ADSORPTION

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Adsorption

- The action of a substance in attracting and holding other materials or particles on its surface

Absorption

- uniform distribution of the substance throughout the bulk, e.g. solution of hydrogen in palladium, solution of gases in liquids.

Sorption

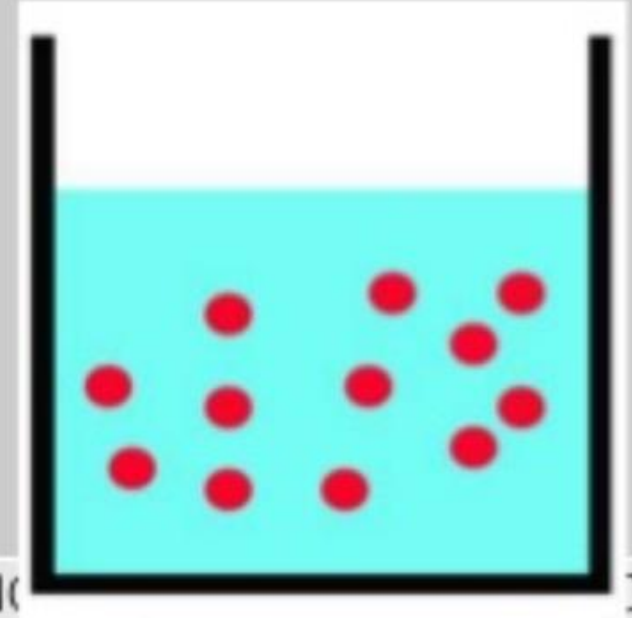
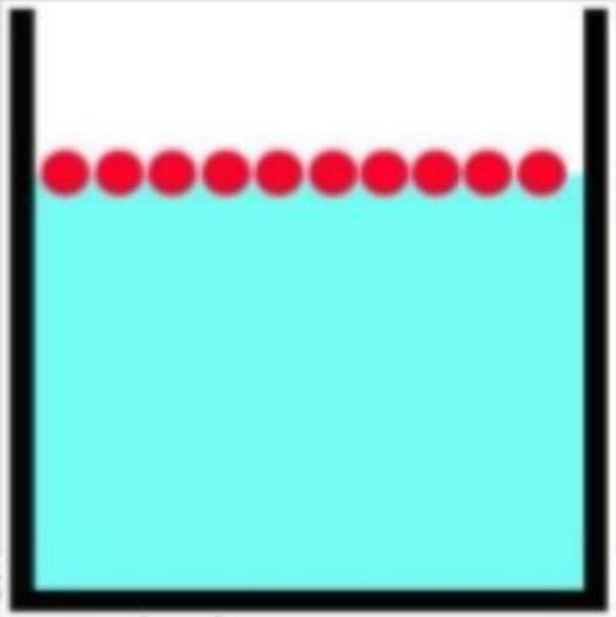
Sorption= Absorption + Adsorption

Desorption

- ADSORBENT: The best adsorbents have coarse pores. For example: silicagel, coal, kaolin, various clays, Kieselguhr.
- ADSORBATE: The substance that has been or is to be adsorbed on a surface/interface.

- LIQUID-LIQUID INTERFACE
- SOLID INTERFACE
- SOLID-GAS INTERFACE

Adsorption at the liquid interface

NEGATIVE ADSORPTION	POSITIVE ADSORPTION
Molecules partitioned in favour of bulk	Molecules partitioned in favour of surface/interface
Increase in the surface tension	Decrease in the surface tension
	
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Adsorption at solid interface

- This is mainly the case for decolorization solutions, chromatography, detergents…
- This adsorption process is just like adsorption at liquid surfaces.

Solid gas interface

- The adsorption event occurs as follows:
- The ion atoms or molecules that form the solid are bonded to each other by bonds
- They are drawn in all directions. Since the forces on the surface of the solid are unbalanced, there will be an attraction force.
- The attraction forces perpendicular to the surface attract particles inside. The energy that draws it is the potential energy of the interior particles
- Meanwhile, the surface particles attract other particles.

Adsorption of Gases by Solids:

- 1) Physical Adsorption (van der waals Adsorption),
- 2) Chemical Adsorption (Active Adsorption).

Physical Adsorption	Chemical Adsorption
Weak van der waals forces	Chemical bonds (ionic or covalent)
Adsorption heat is low	Adsorption heat is high
It is reversable (desorption with temperature increase or pressure reduction)	Irreversible
No activation energy required	Activation energy required
Forms at low temperature and adsorption decreases as temperature increases	Initially adsorption increases with temperature
Non specific	Depends on the formation chemical bonds
A multi-molecular layer is formed	A mono molecular layer is formed

Adsorption Measurement - Adsorption Isotherms:

The relation between the amount of adsorbed matter by the adsorbent at constant temperature and equilibrium pressure or equilibrium concentration are given by adsorption isotherms.

1. Freundlich isotherm
2. Langmuir isotherm
3. BET isotherm (Brunauer-Emmett-Teller)

Freundlich Isotherm

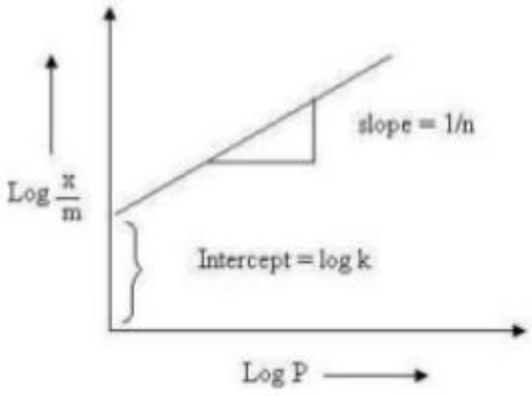
- In 1909, Freundich gave an empirical expression representing the isothermal variation of adsorption of a quantitiy of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as “Freundlich Adsorption Isotherm” or “Freundlich Adsorption Equation”

As per Freundlich adsorption equation

$x/m = k P^{1/n}$

Taking log both sides of equation, we get,

$\log \{x/m\} = \log k + 1/n \log p$



where ‘x’ is the mass of the gas adsorbed on mass ‘m’ of the adsorbent at pressure ‘P’. ‘k’ and ‘n’ are constants that depend on the nature of the adsorbent and the gas at a particular temperature.

Freundlich isotherm only approximately explains the behaviour of adsorption. The value of 1/n can be between 0 and 1, therefore the equation holds good only over a limited range of pressure.

- When $1/n = 0$, x/m is constant, the adsorption is independent of pressure.

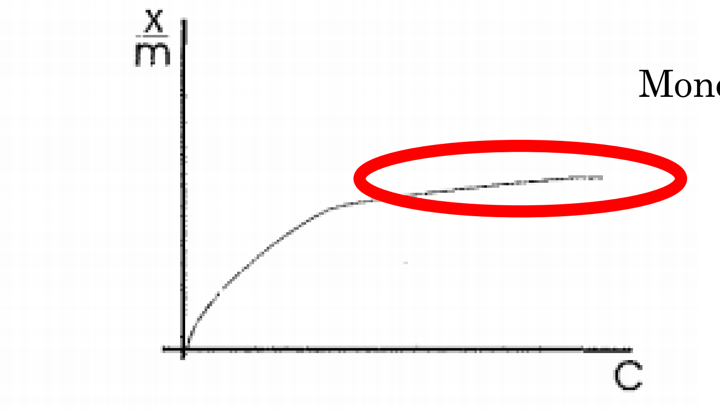
- When $1/n = 1$, $x/m = kP$, i.e. $x/m \propto P$, adsorption is directly proportional to pressure.

Langmuir isotherm:

Assumptions:

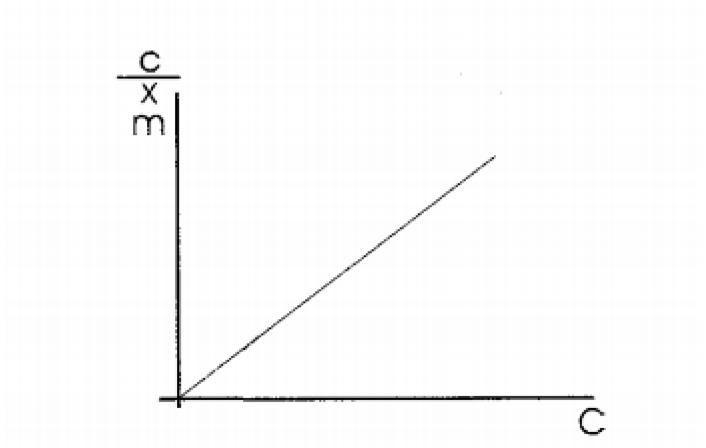
- Monolayer adsorption
- There are unfilled sites on the adsorbent
- adsorption energy on all sides of the surface is the same
- there is no interaction between the molecules retained on the surface.

- The amount of adsorbed gas initially increases with pressure, after a while it reaches its maximum and remains constant despite the pressure increase.
- The point at which the isotherm reaches the plateau indicates the formation of the monolayer on the solid is complete, from which the specific surface area of the solid can be calculated.



Monolayer formation

Langmuir isotherm



$$\frac{x}{m} = \frac{abc}{1+ac}$$

$$\frac{c}{x/m} = \frac{1}{ab} + \frac{1}{b}c$$

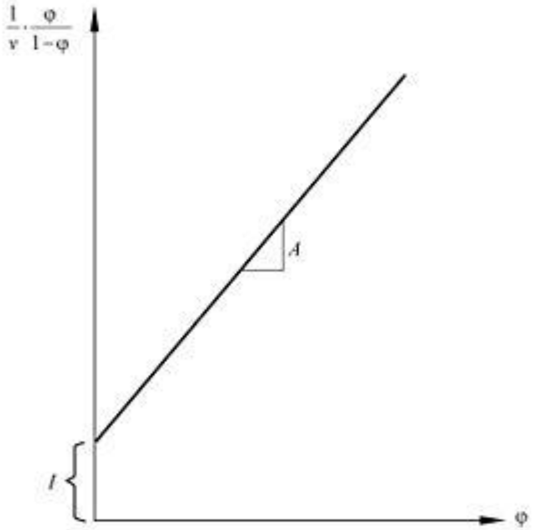
Liner-Langmuir isotherm

- a: adsorption coefficient (gives the value of the interaction between the adsorbed molecules and the bound molecules)
- b: maximum adsorption capacity

BET isotherm :

- Brunauer, Emmett and Teller in 1938 extended Langmuir's ideas to cover adsorption where more than one molecular layer could form. This situation occured at low temperatures and at pressures approaching saturation pressure when an S-shaped isotherm was obtained.
- The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules.
- The most reliable method

$$\frac{1}{v\left[(p_0/p)-1\right]} = \frac{c-1}{v_{\mathrm{m}} c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c},$$



where p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity (for example, in volume units), and v_{m} is the monolayer adsorbed gas quantity. c is the *BET constant*,

Factors Affecting Adsorption:

1) Surface area of the adsorbent: If the surface of the adsorbent material is large, the adsorption will be high.

2) The pressure of the gas used or the concentration of the solution: In dilute solutions, the adsorption is higher than the concentrated solutions.

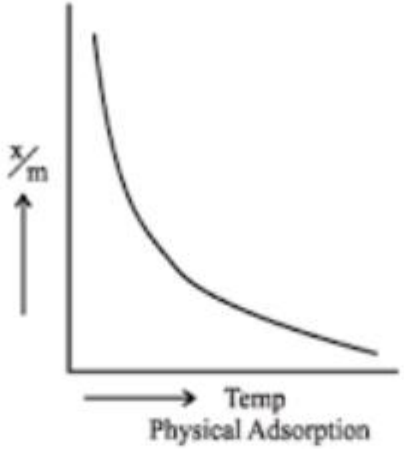
Factors Affecting Adsorption:

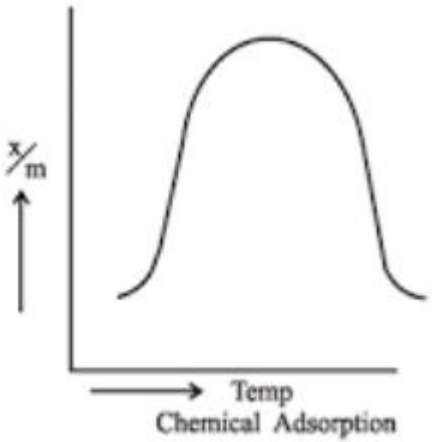
- 3) Effect of solvent: Adsorption is easier to see in solvents where solids are easily dissolved

- 4) Attraction between adsorbent and active ingredient: Adsorbents are different in their ability to adsorb various active substances.

Factors Affecting Adsorption:

- 5) Effect of temperature: Physical adsorption is an exothermic event. At low temperature adsorption is higher. However, the chemical adsorption first increases with rise in temperature and then starts decreasing. The initial increase shows that like chemical reactions, chemical adsorption also needs activation energy.





Factors Affecting Adsorption:

- 6) Effect of the solution pH: If the solid is an electrically charged ion or colloid particle, the effect of pH is an important parameter. The pH of the solution affects the degree of dissociation of the adsorbed material and is more easily adsorbed than non-dissociated molecules.

- 7) Effect of surface active agent: As the surface activity increases, the adsorption increases.

Technological Applications of Adsorption

- Adsorption at solid-gas interface
  - Construction of gas masks
  - Elimination of bad odors from the environment and food
  - Catalysis of gas reactions

- Adsorption at solid-liquid interface
  - Solution color removal
  - Wetting
  - Detergent cleaning
  - Adsorption of bacteria and foreign substances in the water via sand filters
  - Adsorption chromatography
- Adsorption at the liquid-gas interface
  - Foam formation and stabilization

Other examples of adsorption

- Activated charcoal is used as an antidote in various drug poisoning.
- Adsorption of active agents to primary packaging