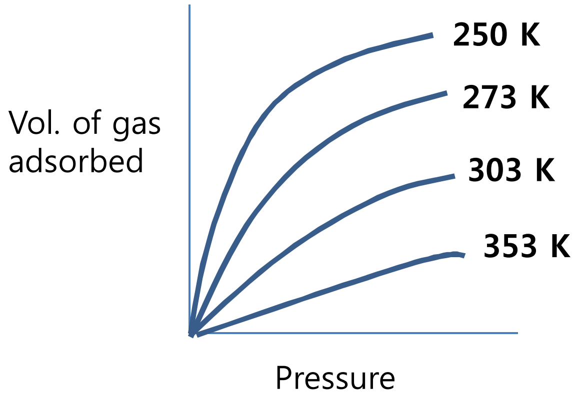
Solid-Gas Interface

- When a gas or vapor is brought into contact with a clean solid surface, some of it will become attached to the surface
  - Solid: adsorbent
  - Gas: adsorbate

- Any solid is capable of adsorbing a certain amount of gas. The extent of adsorption depends on temp. and pressure of the gas, and effective surface area of the solid
  - The most notable adsorbents are highly porous solids.
  - Charcoal, silica gel (~1000 m^2/g)

- The relationship at a give temp between the equilibrium amount of gas adsorbed and the pressure of this gas → adsorption isotherm



- Adsorption reduces the surface energy.

Physical Adsorption and Chemical Adsorption

- Forces involved in the adsorption of gas and vapors.
  - Non-specific (van der Waals): physical adsorption
  - Stronger specific forces (chemical bonding): chemisorption

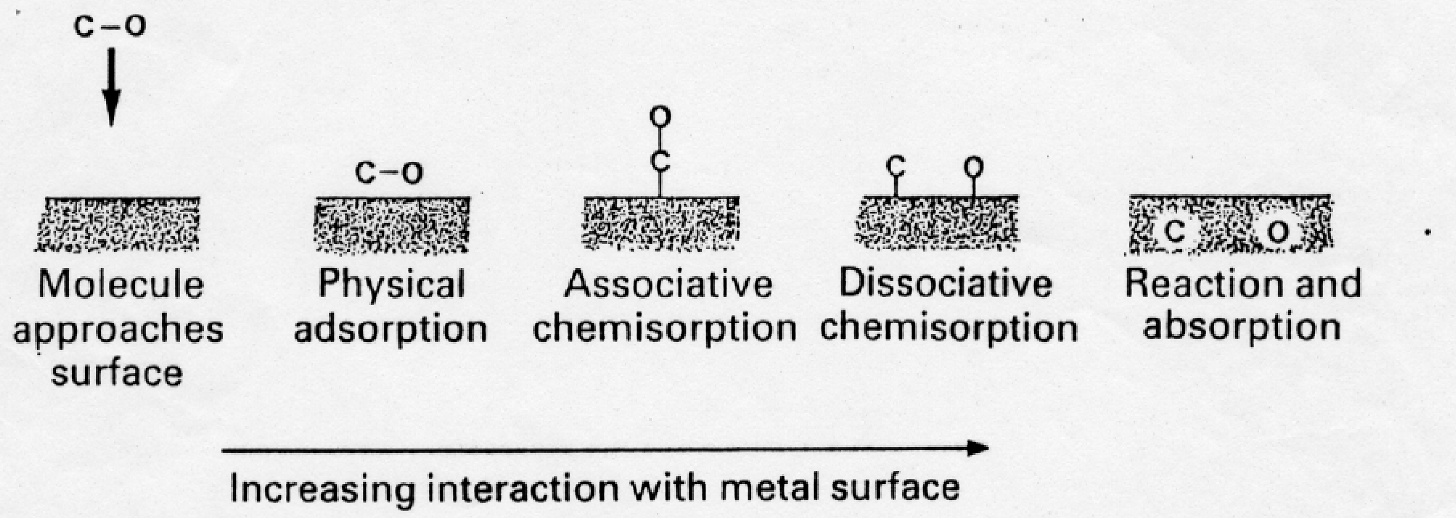


Figure 1.6. Schematic representation of the adsorption, and possible subsequent reaction, of carbon monoxide on various solid surfaces.

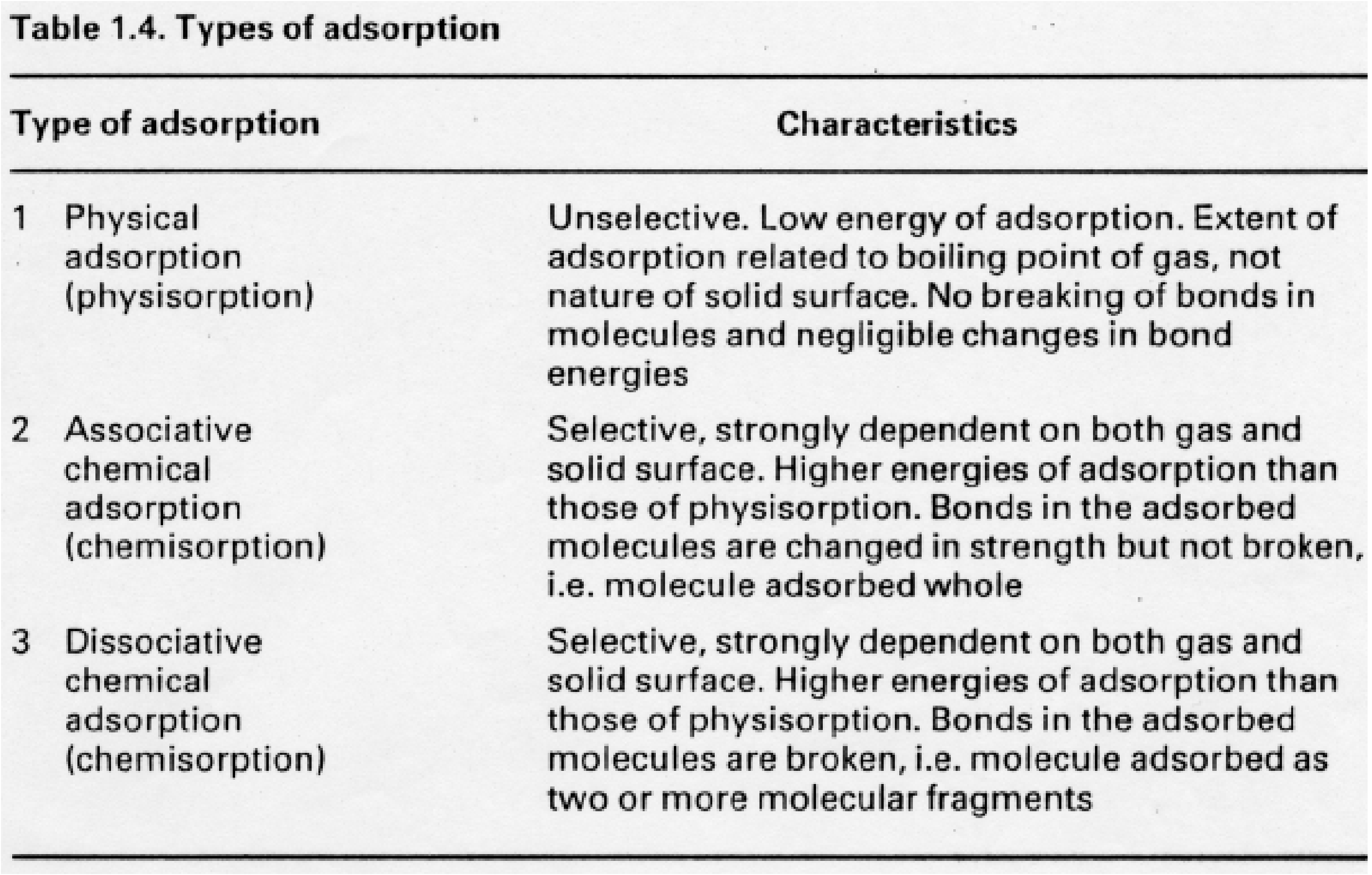


Table 1.4. Types of adsorption

Type of adsorption	Characteristics
1 Physical adsorption (physisorption)	Unselective. Low energy of adsorption. Extent of adsorption related to boiling point of gas, not nature of solid surface. No breaking of bonds in molecules and negligible changes in bond energies
2 Associative chemical adsorption (chemisorption)	Selective, strongly dependent on both gas and solid surface. Higher energies of adsorption than those of physisorption. Bonds in the adsorbed molecules are changed in strength but not broken, i.e. molecule adsorbed whole
3 Dissociative chemical adsorption (chemisorption)	Selective, strongly dependent on both gas and solid surface. Higher energies of adsorption than those of physisorption. Bonds in the adsorbed molecules are broken, i.e. molecule adsorbed as two or more molecular fragments

Physical Adsorption and Chemical Adsorption

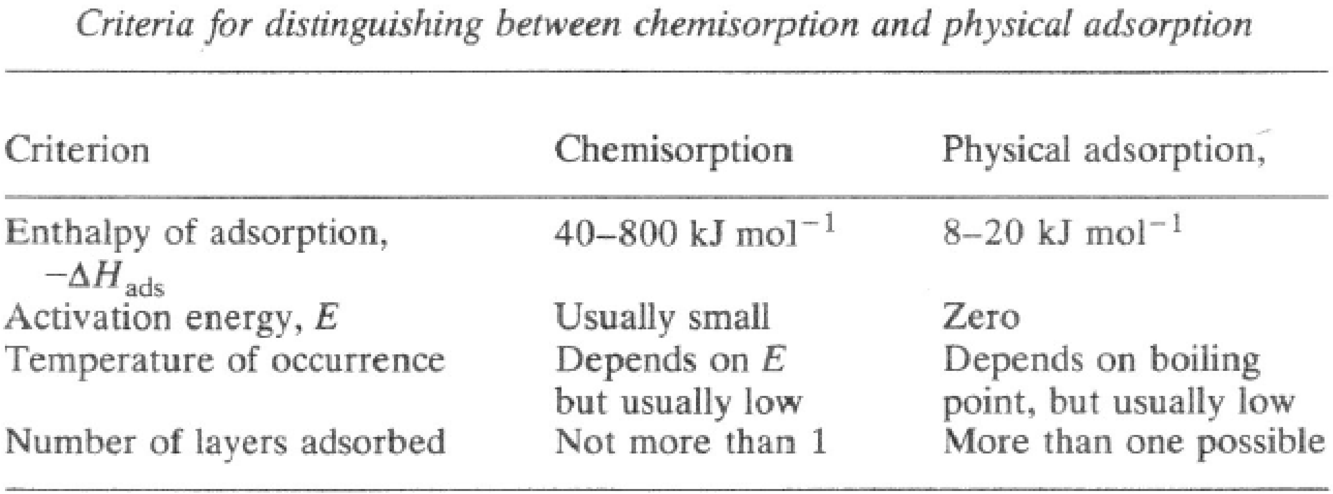
- Adsorption also involves a decrease in free energy

$$\Delta G = \Delta H - T\Delta S$$

$\Delta S < 0$ (more ordered when adsorbed)

Therefore, ΔH also must be negative, i.e., the adsorption of gas and vapors on solids is always an exothermic process.

Consequently, adsorption increases with decreasing temp.



Criteria for distinguishing between chemisorption and physical adsorption

Criterion	Chemisorption	Physical adsorption
Enthalpy of adsorption, $-\Delta H_{ads}$	40–800 kJ mol^{-1}	8–20 kJ mol^{-1}
Activation energy, E	Usually small	Zero
Temperature of occurrence	Depends on E but usually low	Depends on boiling point, but usually low
Number of layers adsorbed	Not more than 1	More than one possible

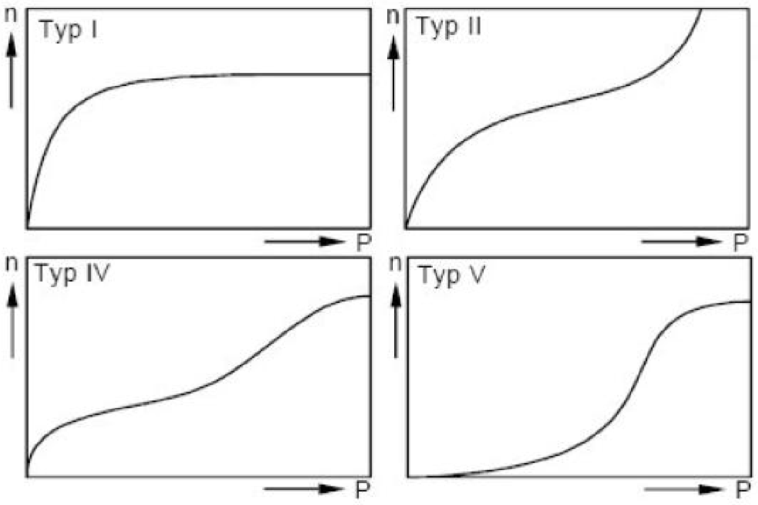
Physical Adsorption and Chemical Adsorption

- Physical adsorption equilibrium: rapid and reversible
- Multilayer physical adsorption is possible.
  - At saturation vapor pressure, physical adsorption becomes continuous with liquefaction.
- Only monomolecular chemisorbed are possible.

  - adsorption is relatively slow and not readily reversible.

Adsorption Isotherm

- How much gas adsorbs at equilibrium as a function of pressure
- Qualitative features of isotherms
  - Types 1-5

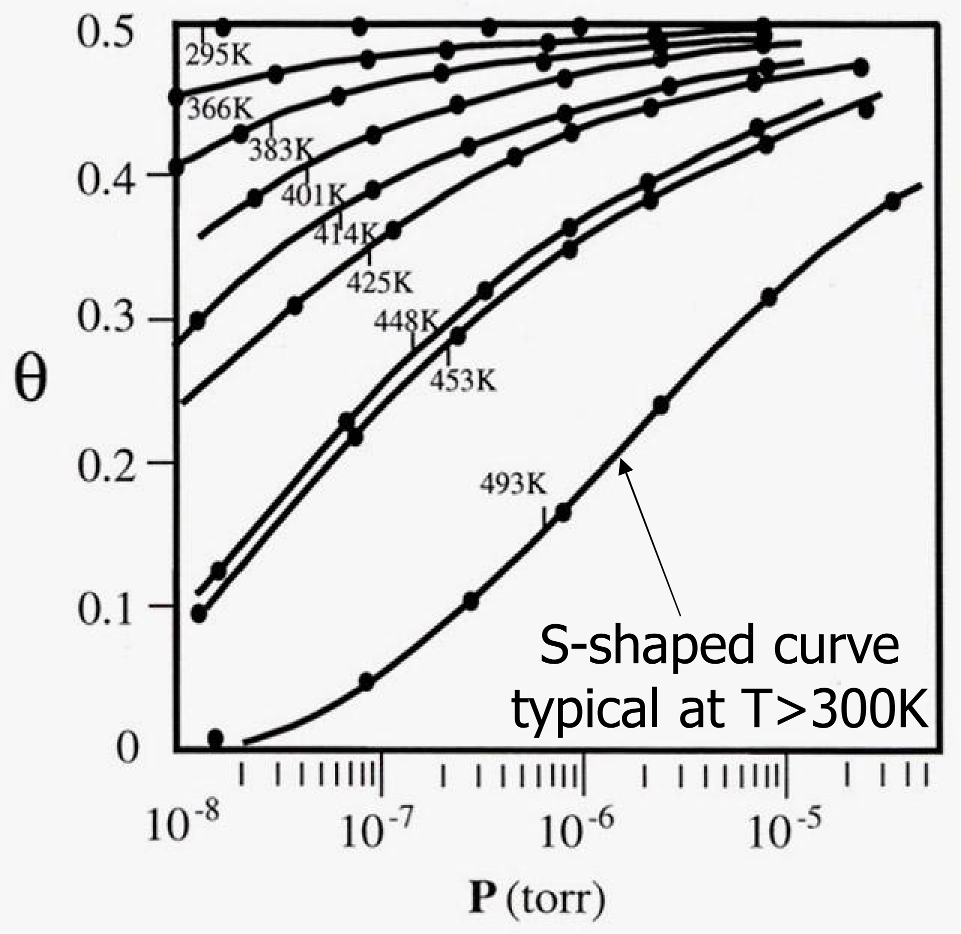


I Benzol/Silicagel bei 303,15 K,
II Wasser/Al_2O_3 bei 303,15 K,
III Brom/Silicagel bei 352 K,
IV Wasser/Silicagel bei 313 K,
V Wasser/Aktivkohle

Some examples of experimental adsorption isotherms

Adsorption Isotherms

- Adsorption Isotherm – amount adsorbed as a function of pressure



S-shaped curve typical at T>300K

Typical S-Shaped Adsorption Curve at Low Pressure

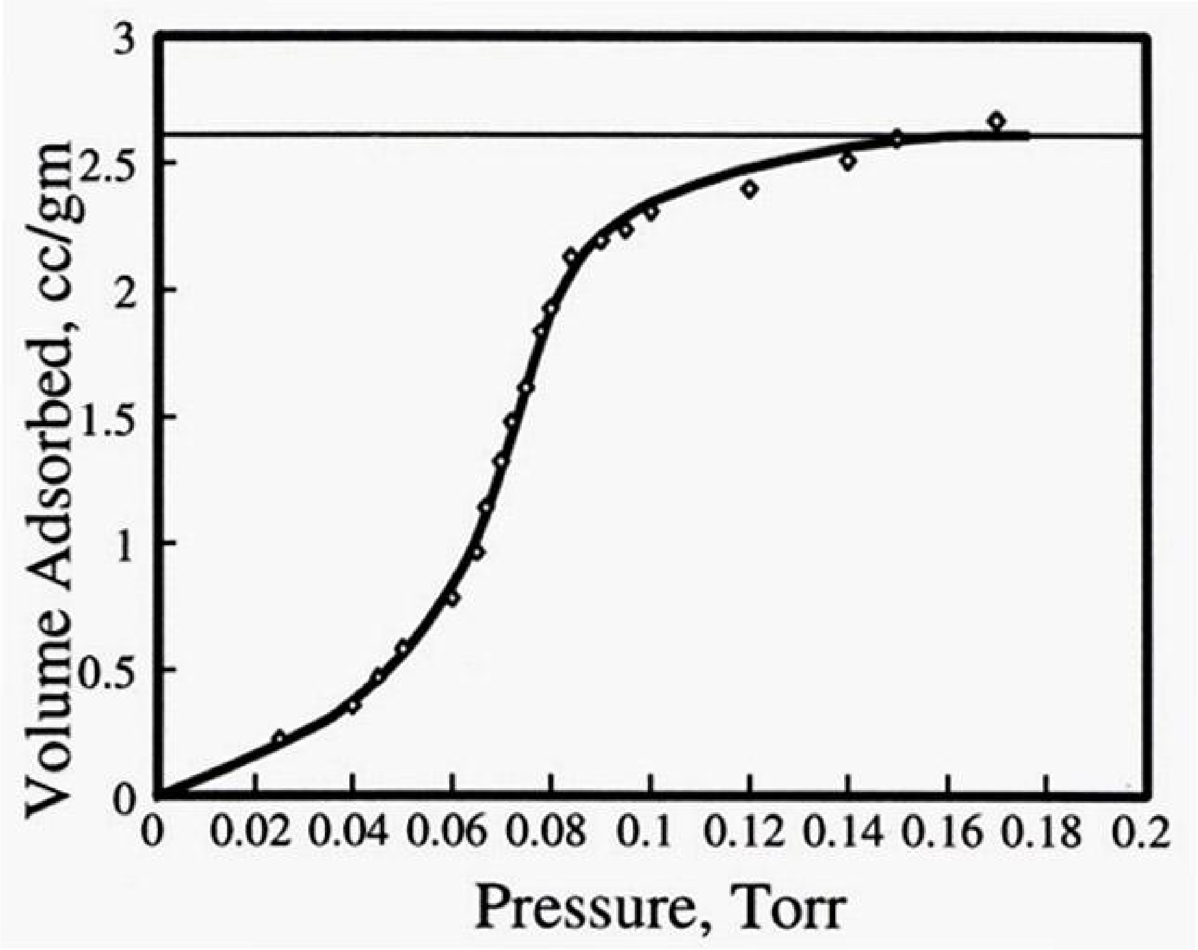


Figure 4.3 A blowup of the low-pressure part of the krypton data in Figure 4.2.

Langmuir's Model of Adsorption:

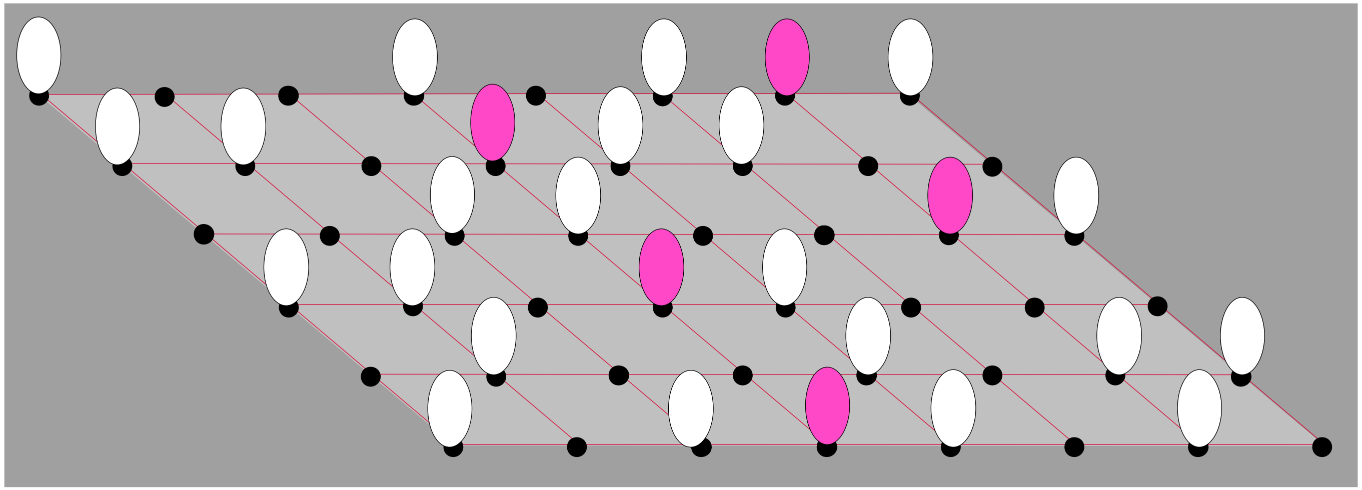


Figure 4.5 Langmuir's model of the structure of the adsorbed layer. The black dots represent possible adsorption sites, while the white and mauve ovals represent adsorbed molecules.

Key Features Of Langmuir's Model

- Finite sites to adsorb gas (all sites are identical)
- Ideal behavior in surface phase (no interactions between adsorbed molecules)
- At low pressures coverages proportional to pressure Eventually surface fills up
  - Adsorption limited by availability of sites
  - If multiple species – competition for sites
  - Maximum coverage 1ML

Kinetic Derivation of Langmuir's Model

Assume equilibrium

$$A_g + Site_{(vacant)} \underset{k_d}{\overset{k_{ad}}{\rightleftarrows}} A_{ad}$$

$$r_{ad} = k_{ad} P_A [Site]$$

$$r_d = k_d [A_{ad}]$$

At equilibrium $r_d = r_{ad}$
Solving

$$\frac{[A_{ad}]}{P_A [Site]} = \frac{k_{ad}}{k_d} = K$$

Suppose there are S sites altogether on solid surface and S_1 are occupied by adsorbed gas

∴ S-S_1 are vacant.

$A_{ad} = S_1$
$Site_{(vacant)} = S - S_1$

$$K = \frac{S_1}{P_A (S - S_1)}$$

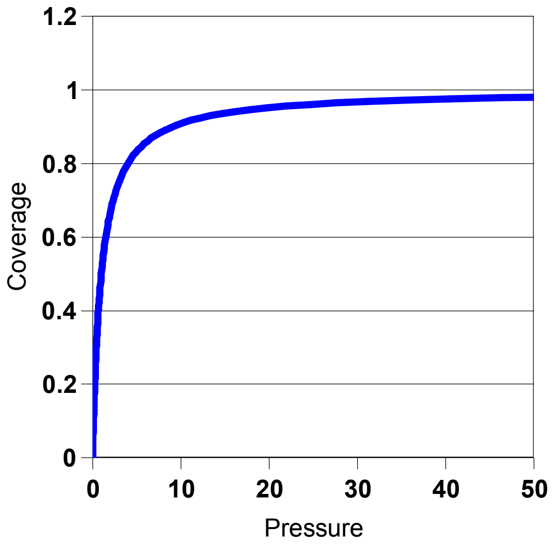
If θ=fraction of sites which are occupied

$$\theta = \frac{S_1}{S} = \text{fractional coverage of surface}$$

$$K = \frac{\theta}{P_A (1-\theta)} \rightarrow \theta = \frac{KP}{1+KP}$$

Langmuir Adsorption Isotherm

Features of Langmuir's Model

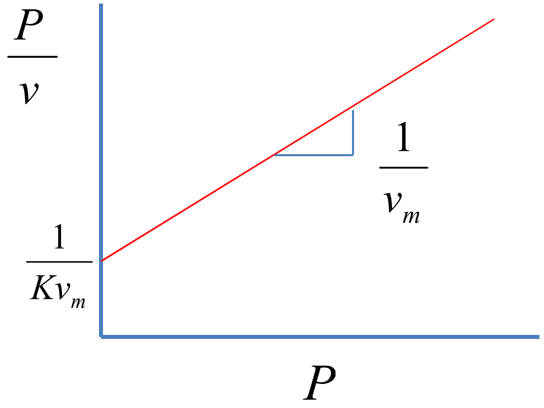


If θ=fraction of sites which are occupied

$$\theta = \frac{v}{v_m}$$

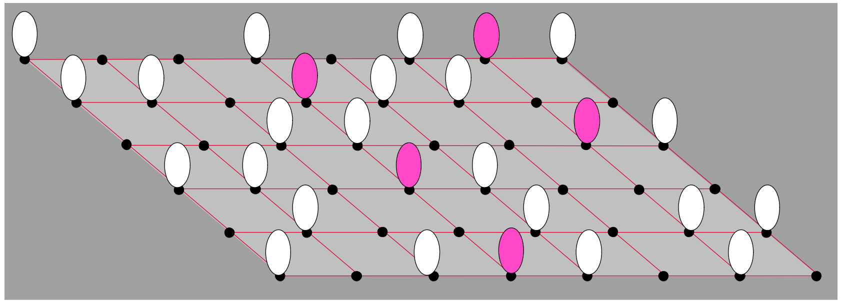
$$v_m = \text{vol of gas adsorbed in a monolayer}$$

$$v = \frac{v_m KP}{1+KP} \quad or \quad \frac{P}{v} = \frac{1}{Kv_m} + \frac{P}{v_m}$$



$$Plot\ \frac{P}{v}\ vs\ P \rightarrow straight\ line$$

Derivation Of Langmuir Isotherm For Competitive Adsorption



$$\frac{[A_{ad}]}{P_A[S]} = K^A_{equ} \qquad \frac{[B_{ad}]}{P_B[S]} = K^B_{equ}$$

$$[S] = [S_o] - [A_{ad}] - [B_{ad}]$$

Solving Equations Simultaneously

$$\theta_A = \frac{K^A_{equ} P_A}{1 + K^A_{equ} P_A + K^B_{equ} P_B} \qquad \theta_B = \frac{K^B_{equ} P_B}{1 + K^A_{equ} P_A + K^B_{equ} P_B}$$

Real Situation: Interactions Between Molecules

Attractive interactions lead to islands

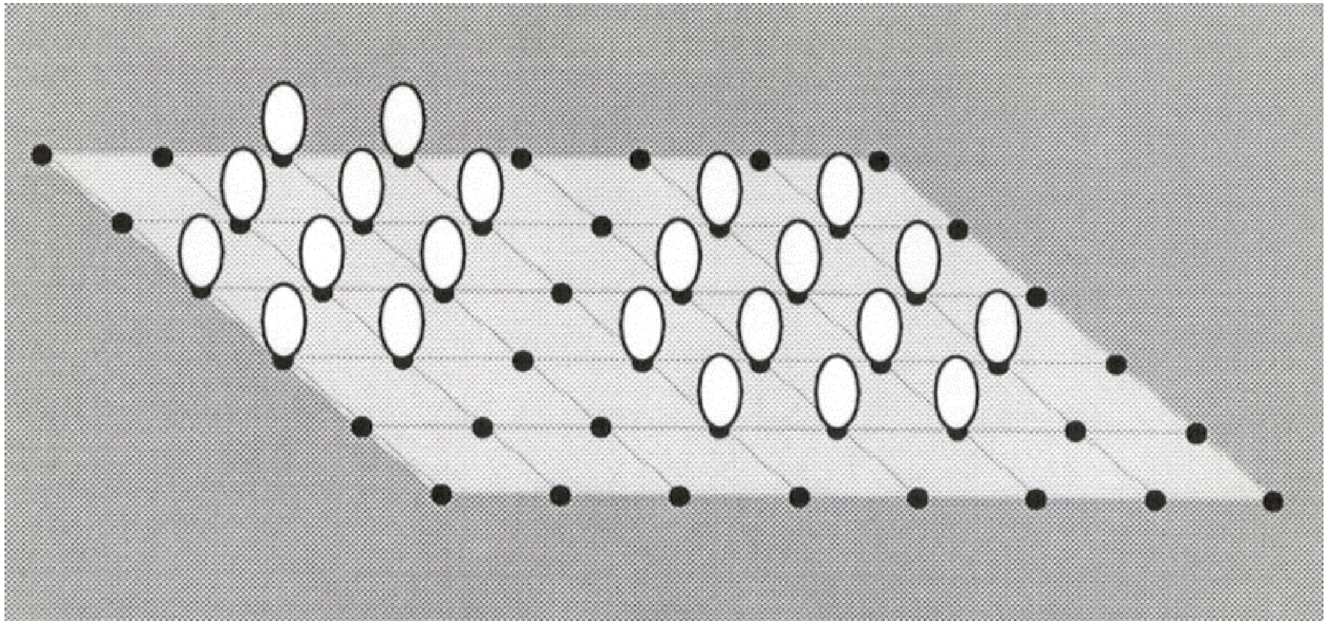


Figure 4.11 **A schematic of island formation on a square surface.**

Repulsive Interactions Order Overlayer Continued

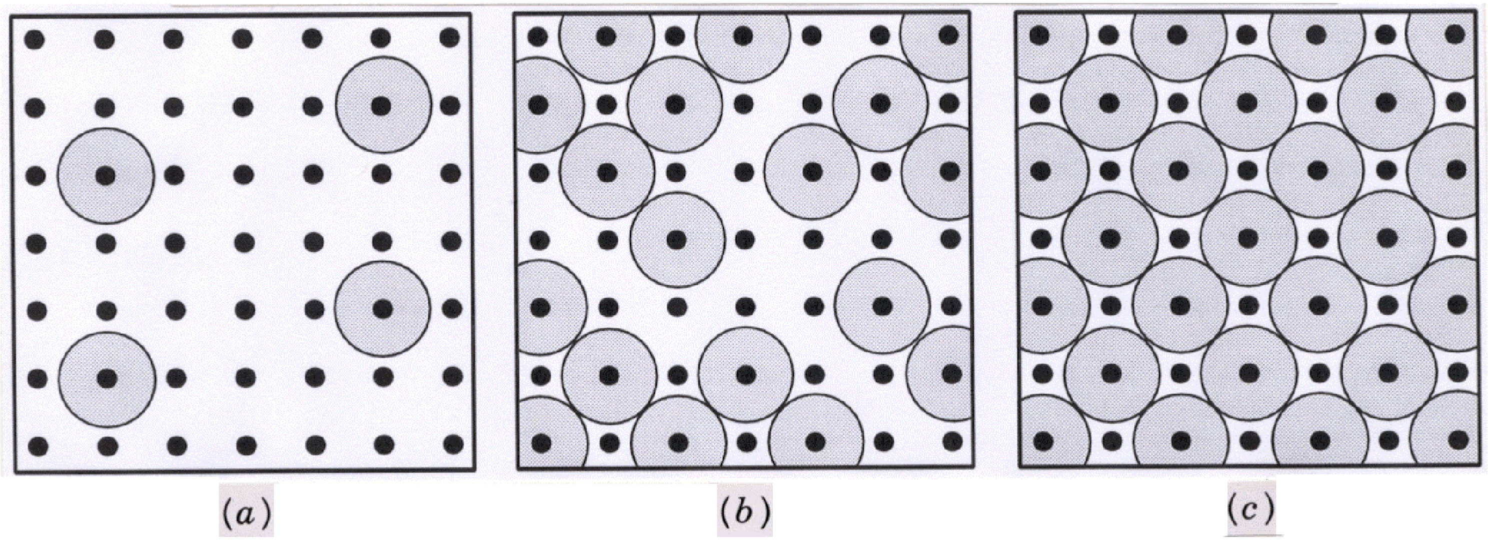


Figure 4.12 Schematic of the adsorbate arrangement that forms when a gas adsorbs onto a square lattice. The small dark circles are possible lattice sites. The large dotted circles are adsorbate molecules.

Complication: Multilayer Adsorption

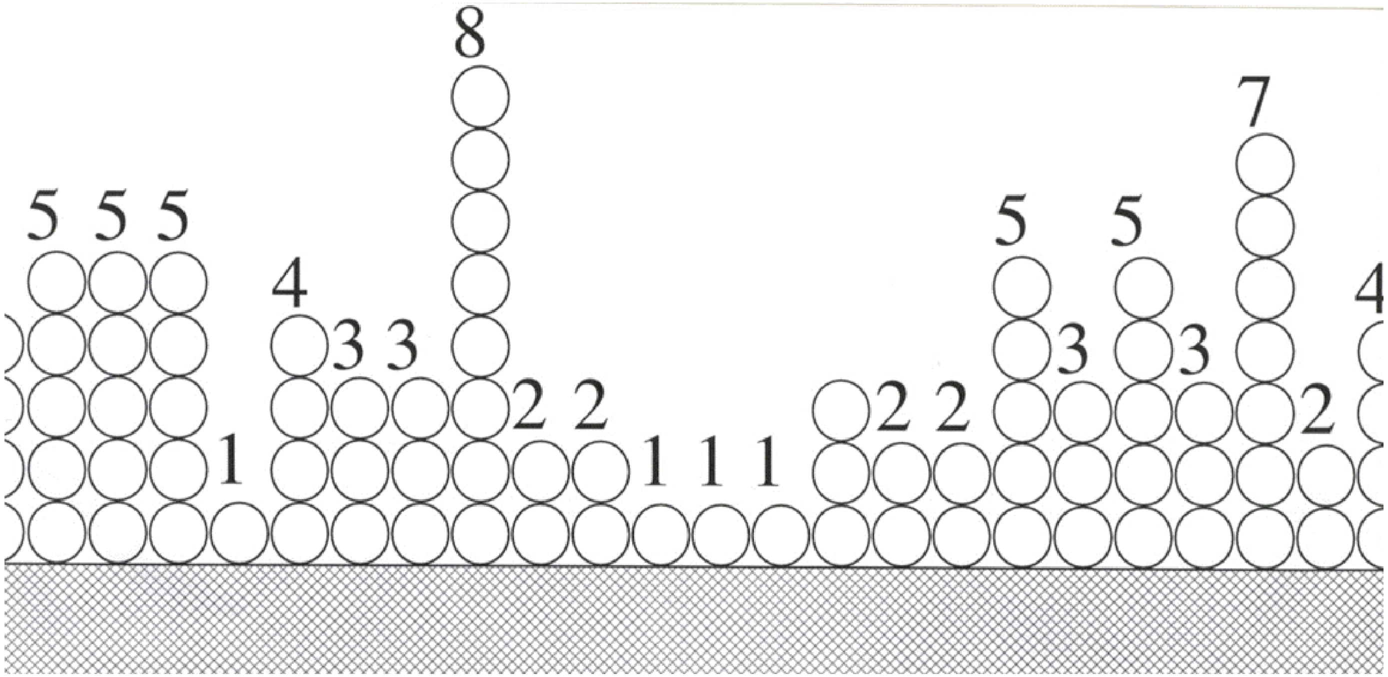
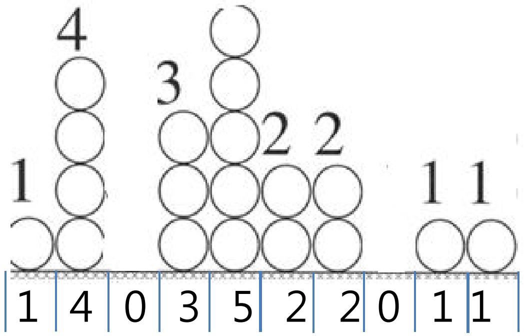


Figure 4.21 Brunauer’s model of multilayer adsorption; that is, a random distribution of sites covered by one, two, three, etc., adsorbate molecules.

Brunauer, Emmett & Teller (BET) Iotherm



Assumed:

1) Langmuir model applies to each layer
2) Adsorption & desorption only possible for exposed layer

S_0: no of sites with no adsorbed molecules
S_1: no of sites with 1 adsorbed molecules
S_2: no of sites with 2 adsorbed molecules
⋮

1st layer $$A_g + vacant\ site \Leftrightarrow A_{ad} \qquad K_1 = \frac{S_1}{PS_0}$$

2nd layer $$A_g + class\ 1\ site \Leftrightarrow A_{ad-2nd\,layer} \qquad K_2 = \frac{S_2}{PS_1}$$

ith layer $$K_i = \frac{S_i}{PS_{i-1}}$$

Then $S_1 = K_1 P S_0$

$S_2 = K_2 P S_1$

$\vdots$

$assumed \;\; K_2 = K_3 = K_4 = \cdots \; etc \neq K_1$

$Let \;\; y = K_1 P, \quad x = K_2 P = K_3 P = \cdots$

$c = K_1 / K_2 \; (= y / x)$

$S_1 = yS_0 = cxC$

$S_2 = xS_1 = cx^2 \, S_0$

$S_3 = xS_2 = cx^3 \, S_0$

$\vdots$

$S_i = xS_{i-1} = cx^i \, S_0$

Total no. of adsorbed molecules:

$$z = S_1 + 2S_2 + 3S_3 + \cdots + iS_i + \cdots$$

$$= \sum_{i=1}^{\infty} iS_i = \sum_{i=1}^{\infty} cS_0 ix^i = cS_0 \sum_{i=1}^{\infty} ix^i$$

Total no. of sites:

$$z_m = S_0 + S_1 + S_2 + \cdots$$

$$= \sum_{i=0}^{\infty} S_i = S_0 + cS_0 \sum_{i=1}^{\infty} x^i$$

$$\theta = \frac{z}{z_m} = \frac{cS_0 \sum ix^i}{S_0 + cS_0 \sum x^i}$$

$$But \quad \sum_{i=1}^{\infty} ix^i = \frac{x}{(1-x)^2} \quad (x < 1)$$

$$\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \quad (x < 1)$$

$$\theta = \frac{v}{v_m} = \frac{cx}{(1-x)^2} \frac{1}{1 + \frac{cx}{1-x}}$$

$$= \frac{cx}{(1-x)(1-x+cx)}$$

$$\theta = \frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)}$$

BET Equation

$$when\ P \to P_0 \quad v \to \infty$$

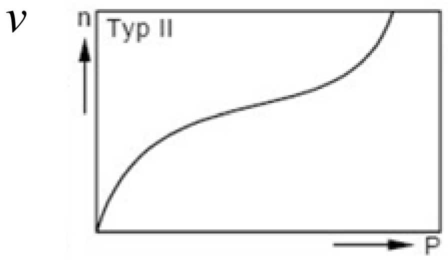
$$x \to 1$$

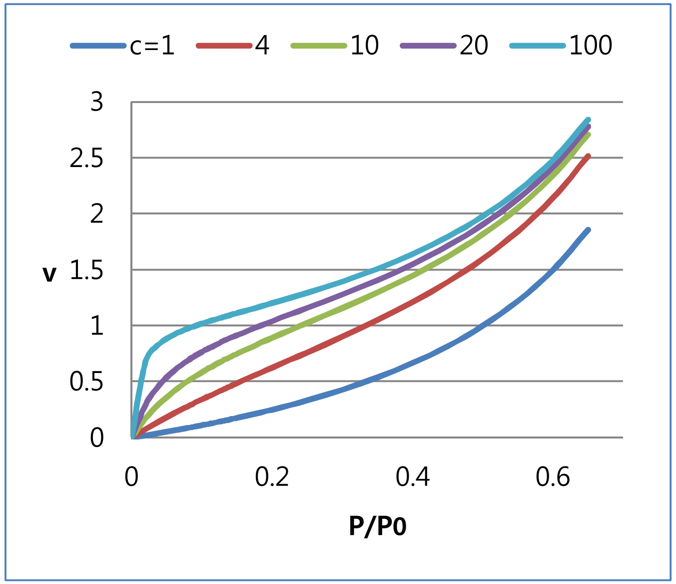
$$x = K_2 P$$

$$1 = K_2 P_0$$

$$K_2 = 1/P_0$$

$$x = P/P_0$$



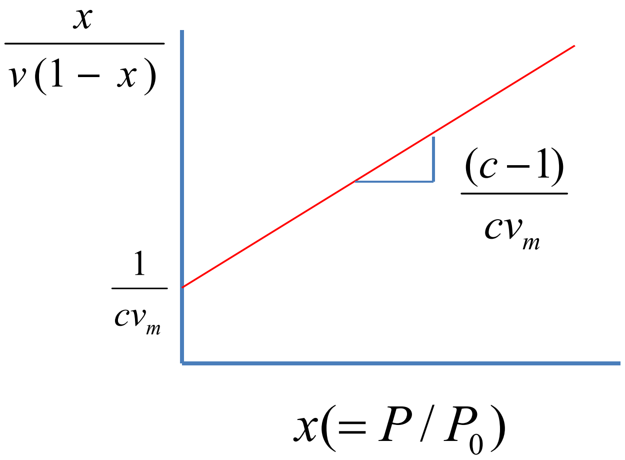


$$c = K_1 / K_2$$

Rearrange BET Eq.

$$\frac{x}{v(1-x)} = \frac{1}{cv_m} + \frac{(c-1)x}{cv_m}$$

$$Plot\ \frac{x}{v(1-x)}\ vs\ \ x \rightarrow straight\ line$$



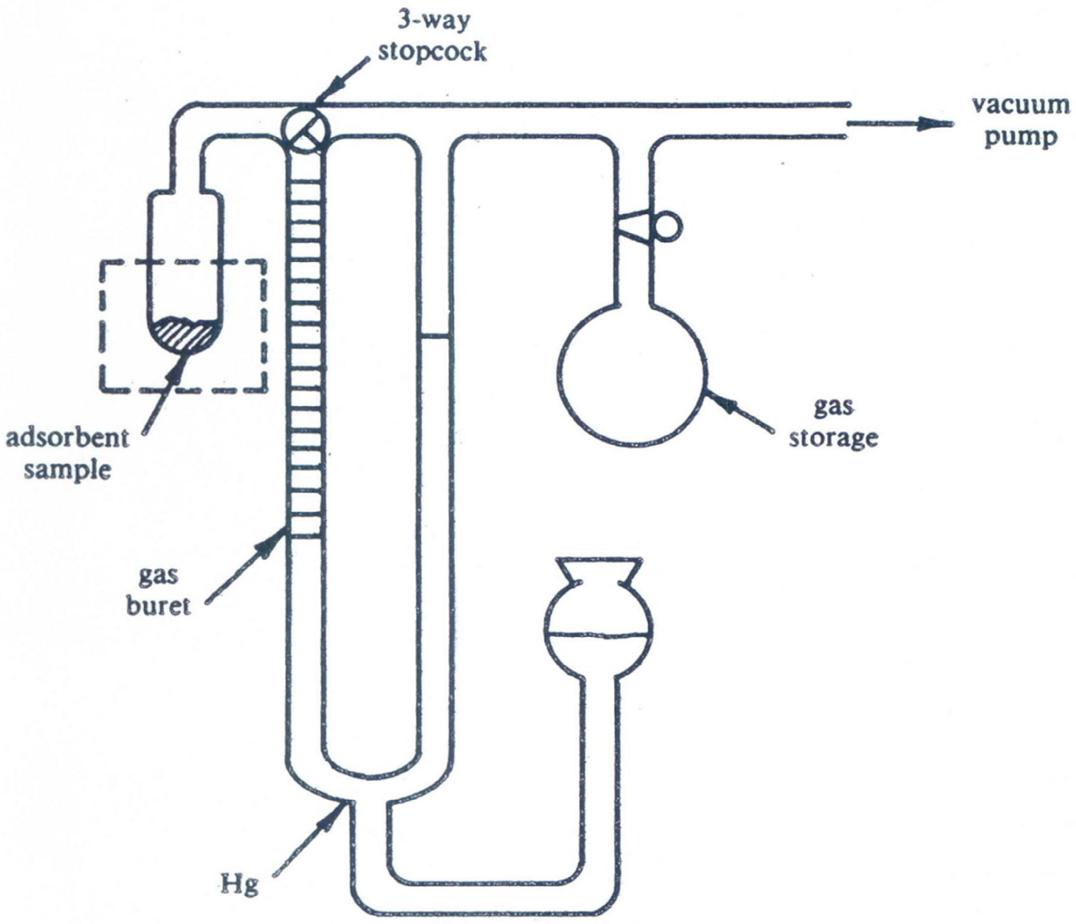


Figure 9.1 Schematic illustration of a gas adsorption apparatus.

Surface Area Measurement

- *Specific surface area:* S_m *, area/mass (cm^2/g, m^2/g)*

$$S_m = \frac{v_m N_{av} \sigma_0}{m v_0} \approx \frac{4.35}{m} v_m \ \ m^2/g \quad for\ N_2$$

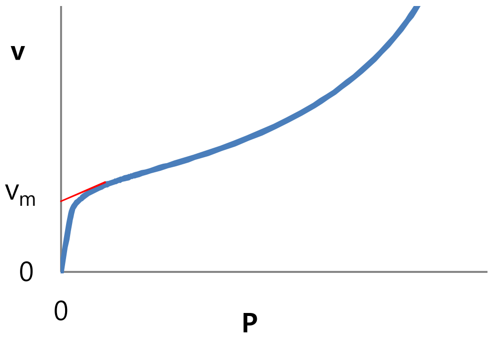
$N_{av} = avogadro's\ No$

$\sigma_0 = area/molecule\ in\ monolayer$

$v_0 = molar\ volume\ of\ gas$

$m = mass\ of\ sample$

Gas	$\sigma_0(\text{Å}^2)$
N_2	16.2
O_2	14.1
Ar	13.8
Kr	19.5

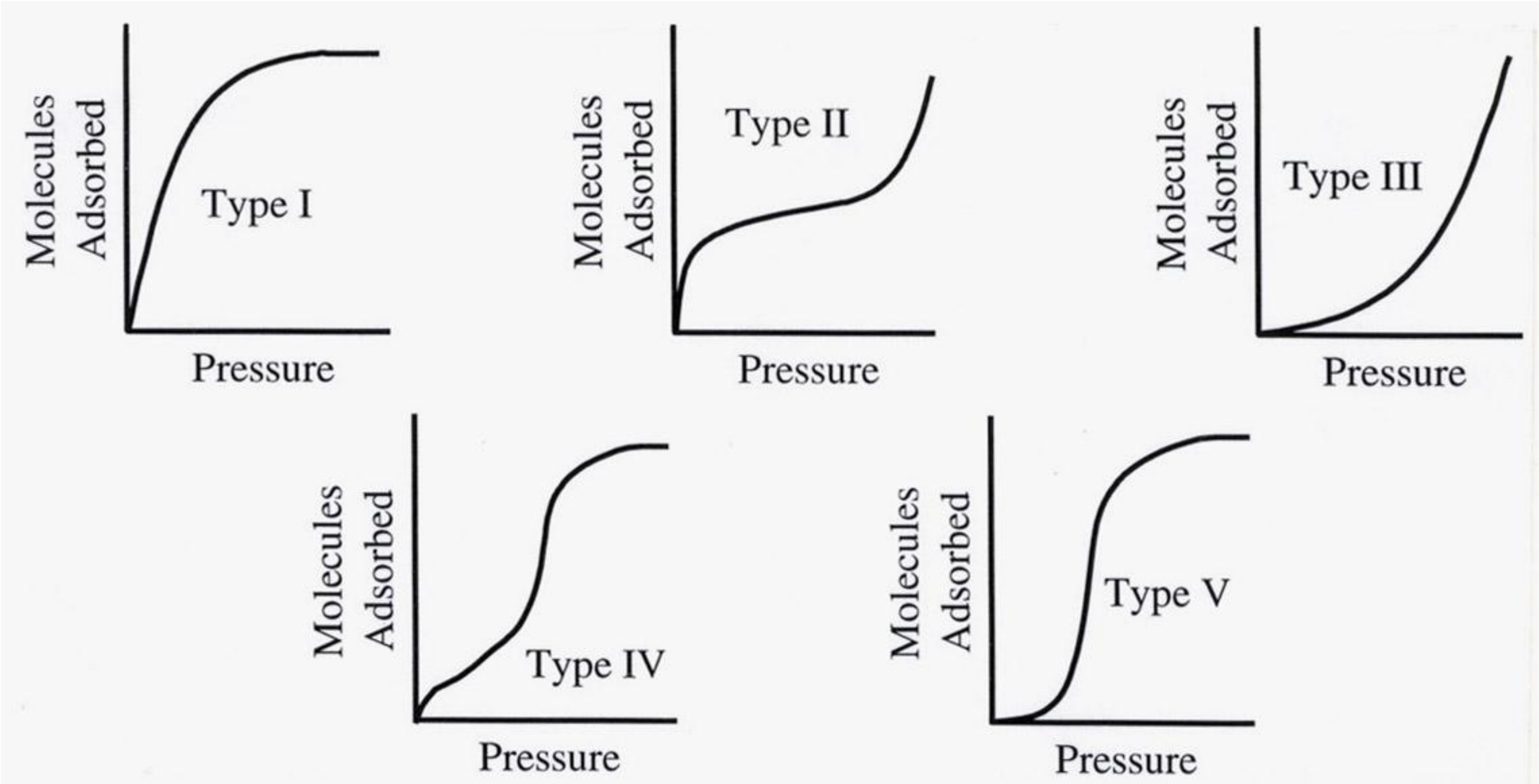


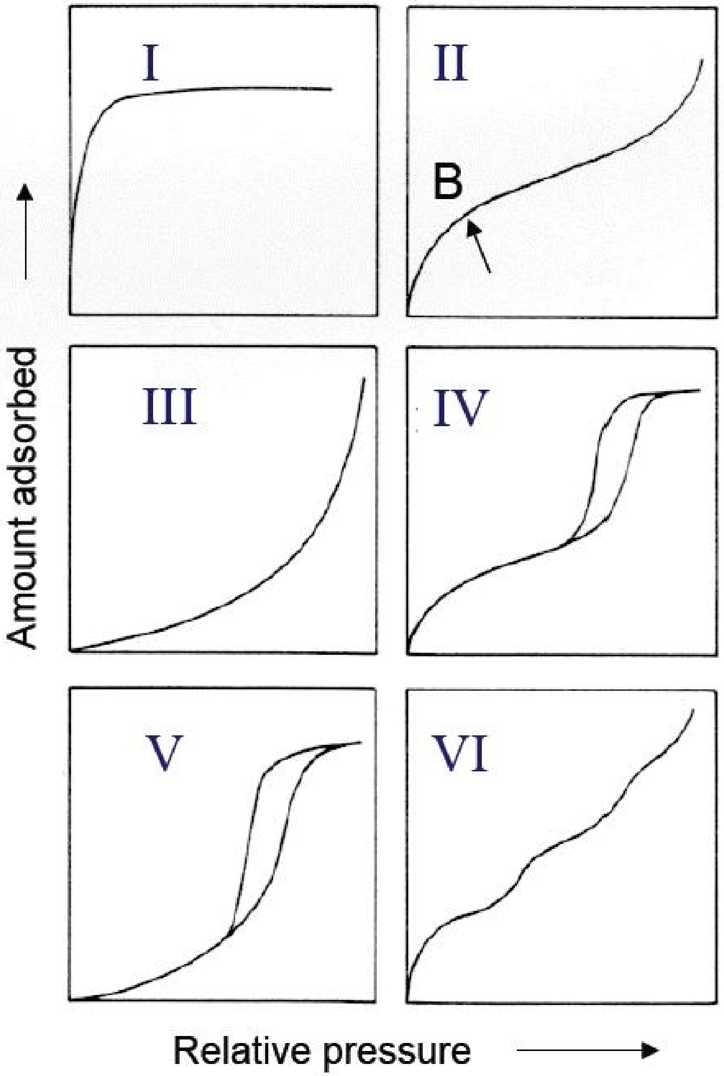
$$\theta = \frac{v}{v_m} = \frac{cx}{(1-x)^2} \frac{1}{1 + \frac{cx}{1-x}}$$

for large c

$$\frac{v}{v_m} \cong \frac{1}{1-x} \quad \text{'single point method'}$$

Why 5 Types Of Adsorption Isotherms?





Adorption in micropores

Adsorption limited to a few molecular layers

true chemisorption

Zeolites, active carbon

Unrestricted monolayer-multilayer adsorption

Nonporous or macroporous adsorbent

B monolayer coverage complete

Weak adsorbtive-adsorbent interactions

Nitrogen on polyethylene

Monolayer-multilayer adsorption and capillary condensation

Complete pore filling

Weak interactions and capillary condensation

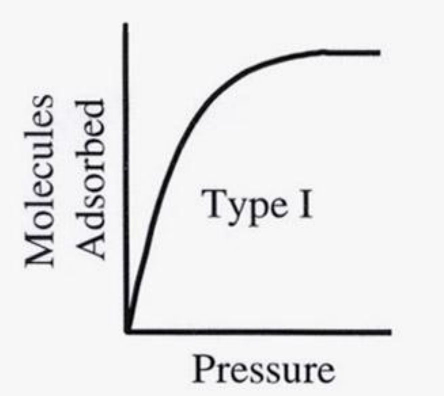
Stepwise multilayer adsorption on a nonporous non-uniform surface

Ar or Kr on graphitized carbon

The Type I isotherm is typical of microporous solids and chemisorption isotherms. Type II is shown by finely divided non-porous solids. Type III and type V are typical of vapor adsorption (i.e. water vapor on hydrophobic materials). Type VI and V feature a hysteresis loop generated by the capillary condensation of the adsorbate in the mesopores of the solid. Finally, the rare type VI step-like isotherm is shown by nitrogen adsorbed on special carbon

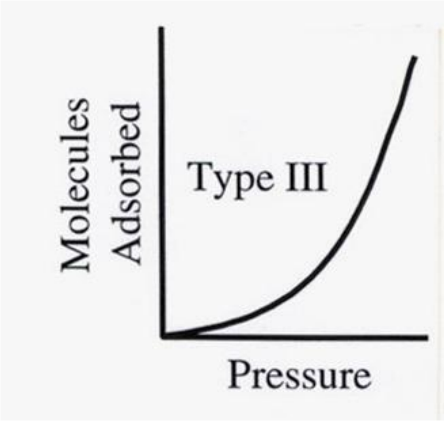
Type I

- Type I arises when only one type of site:
  - Initially surface fills randomly
  - Eventually saturates when surface filled (or pores filled with a porous material)



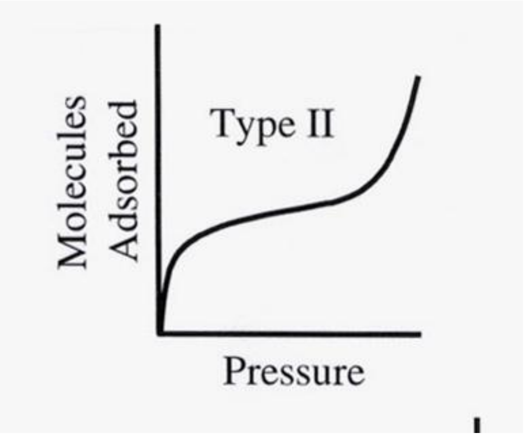
Type III

- Type III arises when there are strong attractive interactions leading to condensation
  - Initially, no adsorption
  - Pressure increases lead to nucleation and growth of islands
  - Eventually liquids condense on the surface



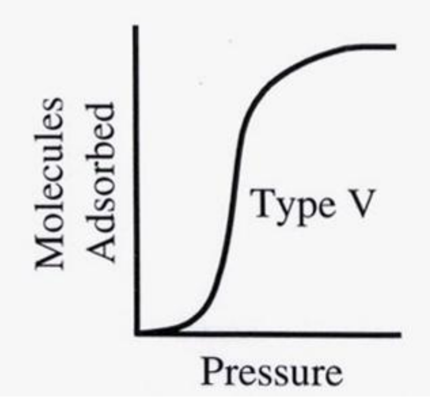
Type II

- Type II arises when the is more than one adsorption site
  - Initial rapid adsorption
  - Saturates when first site filled
  - Second rise when second site fills
- Second site could be a second monolayer, a second site on the surface. In porous materials, it can also be a second type of pore.



Type V

- Type V is another case for attractive interactions
  - Initially no adsorption
  - Next nucleation and growth of islands or liquid drops
  - Coverage saturates when no more space to hold adsorbates



Type IV

- Type V occurs when there are multiple phase transitions due to a mixture of attractive and repulsive interactions
- Can also arise in multilayer adsorption where adsorption on second layer starts before first layer saturates