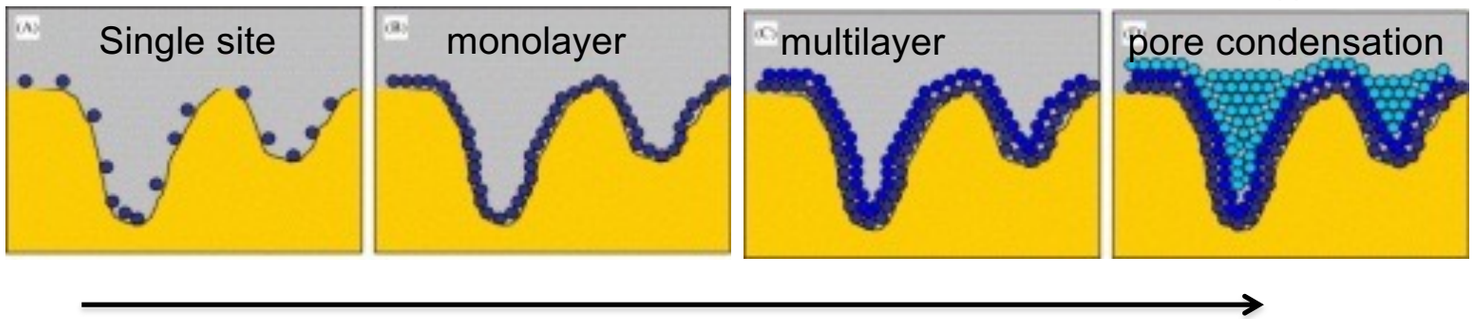




Atomic Force Microscopy (AFM) micrograph of SAM on smooth Si/SiOx (layer thickness 2.1 nm); Lessel *et al Surface and Interface Analysis* 2015

Surface Adsorption

Ho, S. T.; Hutmacher, D. W., *Biomaterials* ***2006, 27, (8), 1362-1376.***

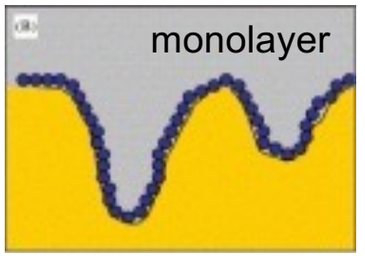


Surface coverage increases with partial pressure in the gas phase

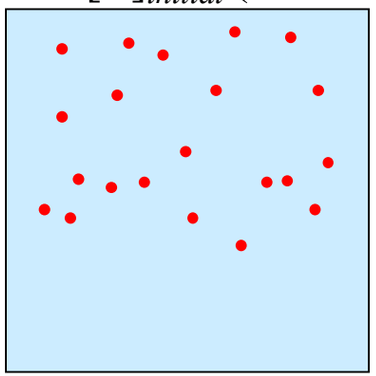
- *Physisorption*: physical adsorption due to van der Waals forces
- Heat is released upon physisorption, typically about 20 kJ mol^{-1}
- *Chemisorption:* chemical bond is formed with the surface
- The enthalpy of chemisorption is much higher (about 200 kJ mol^{-1})
- Bond-breaking upon chemisorption is why surfaces act as catalysts

Adsorption onto Solids

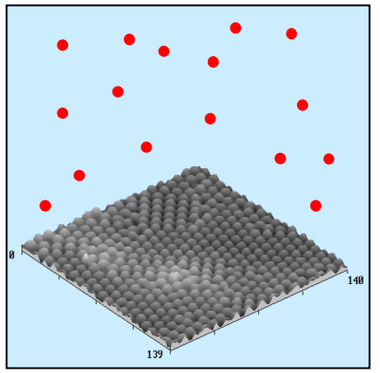
Depletion Adsorption measures the amount removed from a bulk phase (solution or gas) due to adsorption onto a surface. The bulk concentration changes after the solution is exposed to solid.



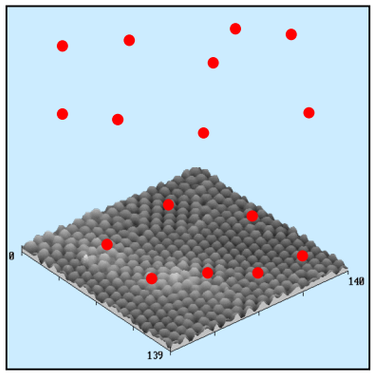
$[X]_{initial}$ (in the bulk)



add solid



→ $[X]_{eq}$ (in the bulk)



$$n_{ads} = ([X]_{initial} - [X]_{eq})V$$

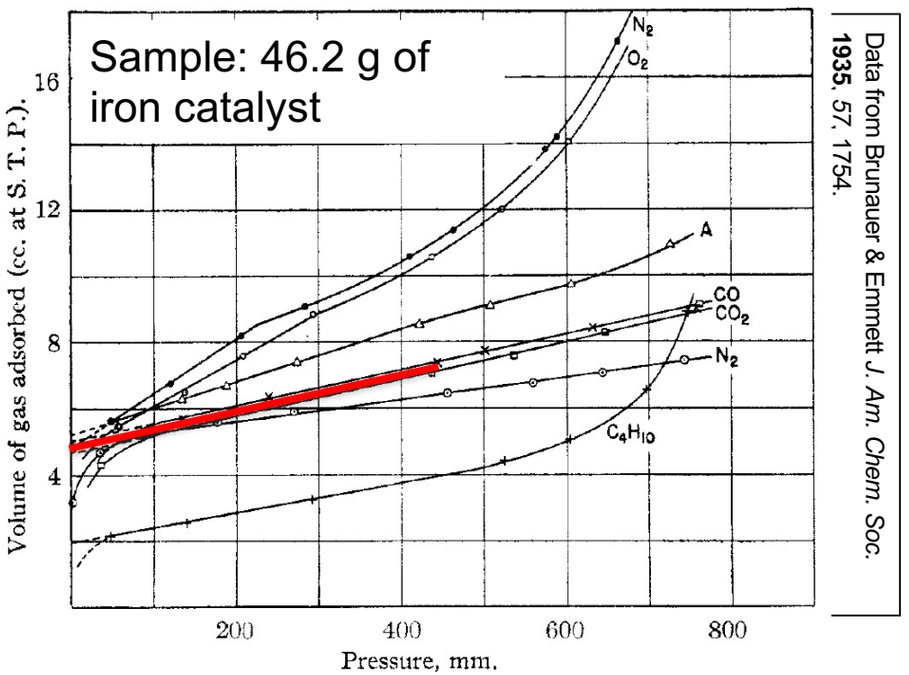
When the solute increases in concentration near the surface there must be a *surface excess* of solute compared with the bulk value. Adsorption can occur both from solutions [X] and from gas (*p*).

Adsorption onto solids from gas phase

Adsorption Isotherm: an "isotherm" expresses the amount of gas adsorbed onto a solid sample as a function of the relative gas pressure p/p^0, where p^0 is the vapour pressure of the gas, at a fixed temperature.

Extract from the paper:
"The extrapolation to zero pressure (of the linear portion between 60 mm and 200 mm) should indicate the volume of gas needed to form a monomolecular layer upon the catalyst."

This is the so-called "Point B method" – now superseded by BET.



Data from Brunauer & Emmett *J. Am. Chem. Soc.* **1935**, *57*, 1754.

Useful to derive surface area and chemistry of a porous sample

Brunauer's five "types" of adsorption isotherm

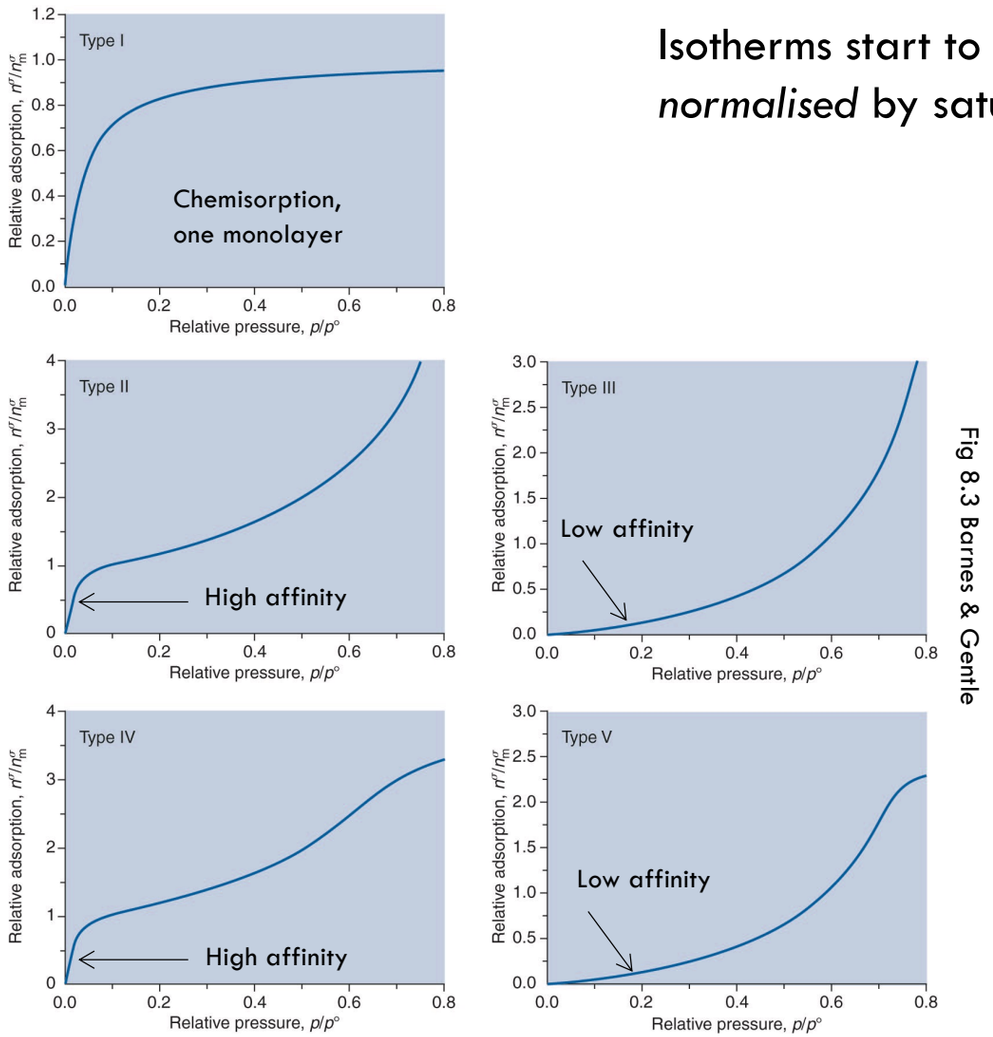


Fig 8.3 Barnes & Gentle

Isotherms start to show similar features when *normalised* by saturation vapour pressure, $P = p/p^0$

Isotherms of type I, II, and IV arise from strong interactions between gas and solid (type I indicates pure chemisorption), and type III and V from weak gas-solid interactions (relatively rare).

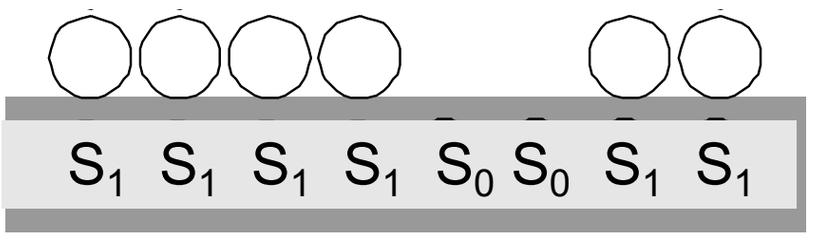
The simplest conceptual models for adsorption are:

- Langmuir
- BET

The Langmuir adsorption isotherm

Q1

- A very simple model
- Relies on three assumptions:
  1. the maximum coverage that can be obtained is one monolayer (chemisorption – works well for Type I isotherms),
  2. every adsorption site is equivalent,
  3. the ability of a particle to bind is independent of whether nearby sites are already occupied



The Langmuir adsorption isotherm

Adsorption is treated as a single equilibrium between bare surface sites, S_0 and a site S_1 covered with adsorbing gas or solute species.

$$X + S_0 \rightleftharpoons S_1$$

This leads to a simple expression for the adsorption isotherm

n_{ads} = amount adsorbed; n_{mono} = amount required to form monolayer

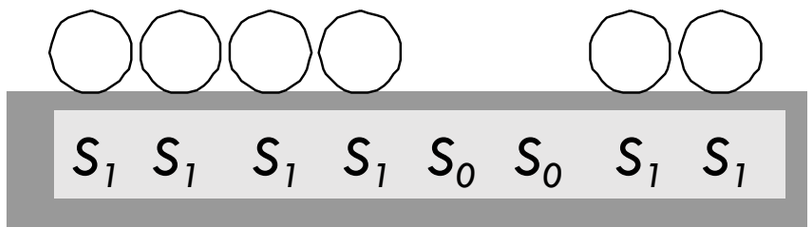
$$\theta = \frac{n_{ads}}{n_{mono}} = \frac{K_1[X]}{1 + K_1[X]}$$

for adsorption of solute of concentration [X]

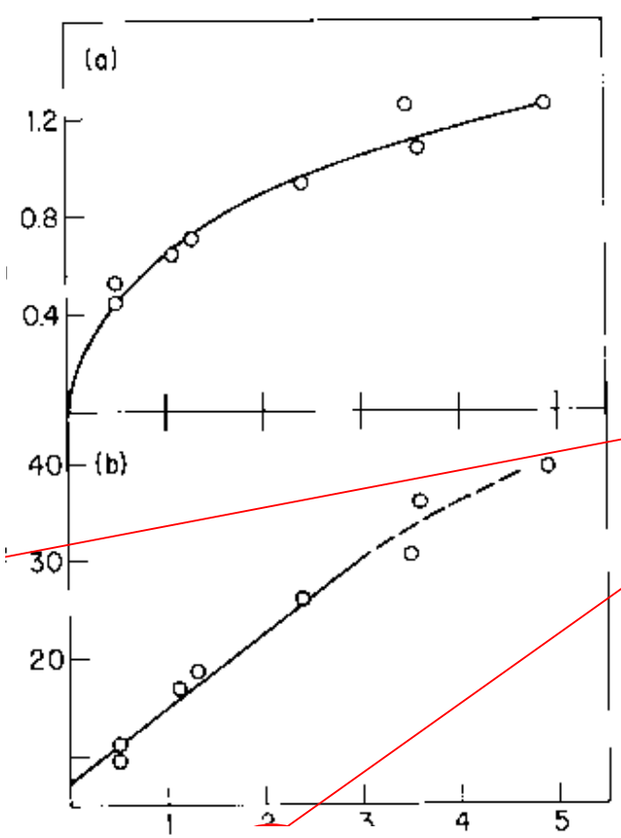
$$\theta = \frac{n_{ads}}{n_{mono}} = \frac{K_1 p}{1 + K_1 p}$$

for adsorption of a gas of pressure *p*

θ is called ***fractional surface coverage***



Linearised Langmuir Isotherm



Benzene on graphite

$$\theta = \frac{n_{ads}}{n_{mono}} = \frac{K_l[X]}{1 + K_l[X]}$$

The Langmuir isotherm can be rearranged into a linear form, i.e. linearised

$$\frac{[X]}{n_{ads}} = \frac{[X]}{n_{mono}} + \frac{1}{K_1 n_{mono}}$$

$$\frac{p}{n_{ads}} = \frac{p}{n_{mono}} + \frac{1}{K_1 n_{mono}}$$

In an experiment, we control [X] or p and measure n_{ads}. From this plot we get our n_{mono} and K_1.

Summary - Langmuir isotherm

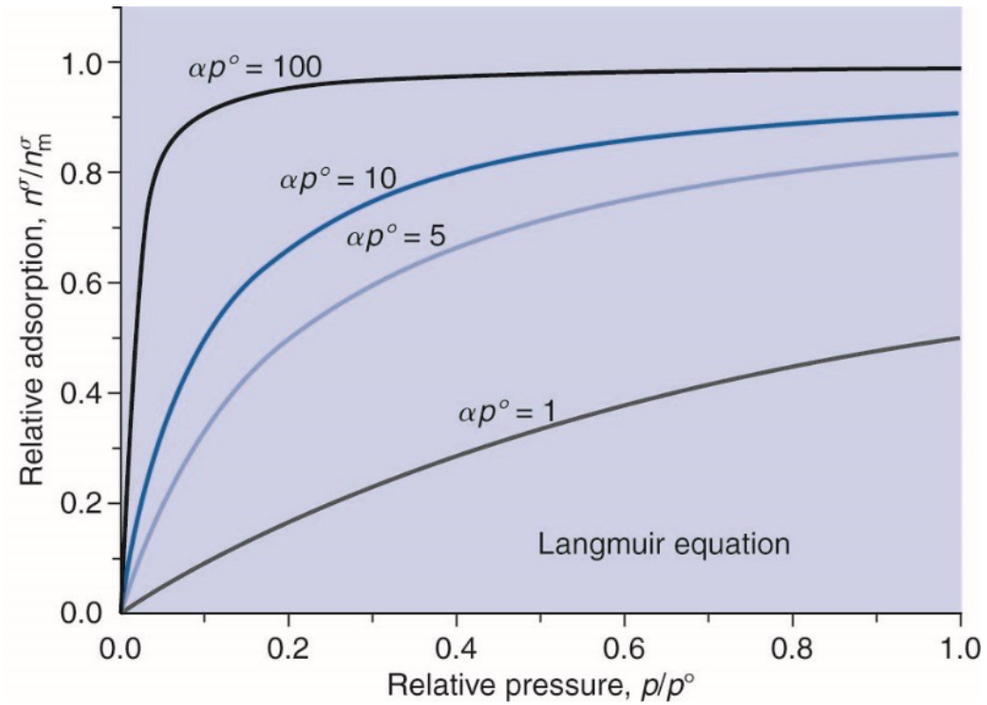


Fig 8.5 Barnes & Gentle

1. Increasing values of K_1 (α in plot) show increasing steepness at low pressures, reflecting increasing affinity between gas and solid.
2. The curves all tend to plateau at 1, which corresponds to a single monolayer (assumption of the Langmuir model)
3. These curves are all of Type I.
4. The result that is obtained from the raw data is $n_{mono;}$ if you know the size of the gas molecules, you can derive the surface area of the solid from $n_{mono.}$
5. It's much easier to get data out of the linearised form of the Langmuir isotherm.

Worksheet - Area of a porous sample

For the adsorption of nitrogen onto a porous sample, monolayer adsorption occurred at 5.0 mg adsorbed nitrogen. If the area occupied by an adsorbed nitrogen molecule is 0.162 nm^2, calculate the surface area of the sample.

Worksheet - Area of a porous sample

For the adsorption of nitrogen onto a porous sample, monolayer adsorption occurred at 5.0 mg adsorbed nitrogen. If the area occupied by an adsorbed nitrogen molecule is 0.162 nm^2, calculate the surface area of the sample.

Answer.
First, we calculate the number of molecules of nitrogen adsorbed in a monolayer.

5.0×10^{-3} g = 5.0×10^{-3} g / 28 g mol^{-1}
= 0.178×10^{-3} mol
= 0.178×10^{-3} mol x 6.022×10^{23} molecules mol^{-1}
= 1.08×10^{20} molecules

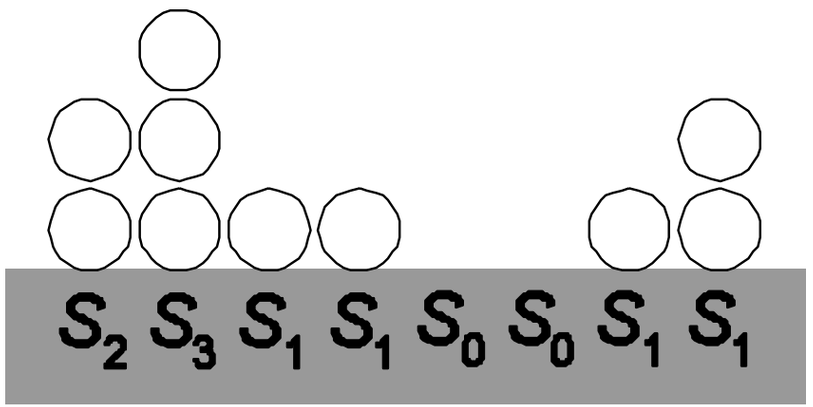
Thus, the total surface area of the porous sample is:

1.08×10^{20} molecules x 0.162×10^{-18} m^2 $molecule^{-1}$ = 17.4 m^2.

The BET (Brunauer, Emmett, Teller) Isotherm

- Slightly more elaborate model – Key assumptions:

1) More than one monolayer can adsorb – up to thick layers, but not too thick
2) Adsorption into layers 2, 3, 4, … all have the same equilibrium constant, *K*. *(not necessarily the same as the first layer's adsorption)*
3) When the layer becomes very thick, then it behaves like the bulk liquid



S_0 sites are bare
S_1 sites are covered by one molecule
S_2 sites are covered by two molecules
S_3 sites are covered by three molecules

The BET Isotherm

Q2

Assumption 2 (equilibrium constants $K_2 = K_3 = \ldots = K$) is important.
This is the same effective equilibrium constant that describes *condensation*.
This can also be thought of in terms of free energy of condensation
$\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$

The BET Equation:

$$\theta = \frac{n_{ads}}{n_{mono}} = \frac{cP}{(1-P)(1+(c-1)P)}$$

θ is called ***fractional surface coverage***.

θ may be >1 if *multilayers* form.

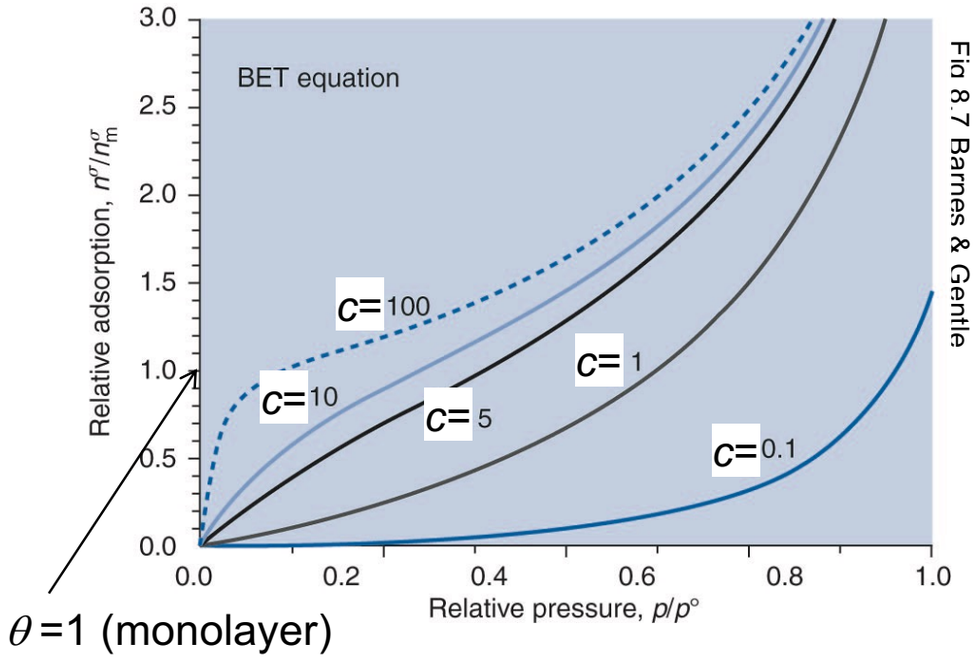
c is the BET parameter, describing the relative ease of adsorption onto the first and all other layers.

$c = K_1/K$

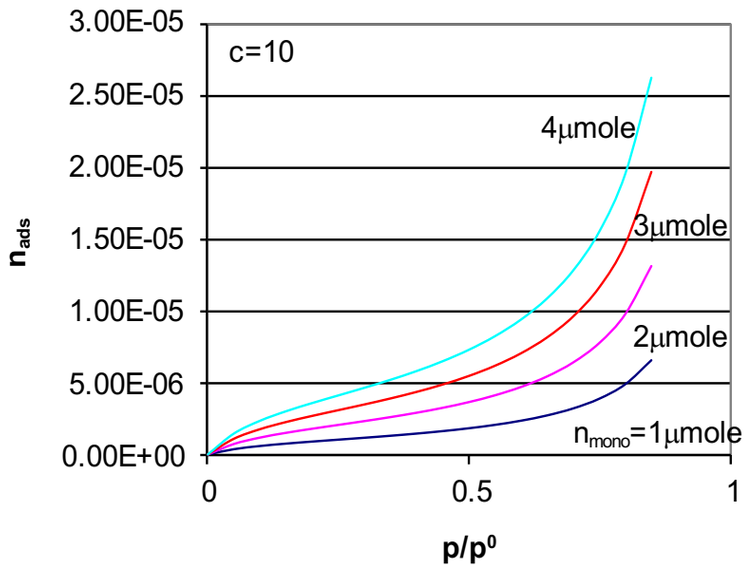
***P* = *p*/*p*^{0} is the partial pressure.** That is, the pressure *relative to the vapour pressure* (where the liquid condenses from the gas).

Changing c and n_{mono}

The BET Equation gives the following isotherms:



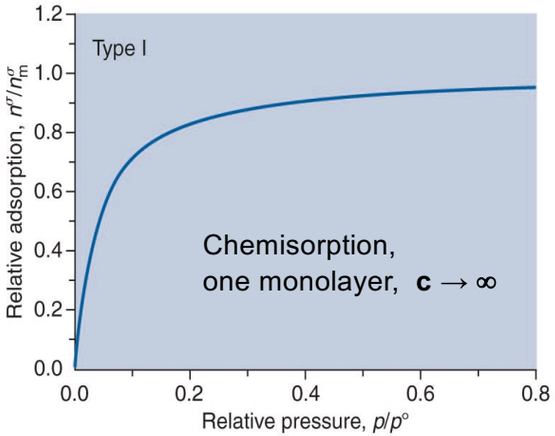
Higher surface area (= higher n_{mono}) changes the y-scale, but not the *shape* of the isotherm.

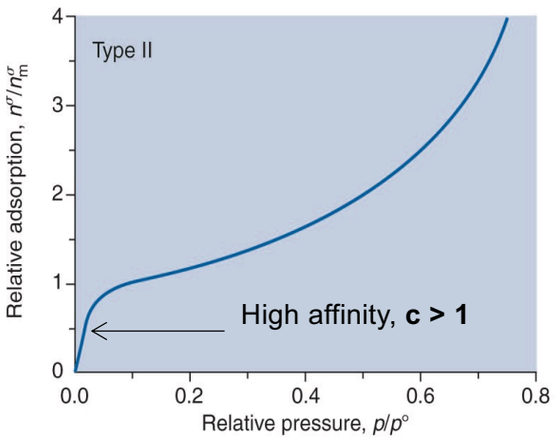


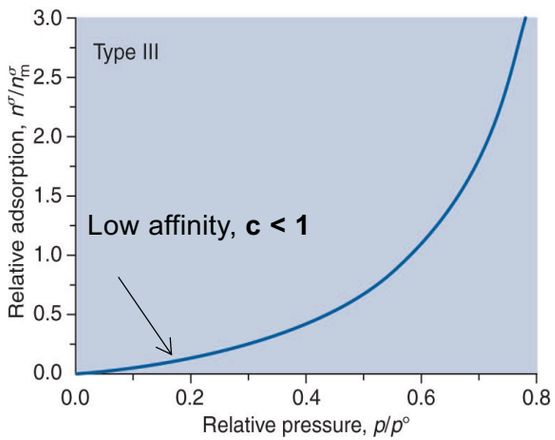
Multilayers always form as the partial pressure approaches p^0.

As c increases, the first layer forms more readily and the "bend" is more pronounced.

Brunauers five "types" of adsorption isotherm

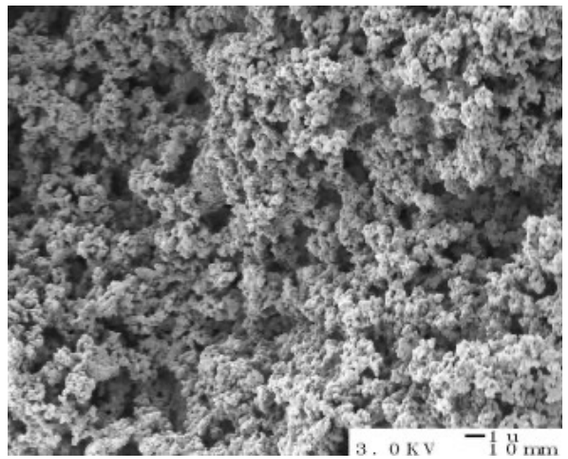






The BET isotherm successfully describes Type I-III isotherms simply by changing the *relative* strength of the interactions between the substrate and the adsorbing molecules, c.

BET model cannot cope with highly porous solids (near their condensation point) – see later.



The linearised BET equation

The BET Equation can be *linearised*, i.e. plotted in such a way that it yields a straight line.

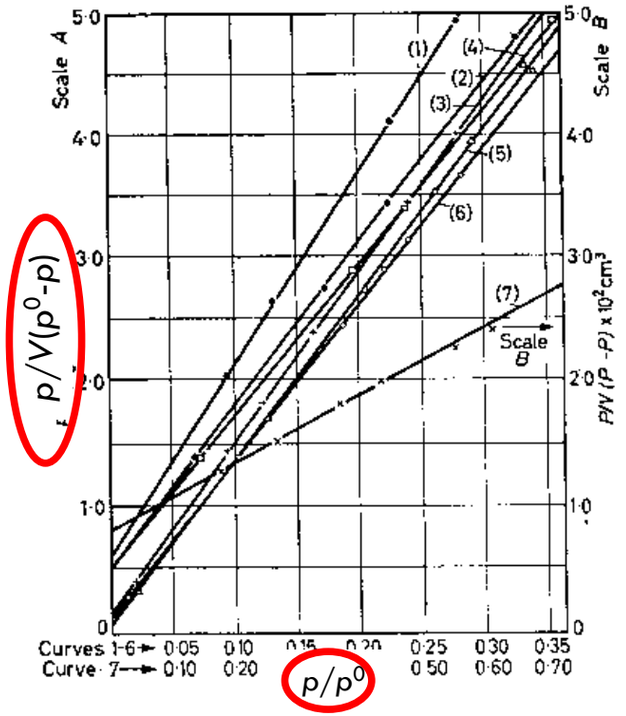
This simplifies obtaining n_{mono} and c.

$$\frac{p}{n_{ads}\left(p^0 - p\right)} = \frac{1}{c\, n_{mono}} + \frac{c - 1}{c\, n_{mono}} \frac{p}{p^0}$$

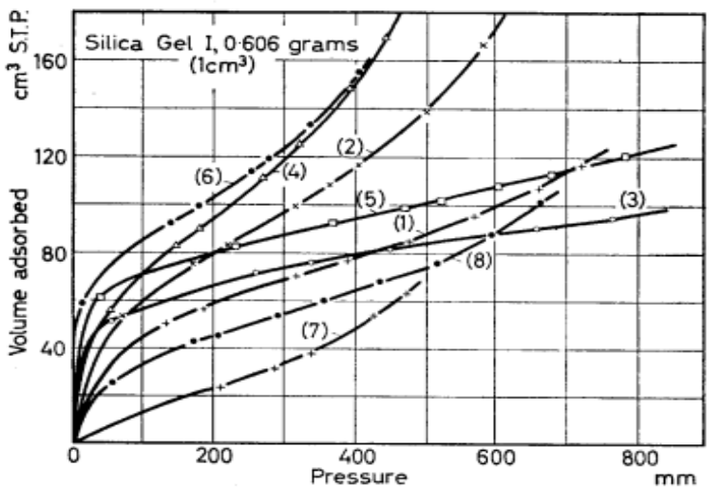
intercept

slope

$$y = b + mx$$



linearised



The linearised BET equation

Equally the BET equation can be written in terms of volume rather than moles

$$\frac{p}{n_{ads}\left(p^0 - p\right)} = \frac{1}{c\, n_{mono}} + \frac{c - 1}{c\, n_{mono}} \frac{p}{p^0}$$

$$\frac{p}{V_{ads}\left(p^0 - p\right)} = \frac{1}{c\, V_{mono}} + \frac{c - 1}{c\, V_{mono}} \frac{p}{p^0}$$

To first approximation, the number of moles *n* and volume *V* can be converted into each other by using the ideal gas equation ($pV = n\,R\,T$).

Exercise

Data for the adsorption of nitrogen gas on silica, when plotted according to the linear form of the BET equation, yields a slope of 319 mol^{-1} and an intercept of 3.35 mol^{-1}. Calculate the surface area of the sample. The effective cross-sectional area of a nitrogen molecule is 0.162 nm^2.

Exercise

Data for the adsorption of nitrogen gas on silica, when plotted according to the linear form of the BET equation, give a slope of 319 mol^{-1} and an intercept of 3.35 mol^{-1}. Calculate the surface area of the sample. The effective cross-sectional area of a nitrogen molecule is 0.162 nm^2.

Answer. In the linear form of the BET equation the slope is:
$(c-1)/(c\ n_{momo}) = 319\ mol^{-1}$
and the intercept is:
$1\ /(c\ n_{mono}) = 3.35\ mol^{-1}$

Substituting the later value into the equation for the slope gives:
$c = 319 \times 1/3.35 + 1 = 96.2$
and inserting this value for c into the equation for the intercept gives:
$n_{mono} = 1/(96.2 \times 3.35) = 3.10 \times 10^{-3}$ mol
The surface area of the sample is then given by the monolayer capacity multiplied by the area per molecule and the Avogadro number:

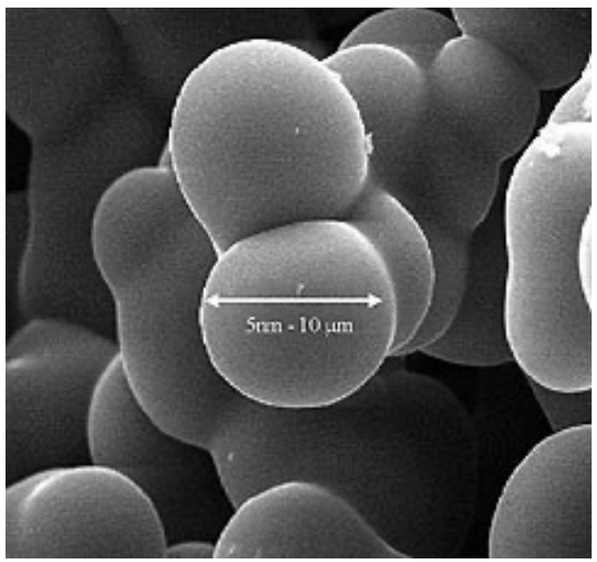
$$\text{Area} = 3.10 \times 10^{-3} \times 0.162 \times 10^{-18} \times 6.02 \times 10^{23} = 302\ m^2$$

Condensation into Pores

• Deviations from the BET model arise from capillary condensation into *pores* in the solid *below saturated vapour pressure*.

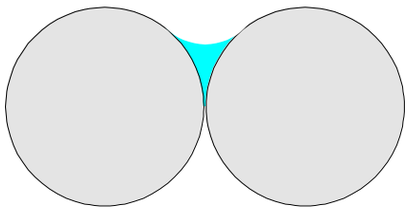
• Once an adsorbed layer is formed, multilayers build up by the same interactions as condensation. That is, the adsorbed layer *wets* the substrate.

E.g. Carbon Aerogel:





Slit pores may form in layered minerals (clays, graphite, talc, MoS_2…)

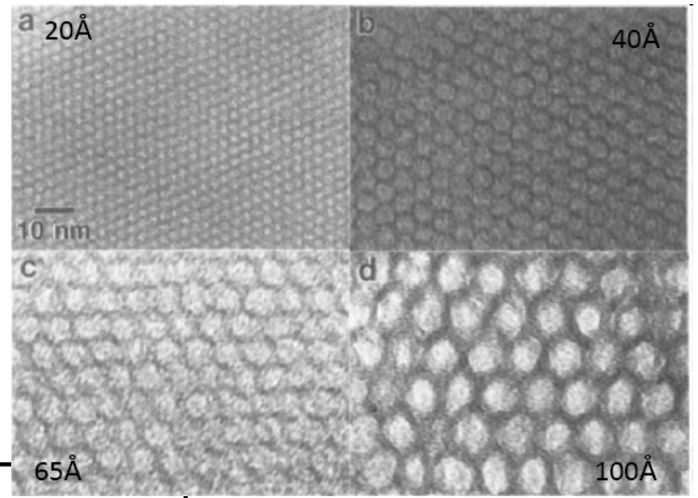


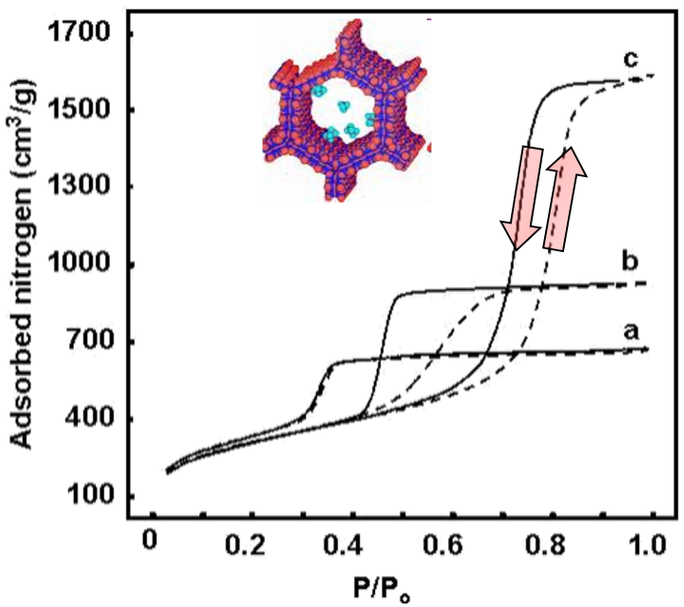
Pores may also form where small particles meet in a powder, especially if the particles are deformable or are sintered to make a permanent connection.

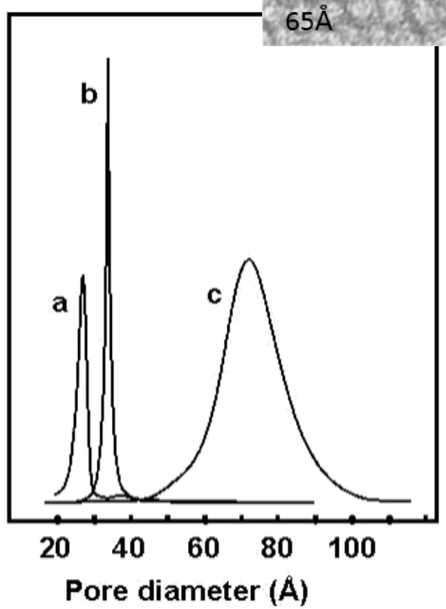
Condensation into Pores

Porous ceramics often show Type IV or V isotherms with pore condensation and even *hysteresis* in the isotherm.

E.g. N_2 adsorption/desorption onto highly porous silica MCM-41:







Learning outcomes

After this lecture you should be able to:

- Define monolayer adsorption and an *adsorption isotherm*
- Describe the key features of the Langmuir and BET model isotherms, including the effect of the model parameters K, c, and n_{mono}.
- Explain how the Langmuir and BET model isotherms relate to Brunauer's five types of isotherms.
- Fit experimental adsorption isotherm data to a Langmuir or BET isotherm and use this to deduce the adsorption mechanism and determine n_{mono}.
- Understand the meaning of monolayer coverage and use this to calculate the specific surface area of a solid.