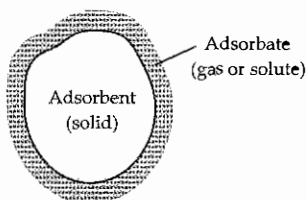


Surface Chemistry

- Surface chemistry can be roughly defined as the study of chemical reactions at interface of two bulk phases. The bulk phases may be solid-gas, liquid-liquid, liquid-gas. Surface chemistry includes heterogeneous catalysis, adsorption, and it also overlaps with electro-chemistry.

ADSORPTION

- The phenomenon of attracting and retaining the molecules of a substance on the surface of a solid or a liquid resulting into higher concentration of the molecules on the surface than in the bulk is called **adsorption**.
- The molecular species which accumulates at the surface is known as **adsorbate** and the material on whose surface the adsorption takes place is called **adsorbent**.



- The adsorption of gases on metal surfaces is called **occlusion**.

Key points

Adsorption + absorption \longrightarrow **sorption**
 Reverse of adsorption \longrightarrow **desorption**

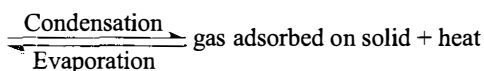
- **Types of adsorption** : Depending on forces which hold the adsorbate on the surface of adsorbent, adsorption is divided into two classes.
 - **Physical adsorption** : When the particles are held to the surface by the physical forces like van der Waals forces, the adsorption is called physical adsorption or physisorption. The extent of physical adsorption decreases with increase in temperature since it is an exothermic reaction.
 - **Chemical adsorption** : When the particles are held to the surface by the chemical forces or by chemical bonds, the adsorption is called chemical adsorption or chemisorption. With increase in temperature chemisorption increases to some extent and then decreases.

Characteristics of Adsorption

Property	Physisorption	Chemisorption
Enthalpy	Low enthalpy, is the order of 20-40 kJ mol ⁻¹	High enthalpy, is the order of 80-240 kJ mol ⁻¹
Reversibility	Reversible process	Irreversible process
Effect of temperature	With the increase in temperature, extent of adsorption decreases because adsorption is an exothermic process and kinetic energy of gas molecules increases with temperature.	Chemisorption first increases with temperature upto a certain extent and then decreases. A gas adsorbed at low temperature by physical adsorption may change into chemisorption at high temperature.
Selectivity	Not selective in nature. Does not depend upon the nature or chemical properties of gas and adsorbent.	Highly selective in nature. Depends upon the nature of gas and adsorbent.
Nature and state of adsorbate	The extent of adsorption depends upon the ease of liquefaction of the gas.	The state of adsorbed molecules may be different from that in the bulk.
Activation energy	No appreciable energy needed.	High activation energy needed.
Pressure	Increase in pressure increases adsorption.	Increase in pressure decreases adsorption.
Layers	Multimolecular layer.	Mono-molecular layer.

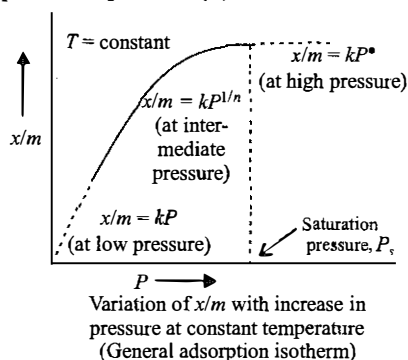
Factors Affecting Adsorption of Gases on Solids

- **Nature of adsorbate (gas)** : More readily soluble and easily liquefiable gases such as NH_3 , HCl , SO_2 , Cl_2 etc. are adsorbed more easily than the permanent gases such as H_2 , N_2 and O_2 . The ease of liquefaction of gases depends on its critical temperature. Higher the T_c , more easily it will liquefy.
- **Nature of adsorbent (solid)** : The substance which is highly porous or finely divided, will have large adsorption power. Most common adsorbents are activated carbon, silica gel, aluminium oxide and clay.
- **Surface area of solid** : The surface area per gram of the adsorbent is called specific area. Larger is the specific area of solid, greater will be the adsorbing capacity.
- **Temperature** : Adsorption is an exothermic process therefore as temperature increases, adsorption decreases. Gas (adsorbate) + solid (adsorbent)

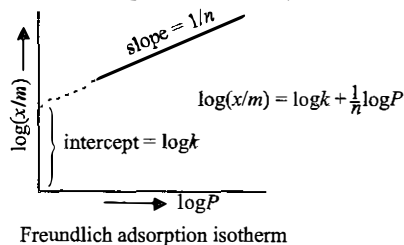


But chemisorption first increases with temperature and after a particular extent, decreases with increase in temperature.

- **Pressure** : At constant temperature, the adsorption of a gas increases with increase in pressure.
- **Adsorption isotherm** : A graph between the amount (x/m) adsorbed by an adsorbent and the equilibrium pressure of the adsorbate at a constant temperature is called the adsorption isotherm.
- A relationship between the amount adsorbed (x/m) and the equilibrium pressure (P) can be obtained as follows:



- In the intermediate range of pressure $x/m = kP^{1/n}$ (was originally put forward by Freundlich and is known as **Freundlich adsorption isotherm**).



- This type of adsorption is also affected by temperature and concentration.

$$i.e., x/m = kC^{1/n} \quad (\text{where } n > 1).$$

Drawbacks of Freundlich adsorption isotherm

- Role of surface area of adsorbent is not considered.
- It is only applicable for physical adsorption because it considers multimolecular layer of adsorption.
- Unable to explain why the degree of adsorption is constant at higher pressure.
- **Langmuir adsorption isotherm** : Langmuir postulated the following theory of adsorption.
- Gases form unimolecular layer of adsorption on the surface of adsorbate.
- Dynamic equilibrium exists on the surface of the adsorbent *i.e.* two opposite processes take place simultaneously on the surface of adsorbent.
- Gases undergoing adsorption behave ideally.
- According to Langmuir, the degree of adsorption is directly proportional to the θ , *i.e.*, fraction of surface area occupied.

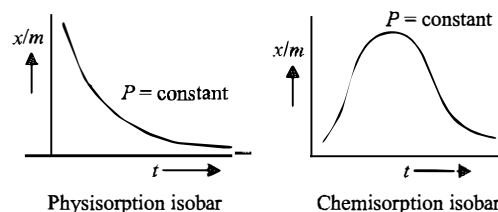
$$\frac{x}{m} \propto \theta = \frac{x}{m} = k_3 \theta$$

$$\frac{x}{m} = k_3 \cdot \frac{bp}{1+bp} \quad \text{or} \quad \frac{x}{m} = \frac{ap}{1+bp}$$

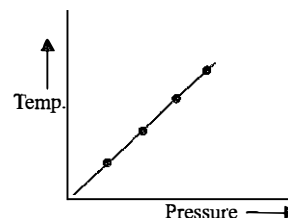
[Langmuir adsorption isotherm]

where $k_3 b = a$, another constant.

- A graph drawn between degree of adsorption (x/m) and temperature t at a constant pressure of adsorbate gas is known as **adsorption isobar**.



- The plot of temperature versus pressure for a given amount of adsorption is called **adsorption isostere**.



CATALYSIS

- Berzelius first used the term catalyst to describe a substance which accelerates the rate of chemical reaction. Berzelius defined the term catalysis as "the phenomenon in which the presence of a foreign substance speeds up the reaction rate without being used up in that reaction" and the substance which is used for the catalysis is known as catalyst. Therefore "catalyst is a substance which can change the speed of a reaction without being used up in that reaction." Catalyst decreases the activation energy of a chemical reaction without itself being changed at the end of the chemical reaction.