



Surface Chemistry



It deals with the phenomena that occurs at **surfaces or interfaces**

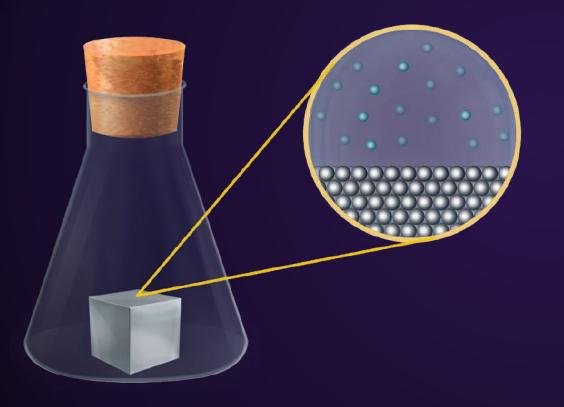
Surface or interface is represented by separating the **bulk** phases by a hyphen or a slash. E.g., solid-gas or solid/gas

The bulk phases that we come across in surface chemistry may be **pure compounds or solutions**. Surface/Interface: Boundary that separates two bulk phases

Bulk: Present in large amounts



Solid-gas (solid/gas)



Liquid-liquid (liquid/liquid)



Surface/Interface



There is **no interface** between gases, due to complete **miscibility**

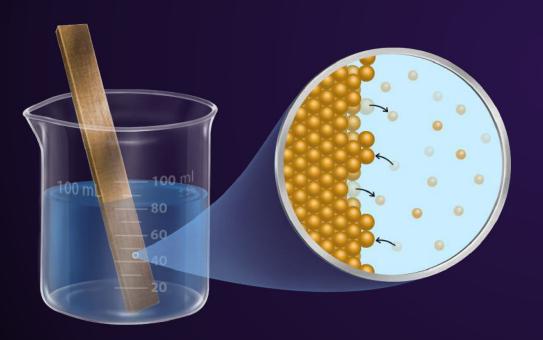
The surface/ interface is normally a **few molecules thick**.

Its **area** depends on the **size** of the particles of **bulk** phases.

Applications



Surface chemistry finds many applications in **industry, analytical work, and daily-life situations**.



Electrochemical equilibrium at solid liquid interface





Clean Surfaces



Every surface can't be considered to conduct surface studies meticulously.

Ultra clean surfaces are required to conduct the surface studies.

Such metal surfaces are obtained under very **high vacuum** (10⁻⁸ to 10⁻⁹ Pa)

Need to be stored in vacuum otherwise they interact with air (e.g.: O_2 , N_{2} , etc.)

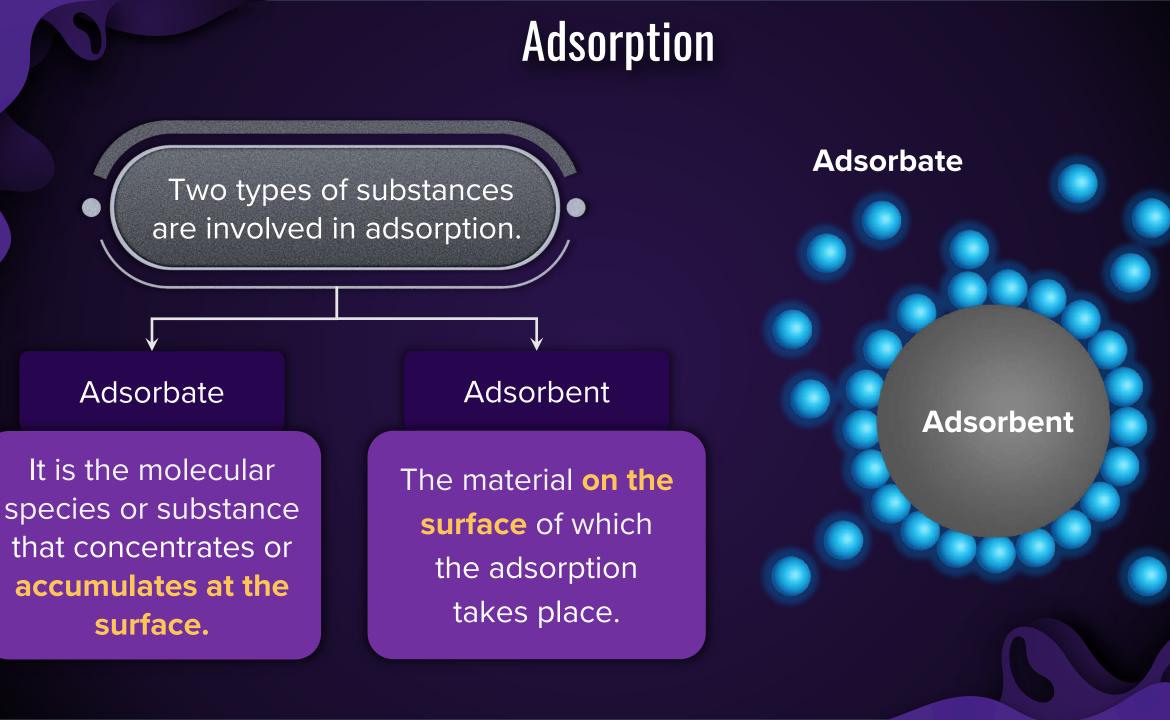
Adsorption

B

Solid surface has tendency to **attract and retain** other phase particles.

Such particles **remain at surface** without moving deep into the bulk.

It is the **accumulation** of molecular species at the **surface** rather than in the bulk of a solid or liquid.



Adsorption



Adsorption is essentially a **surface phenomenon**.

Solids, particularly in finely divided state have large surface area. **Gases** like O_2 , H_2 , CO, CI_2 , NH₃, or SO₂ are taken in a closed vessel containing **charcoal**

Examples

Therefore, charcoal, silica gel, alumina gel, clay, etc. act as **good adsorbents**. The **air** becomes **dry** in the presence of **silica gel**.

Desorption



Desorption

The process of removing an adsorbed substance (adsorbate) from a surface on which it is adsorbed (adsorbent).

Absorption



Example

Anhydrous CaCl₂

The phenomenon in which the particles of gas or liquid get **uniformly distributed** throughout the **body** of the solid.

Absorption vs Adsorption



Absorption	Adsorption
The substance is uniformly distributed throughout the bulk of the solid.	The substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent.
The concentration is uniform throughout the bulk of the material.	The concentration of the adsorbate increases only at the surface of the adsorbent.

Absorption vs Adsorption



Absorption	Adsorption
lt is a bulk phenomenon.	It is a surface phenomenon.
Absorption occurs at a uniform rate.	Adsorption is rapid in the beginning and its rate slowly decreases.
It is a slow process.	lt is a <mark>fast</mark> process.
E.g.: Water vapours are absorbed by anhydrous calcium chloride.	E.g.: Water vapours are adsorbed by silica gel.





When absorption and adsorption of the **same substance** take place simultaneously, it is known as **sorption**.

For example, dyes get adsorbed as well as absorbed in cotton fibre.

Mechanism of Adsorption

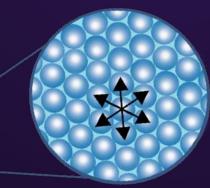


Surface particles of the adsorbent are not in the same environment as the particles inside the bulk.

Inside the adsorbent

All the forces acting between the particles are mutually **balanced**.





Mechanism of Adsorption



On the surface the particles are not surrounded by same particles on all sides. Unbalanced or

residual forces

Are responsible for attracting the adsorbate particles on its surface

Thermodynamics of Adsorption

2

B

Adsorption involves a decrease in residual forces or surface energy. The **freedom of movement** of gaseous adsorbate particles is **restricted** due to adsorption.

Energy is released, so the **heat of adsorption** is negative.

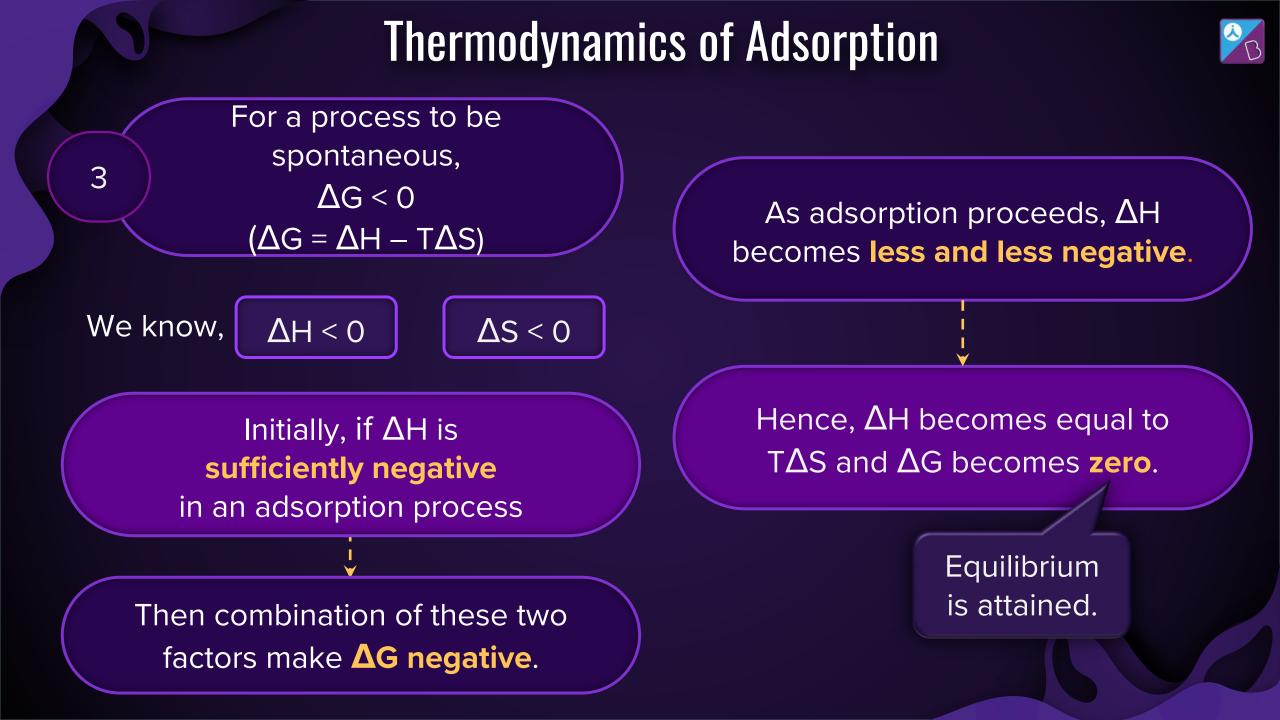
Adsorption is always

exothermic.

Entropy decreases

ΔS < 0

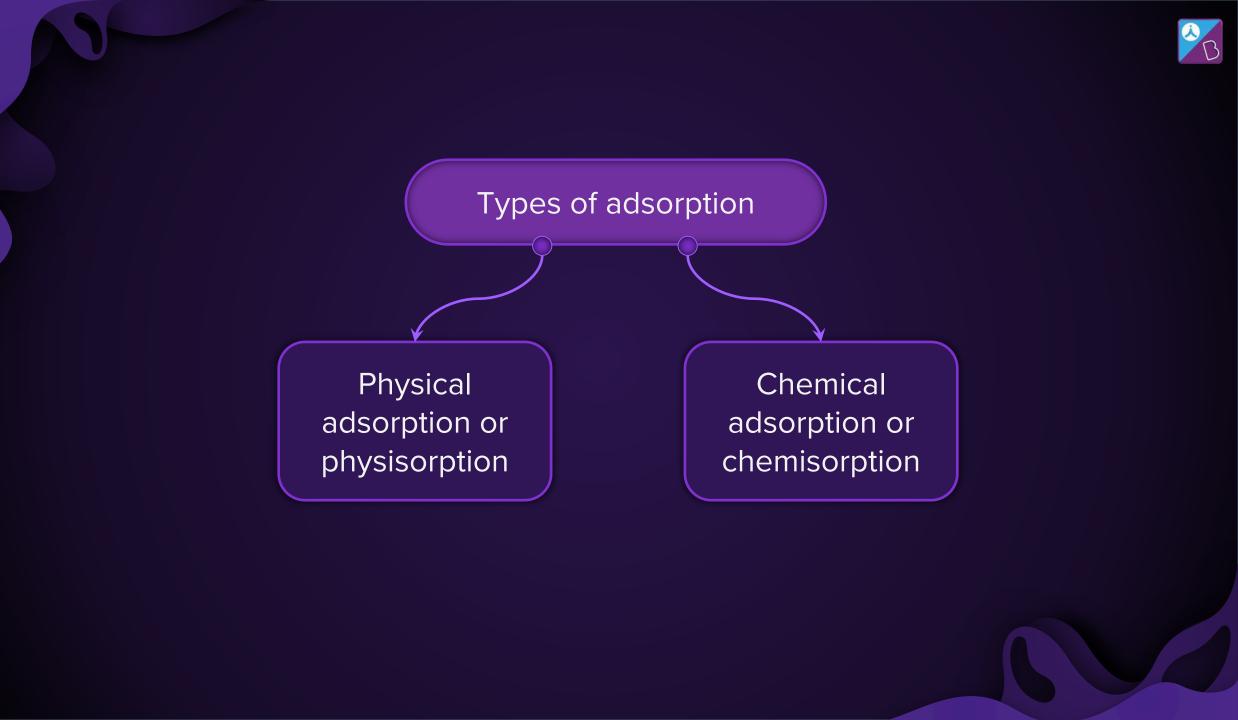
 $\Delta H < 0$



Enthalpy of Adsorption ($\Delta H_{Adsorption}$)

It is the amount of **heat released** when **1 mole** of an adsorbate gets adsorbed on a particular adsorbent at adsorption **equilibrium**.

It depends on the nature of both adsorbent and adsorbate.



Physical Adsorption

If accumulation of a gas on the surface of a solid, Force of attraction: **van der Waals**' forces. Temperature favoured: **Low** Layer: **Multilayered**

> van der Waals forces

Adsorbent

Adsorbate



Multilayer

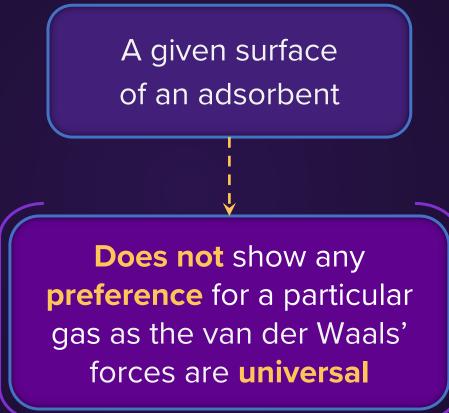
Characteristics of Physisorption





Lack of Specificity





Nature of Adsorbate

Having **higher** critical temperatures (T_C)

Generally,

Easily liquefiable gases are readily adsorbed.

As van der Waals forces are **stronger** for gases having **higher T_C**

Example

$$T_{C} (SO_{2}) = 630 \text{ K \& } T_{C}$$

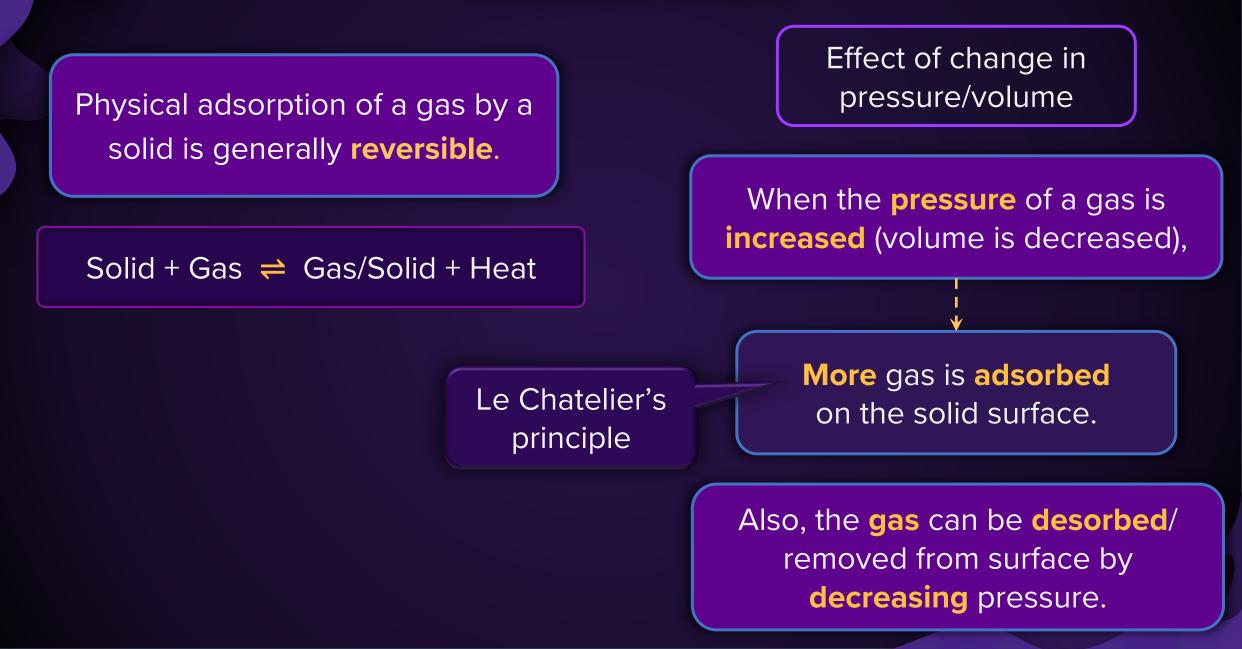
 $(CH_{4}) = 190 \text{ K}$

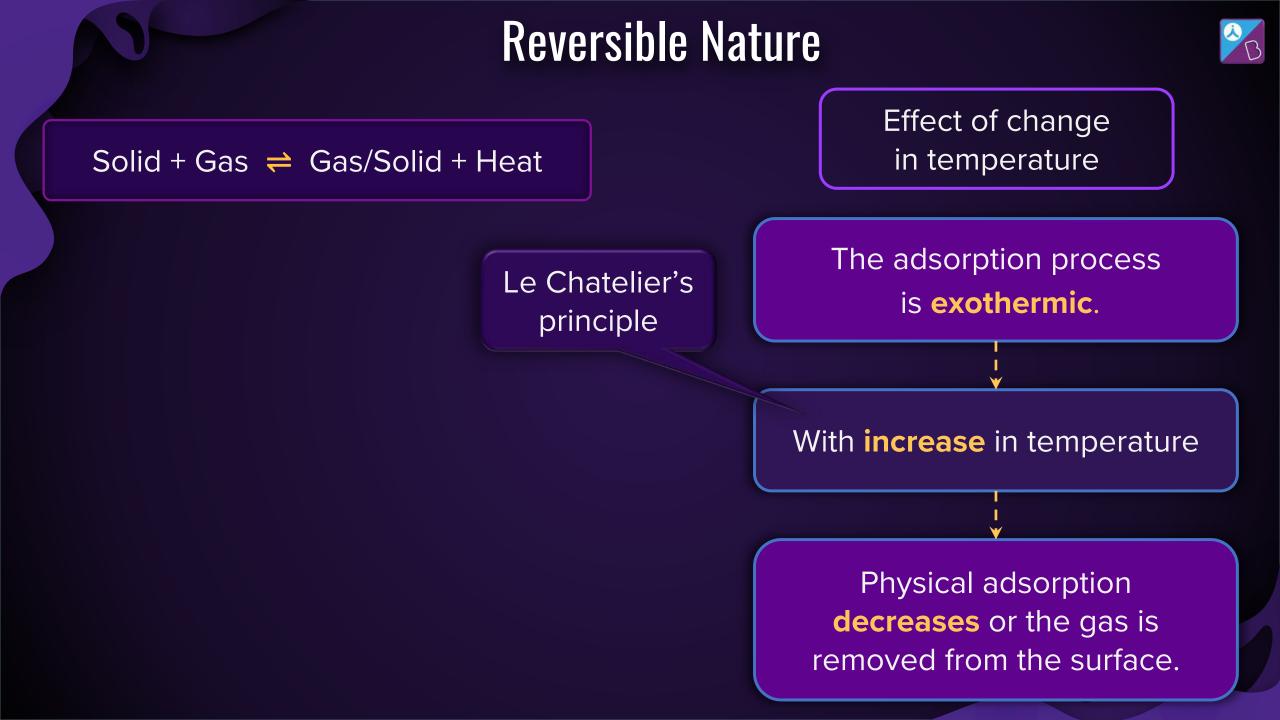
1 g of activated charcoal adsorbs more sulphur dioxide than methane.



Reversible Nature







Surface Area of Adsorbent



The extent of physisorption increases with the increase in surface area of the adsorbent Thus, **finely divided** metals and **porous** substances having large surface areas are **good adsorbents**

Enthalpy of Adsorption



Physical adsorption is an **exothermic** process but enthalpy of adsorption is **very low.**

(20-40) kJ mol⁻¹

Reason

As weak physical forces like van der Waals' forces are involved, the attraction between the adsorbate and the adsorbent is low.

Chemical Adsorption



The adsorption in which gas **molecules or atoms** of the adsorbate are **held** to the solid surface of the adsorbent by the **chemical bonds**. Chemical **bonds** may be **covalent or ionic** in nature

Generally, occurs at high temperature and is monolayer adsorption

Chemisorption involves a high activation energy, often referred to as activated adsorption.

Characteristics of Chemisorption





High Specificity



Example

Chemisorption occurs only if there is a possibility of chemical bonding between adsorbent and adsorbate



2

Oxygen is adsorbed on metals by virtue of oxide formation.

Hydrogen is adsorbed by **transition metals** due to **hydride** formation.

Irreversibility



Effect of change in temperature

Although chemisorption is an **exothermic** process, it is **very slow** at **low temperature** due to **high activation energy**.

Effect of change in pressure

Usually, **high** pressure is **favourable** for chemisorption.

As chemisorption involves compound formation. It is usually irreversible in nature.

Surface Area of Adsorbent



Chemisorption also **increases** with an increase in the surface area of the adsorbent.

Enthalpy of Adsorption



As chemical bond

formation is involved,

enthalpy of adsorption is high

(80–240) kJ mol⁻¹



Physisorption vs Chemisorption



Property	Physisorption	Chemisorption
Nature of adsorption	<mark>Weak</mark> (van der Waals' forces)	Strong (Chemical bond formation)
Specificity of adsorption	Not specific	Highly specific
Reversibility of adsorption	Reversible	Irreversible
Temperature at which adsorption is more pronounced	Low temperature	High temperature
Effect of change in temperature	Decreases with rise in temperature	Increases with rise in temperature
Enthalpy of adsorption	Low (20-40 kJ mol ⁻¹)	High (80-240 kJ mol ⁻¹)

Physisorption vs Chemisorption



Property	Physisorption	Chemisorption
Nature of adsorbate layer	Multi-layered (at high pressure)	Mono-layered
Energy of activation	Low	Significantly high
Rate	Rapid/Fast	Slow
Ease of desorption	Easy , since van der Waals forces are involved	Not easy , since chemical forces are involved
Nature of gas	More easily liquifiable gases are adsorbed readily	Gases which can react with the adsorbent show chemisorption





As **temperature** increases

A physisorption, at low temperature, may **pass into** chemisorption, as the temperature is **increased**.

Dihydrogen is first adsorbed on nickel by van der Waals' force.

Physisorption

Chemisorption

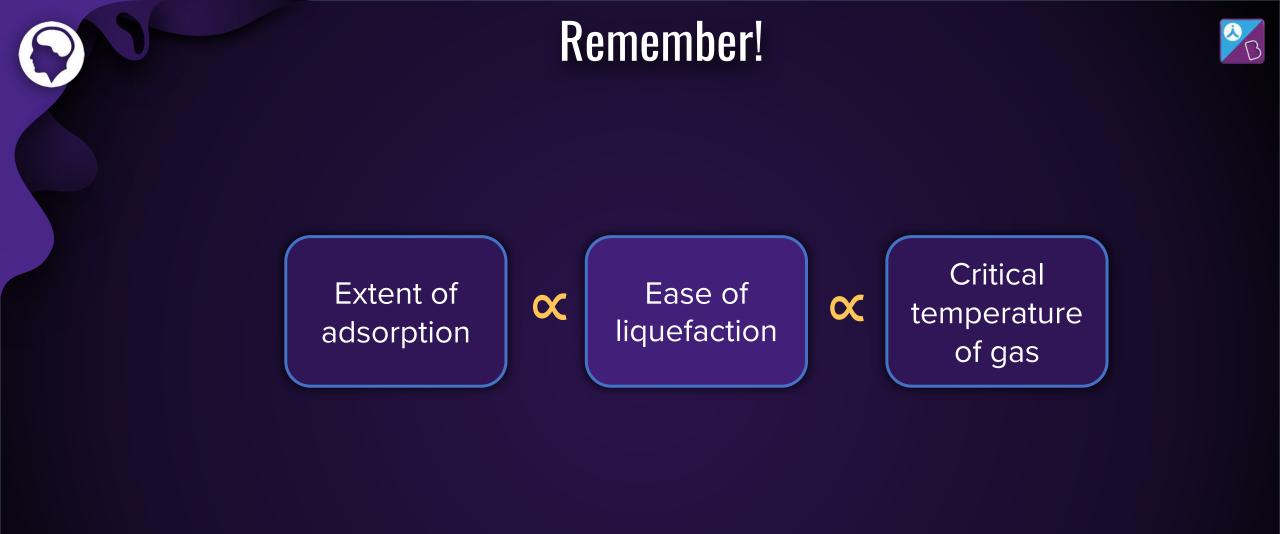
Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface.

Competitive Adsorption



When an adsorbent is in contact with **more than one** species There will be competition amongst them to get adsorbed on the surface of the adsorbent.

Factor Affecting Adsorption of Gases on Solids Nature of gases (adsorbate) Nature of adsorbent Effect of temperature Effect of pressure



Nature of Adsorbent



Extent of adsorption



Surface area of solid

So, **finely divided** adsorbents are **more efficient** than normal one. Activated charcoal, clay etc., can adsorb gases which are **easily liquified.** Gases such as H_2 , N_2 and O_2 are generally adsorbed on finely divided transition metals Ni and Co.

Effect of Temperature



We know,

Adsorbent (s) + Adsorbate (g) \rightleftharpoons [Adsorbent---Adsorbate] + Δ H



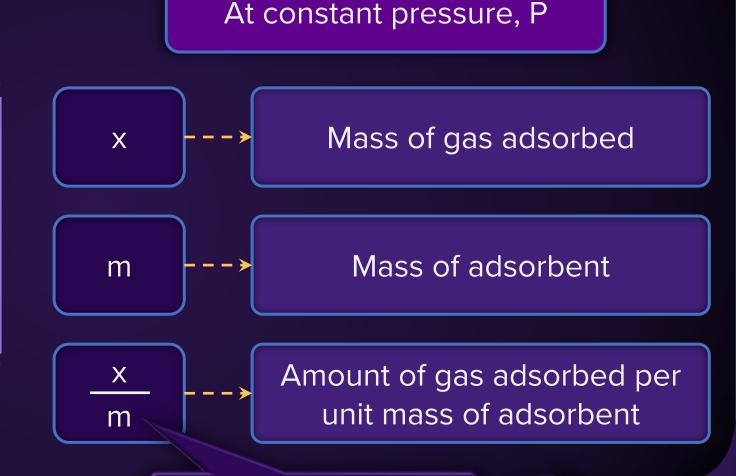
According to Le-Chatelier's principle

Adsorption Isobar



At constant pressure,

The variation in the amount of gas adsorbed by the adsorbent with temperature can be expressed by a curve termed as adsorption isobar

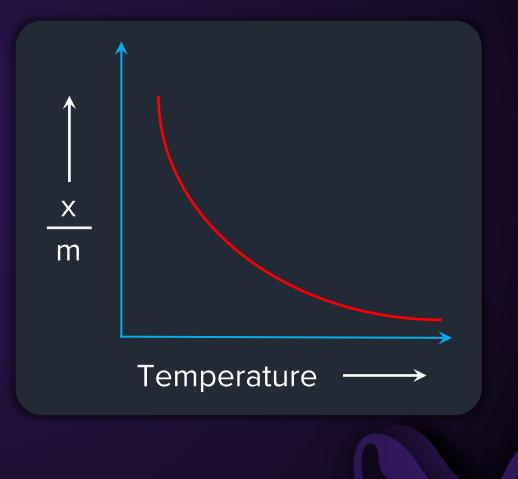


Extent of adsorption

Adsorption Isobar for Physisorption

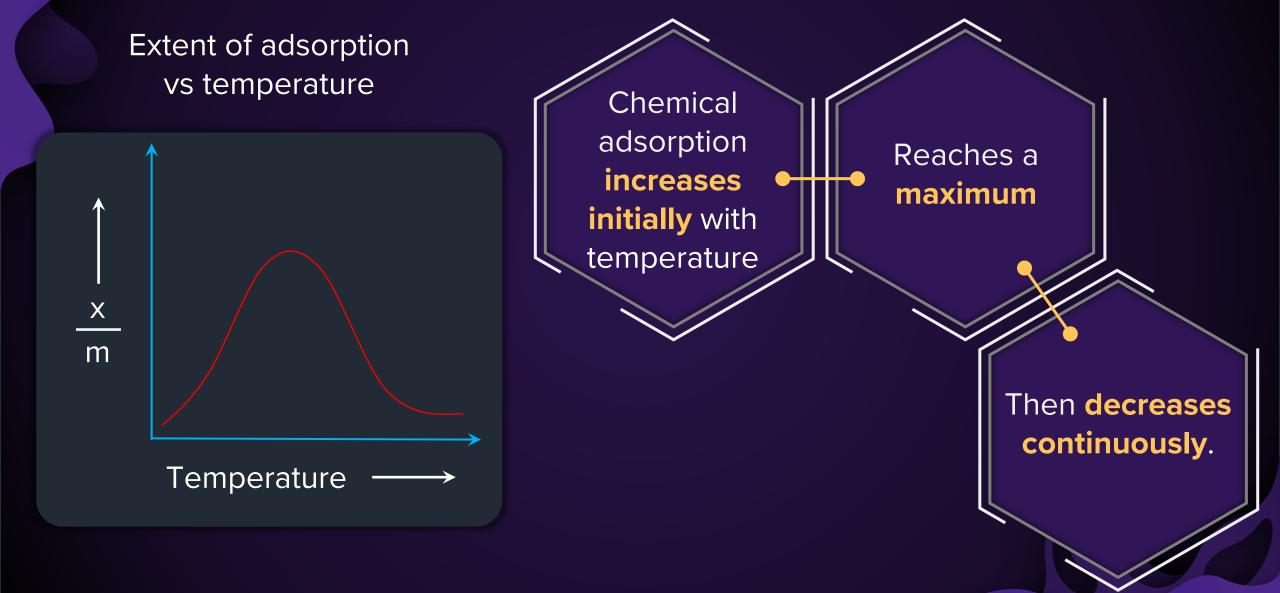
With **increase** in temperature, physical adsorption **decreases** continuously

Extent of adsorption vs temperature



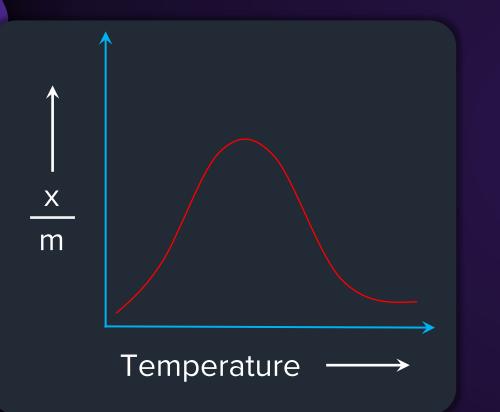
Adsorption Isobar for Chemisorption





Adsorption Isobar for Chemisorption

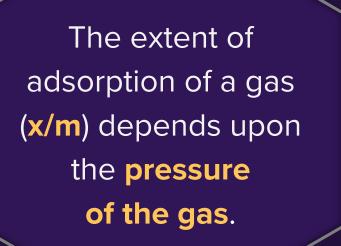
Extent of adsorption vs temperature



There is an increase in the chemisorption initially because **activation energy** is required to **initiate** the process

So, chemical adsorption is also known as **'activated adsorption'**

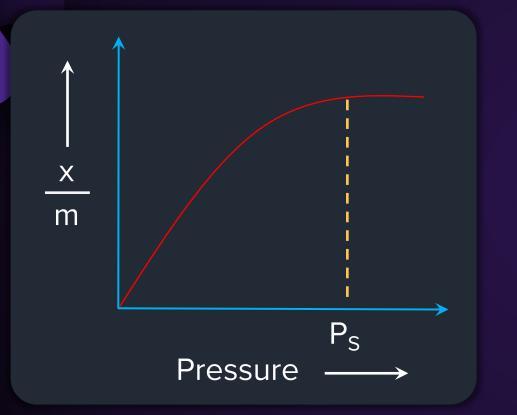
Effect of Pressure





Adsorption Isotherm



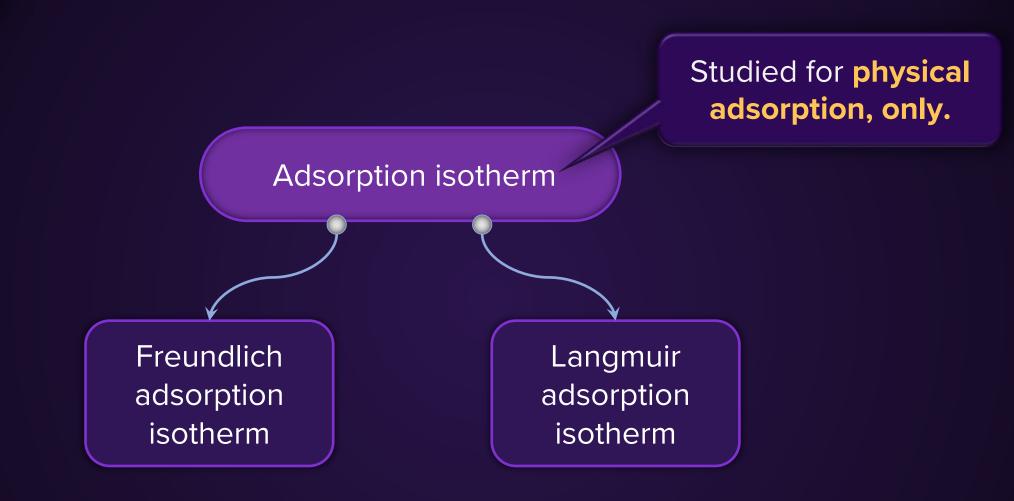


At constant temperature,

Adsorption isotherm is a curve representing variation in the **amount of gas adsorbed** by the adsorbent with pressure

Extent of adsorption (x/m) increases with pressure, it becomes maximum corresponding to a pressure P_s, called saturation pressure

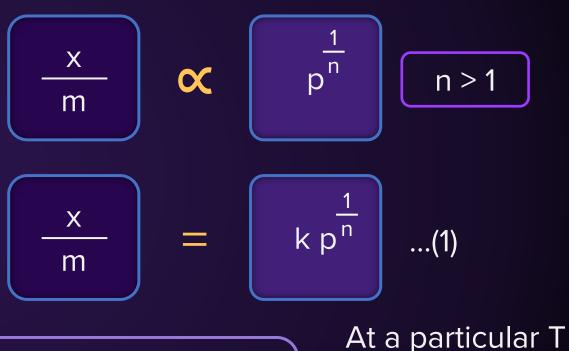








The relationship can be expressed as,



Where, k and n: Constants x: Mass of gas adsorbed m: Mass of adsorbent

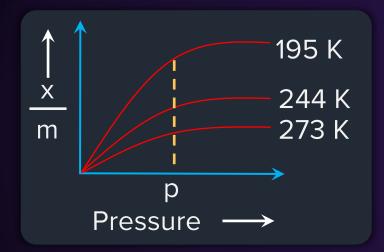
Depends on the nature of gas and adsorbent

Freundlich gave an empirical relationship between the extent of adsorption(x/m) and pressure, at a particular temperature.



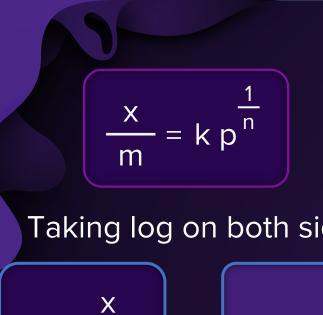
 $\frac{x}{m}$ vs pressure

(at different temperatures)



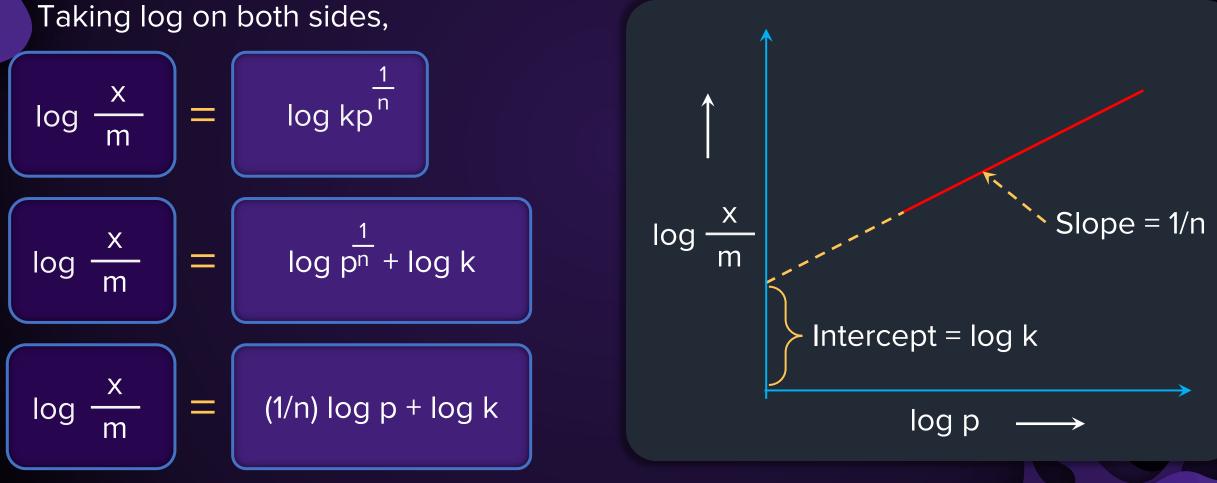
At a fixed pressure, there is a **decrease** in physical adsorption with **increase** in temperature.

The curves at different temperatures approach saturation at high pressure.



B

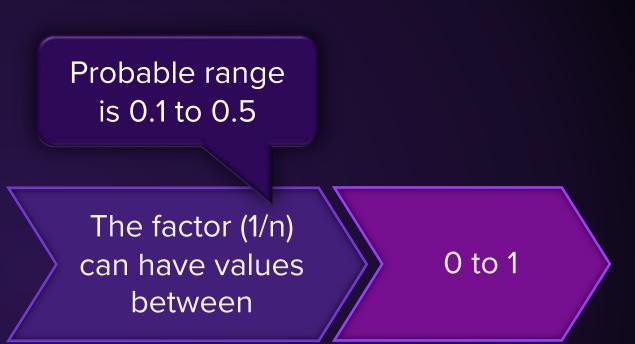
Compare with straight line equation, y = mx + c





Freundlich isotherm is **valid** if the plot is a **straight line.**

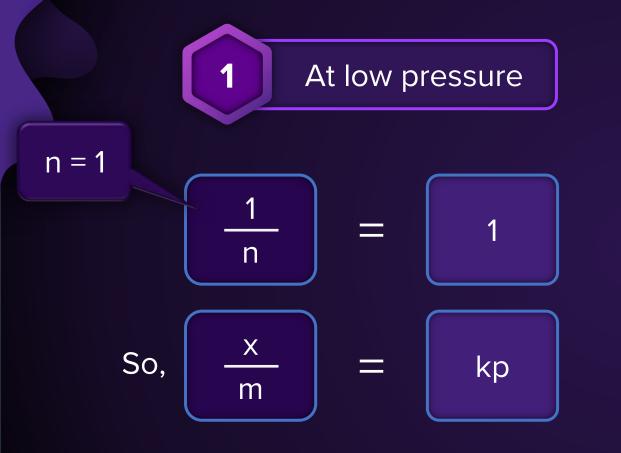
It explains the behavior of adsorption in an **approximate** manner.

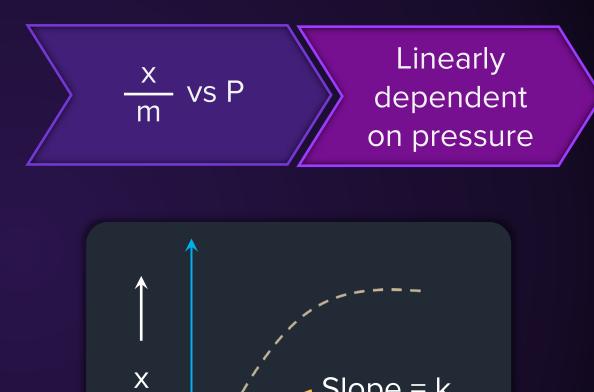


Freundlich isotherm **holds** good over a **limited range** of pressure.

Adsorption Isotherm Under Different Pressure Ranges





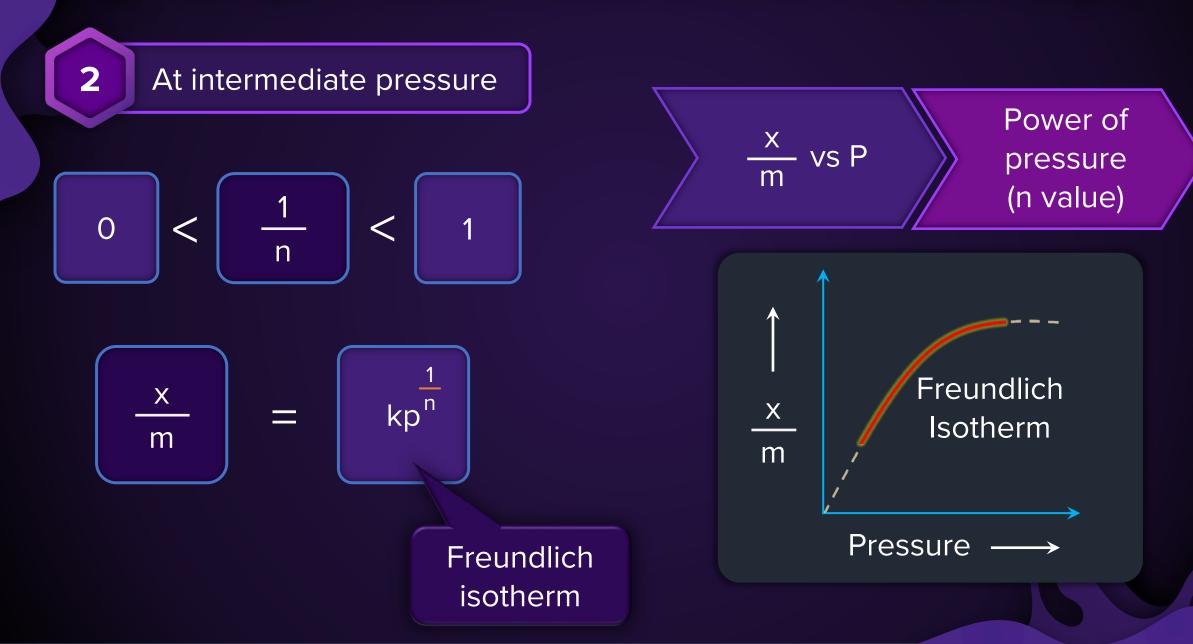


Slope = k Straight line Pressure \longrightarrow

m

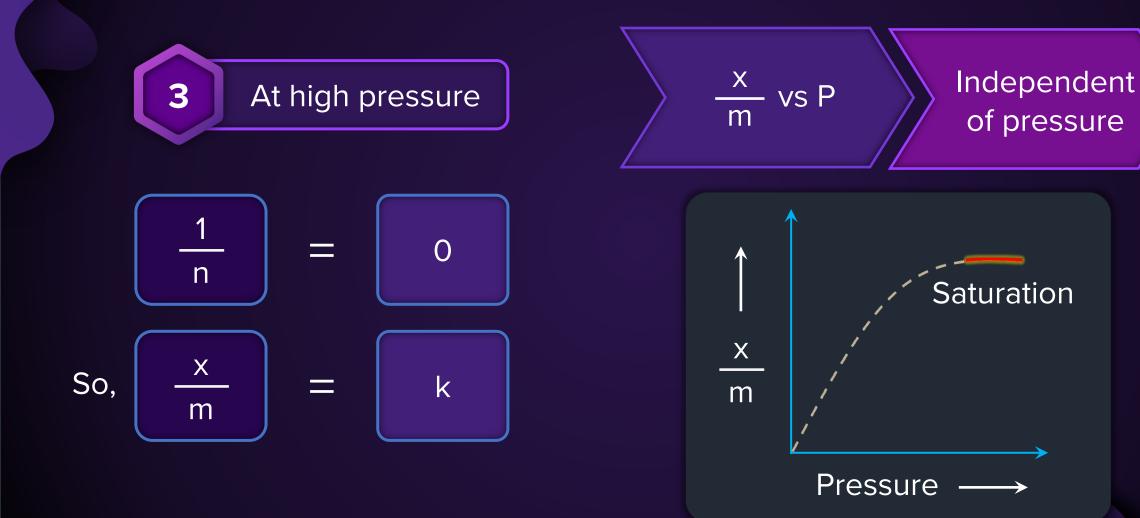
Adsorption Isotherm Under Different Pressure Ranges





Adsorption Isotherm Under Different Pressure Ranges





Drawbacks of Freundlich Adsorption Isotherm

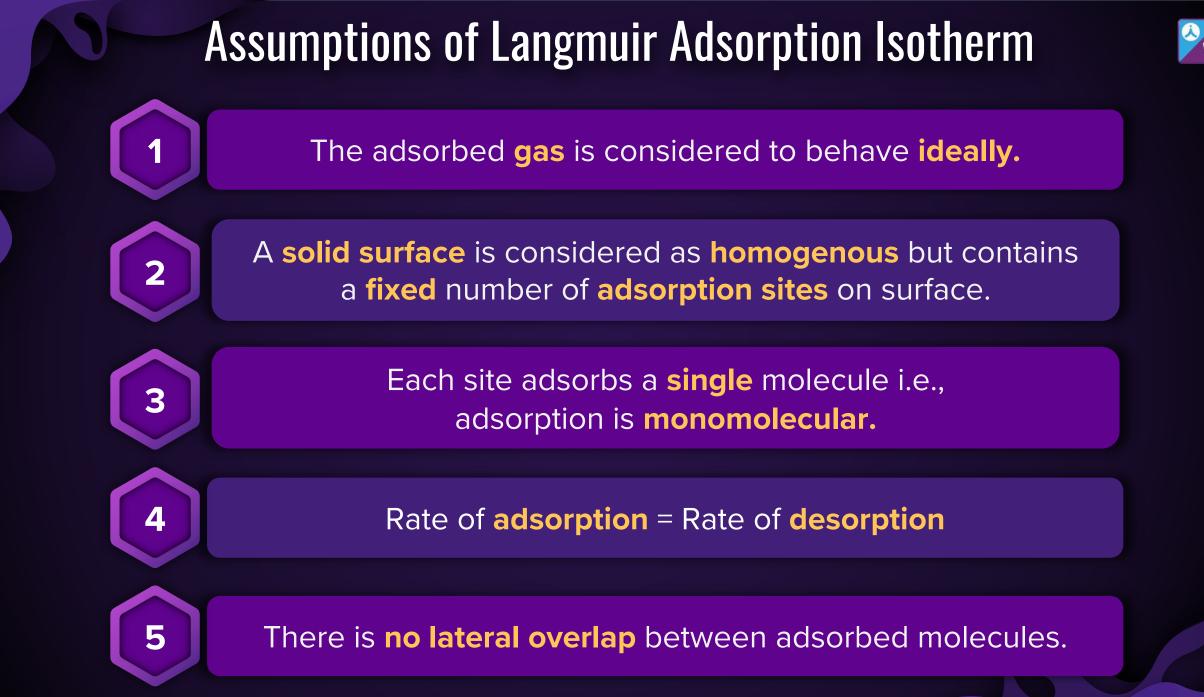


It holds good for a limited range of pressure of the gas, but generally, fails at high pressure.

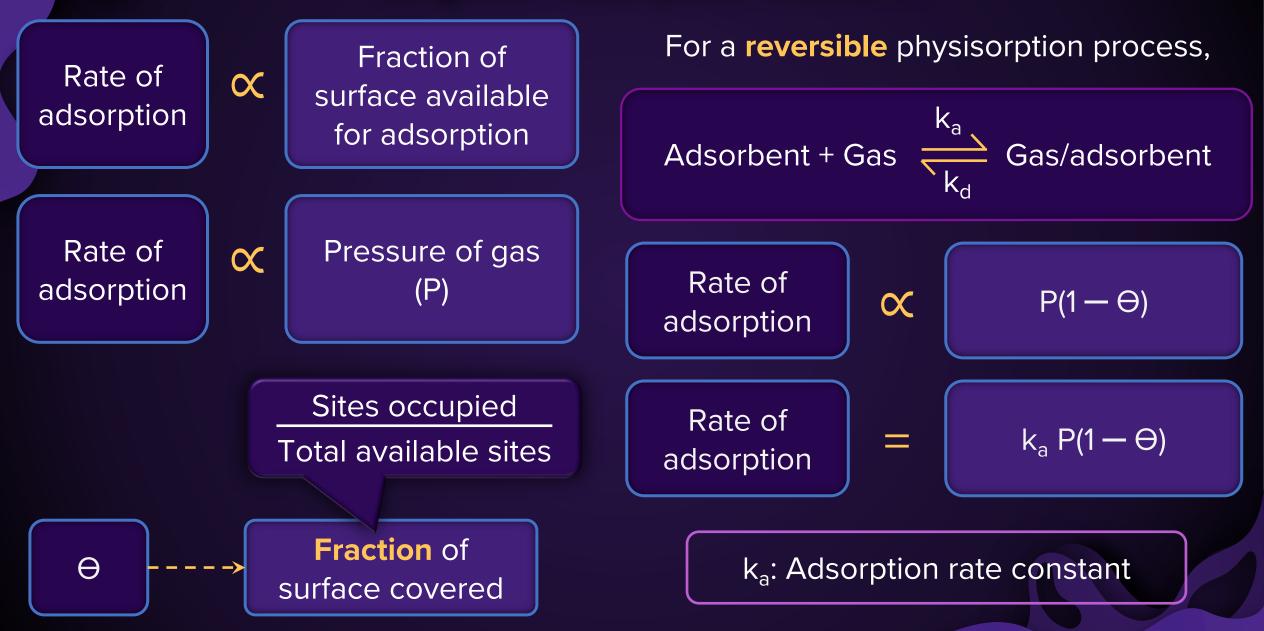
Saturation at high pressure



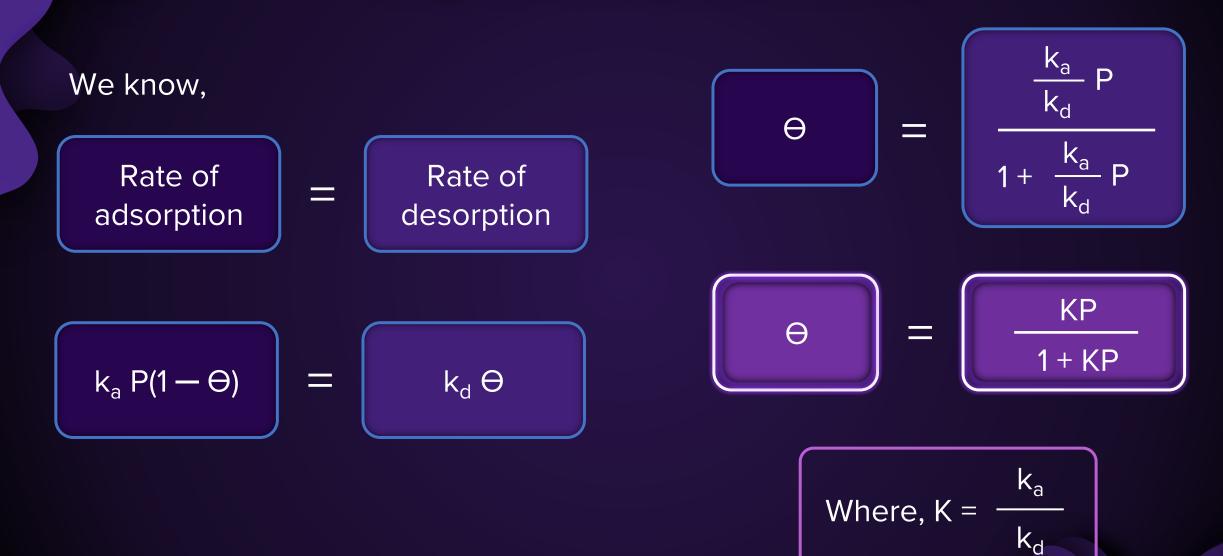
The isotherm is **applicable** when the adsorbate forms a **unimolecular layer** on the adsorbent surface.









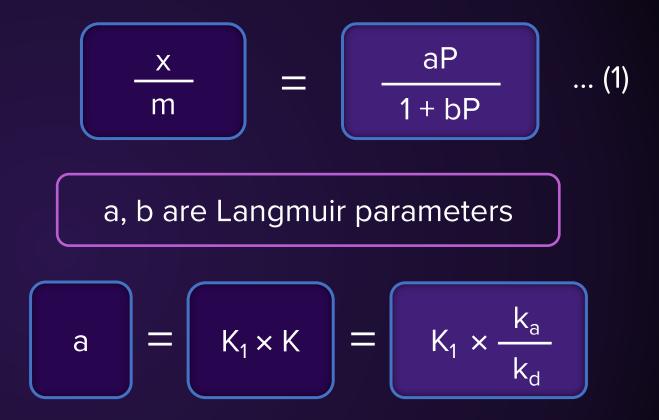


According to Langmuir, extent of adsorption is proportional to Θ





K₁ is a proportionality constant

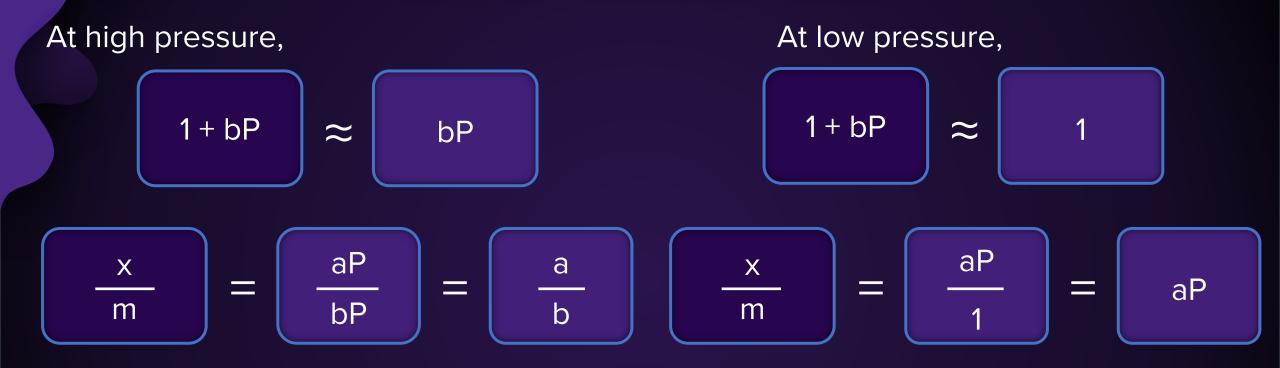






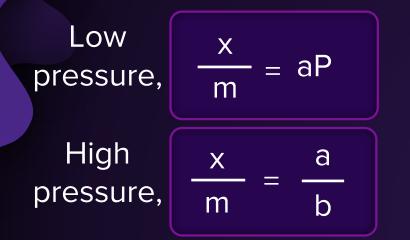




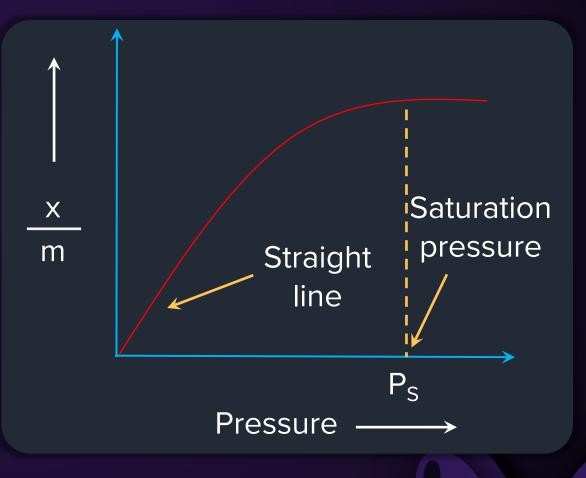


x/m becomes independent of pressure i.e., the surface is fully covered and change in pressure has no effect on further adsorption.

x/m **increases linearly** with pressure

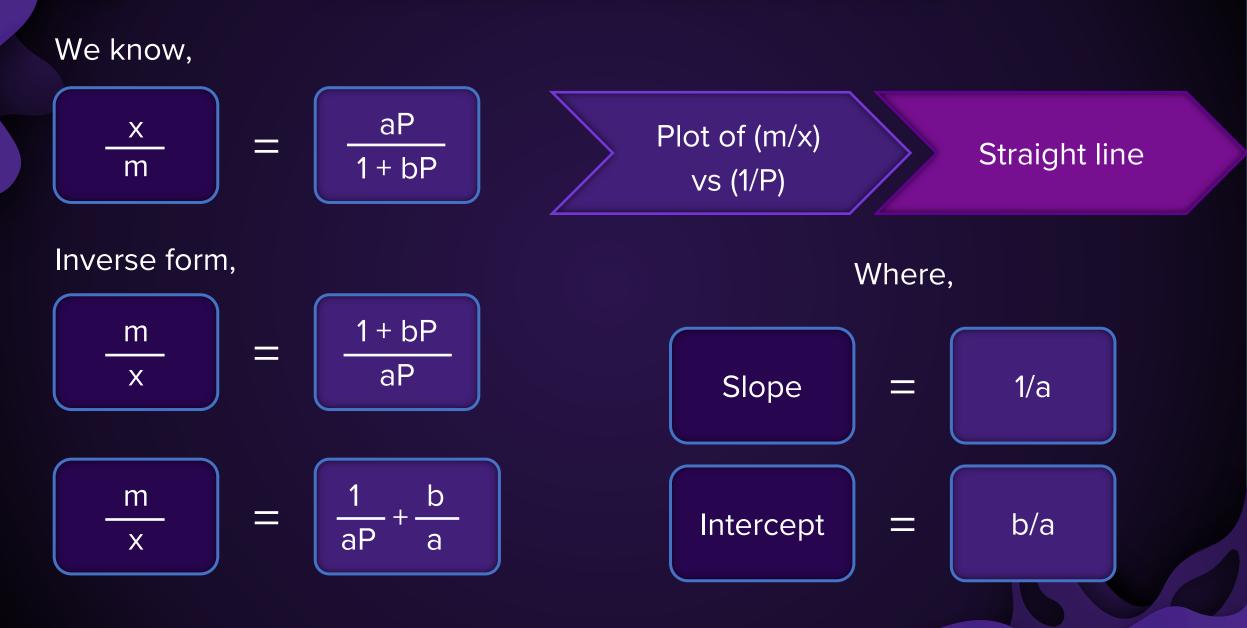


We know, for adsorption isotherm

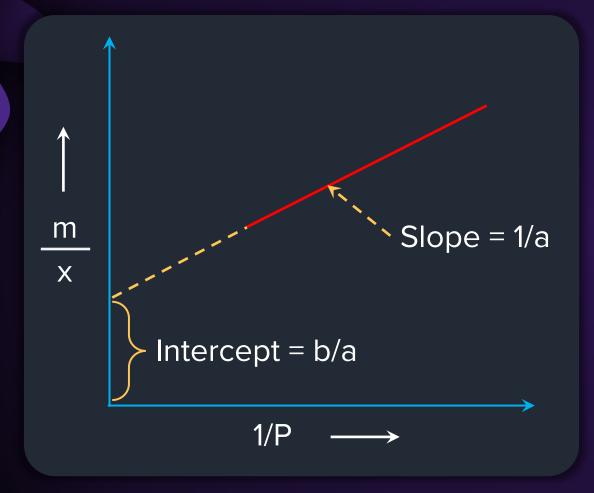


Determination of Values of a and b





Determination of Values of a and b



Values of a and b can be determined using the slope and intercept of the m/x vs 1/P curve

Adsorption from Solution Phase

B

Solids can adsorb solutes **from a solution.**

Example:

A solution of acetic acid in water is shaken with charcoal.

A part of the **acid is adsorbed** by the charcoal, and the **concentration** of the acid **decreases**.

Characteristics of Adsorption from Solution Phase



The **extent** of adsorption **increases** with **increase** in the **surface area** of adsorbent.



The **extent** of adsorption **decreases** with **increase** in **temperature**.



The extent of adsorption depends on the concentration of the solute in solution.



The **extent** of adsorption **depends** on the **nature** of the **adsorbent** and the **adsorbate**.

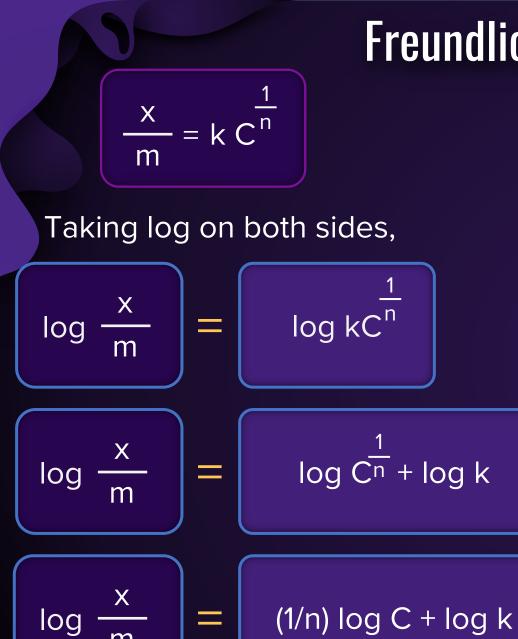
Characteristics of Adsorption from Solution Phase



Freundlich's equation approximately describes the **behaviour of adsorption** from the solution.



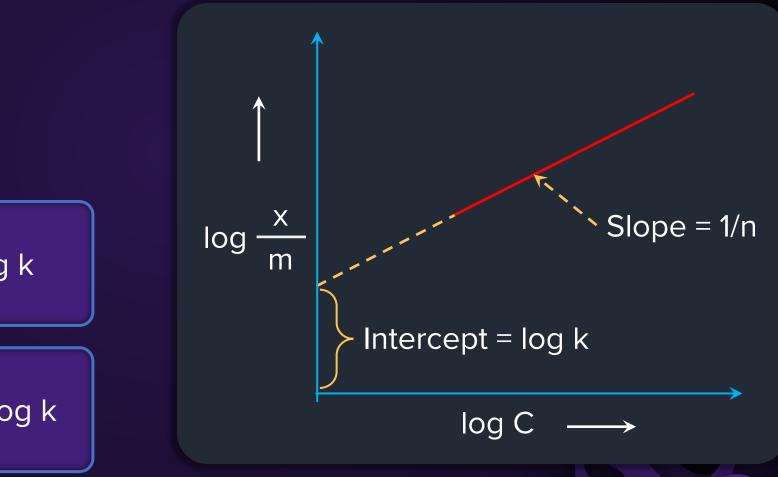
But for the solution phase, concentration of the solution is taken in account instead of pressure. C : The equilibrium concentration of solute k : Constant n : Constant, (n > 1) (x/m) : Extent of adsorption



m

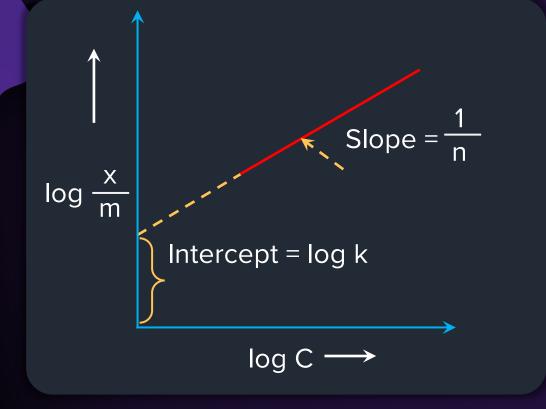
Freundlich Adsorption Isotherm

Compare with straight line equation, y = mx + c



Characteristics of Adsorption from Solution Phase





Validity of Freundlich isotherm can be established if plot of log x/m vs log C is a straight line.





A chemical substance that can **alter** the **rate** of a reaction, by providing an **alternative** pathway.

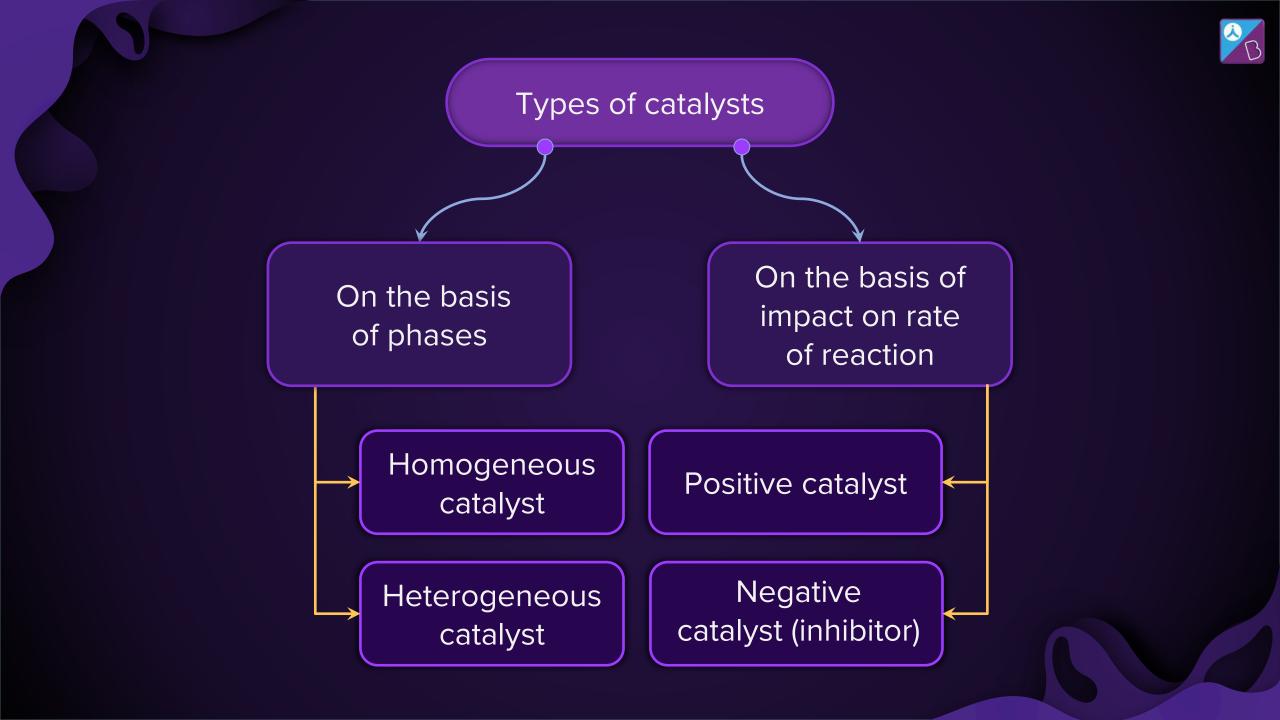
$$2\text{KCIO}_3 \xrightarrow{\text{MnO}_2} 2\text{KCI} + 3\text{O}_2$$

Normally, KCIO₃ is heated to **high** temperature

When catalyst MnO₂ is used, reaction occurs at a **low** temperature and **rapidly**

653-873 K

473-633 K



Homogeneous Catalyst

B

The process in which the catalysts and reactants are in the **same phase** process is called as **homogeneous catalysis**.

The catalyst is called a **homogeneous catalyst**.

Example:

(i)

(ii)

Hydrolysis of ester (acidic medium)

 $CH_3COOC_2H_5(\ell) + H_2O(\ell) \xrightarrow{HCI(\ell)} CH_3COOH(aq) + C_2H_5OH(aq)$

Oxidation of sulphur dioxide

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

Heterogeneous Catalyst



The process in which the catalysts and reactants are in **different phase** process is called as **heterogeneous catalysis**. Example:

Decomposition of H_2O_2

$$\begin{array}{c} \mathsf{MnO}_2 \text{ (s)}\\ \mathsf{2H}_2\mathsf{O}_2 \text{ (l)} & \longrightarrow \mathsf{H}_2\mathsf{O} \text{ (l)} + \mathsf{O}_2 \text{ (g)} \end{array}$$

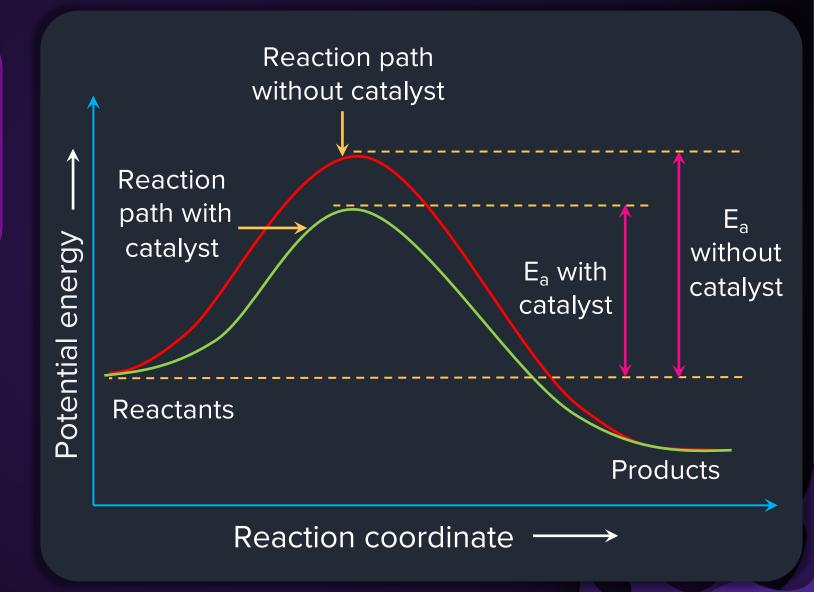
The catalyst is called a **heterogeneous catalyst**.

$$N_2$$
 (g) + 3 H_2 (g) $\xrightarrow{\text{Fe (s)}}$ 2 NH_3 (g)

Positive Catalyst



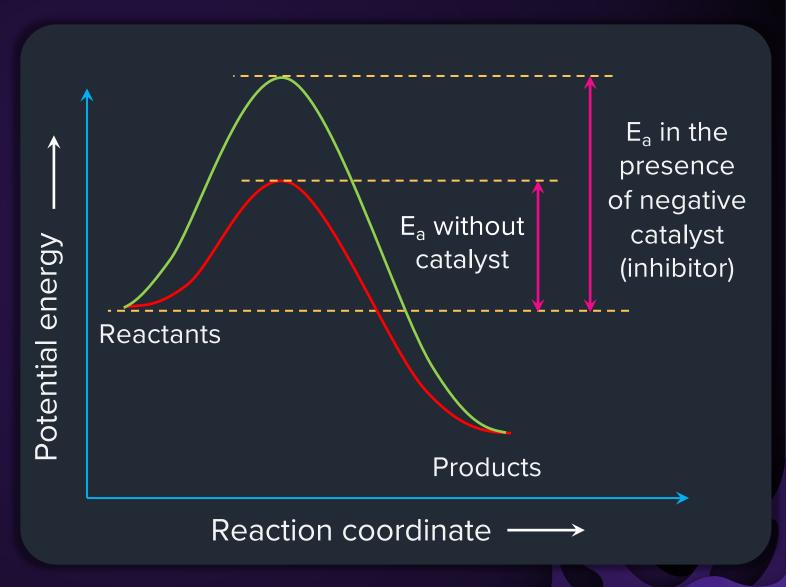
A positive catalyst increases the reaction rate by reducing the activation energy barrier.



Negative Catalyst

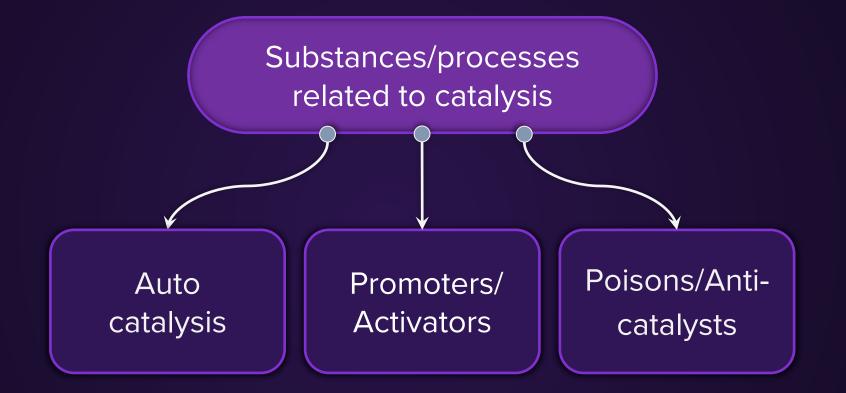


A negative catalyst decreases the reaction rate by increasing the activation energy barrier.



Other Important Terms





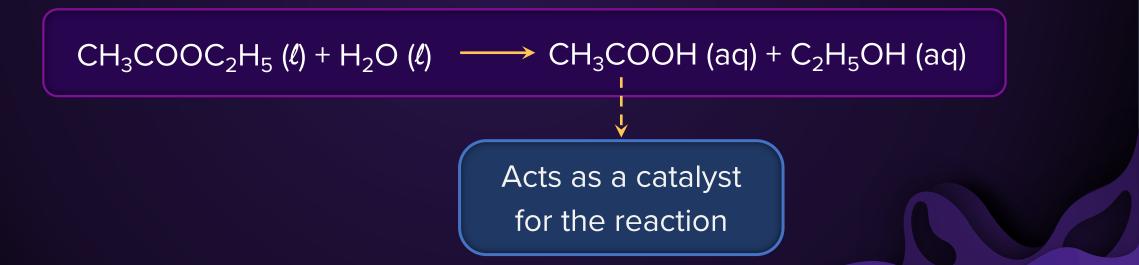


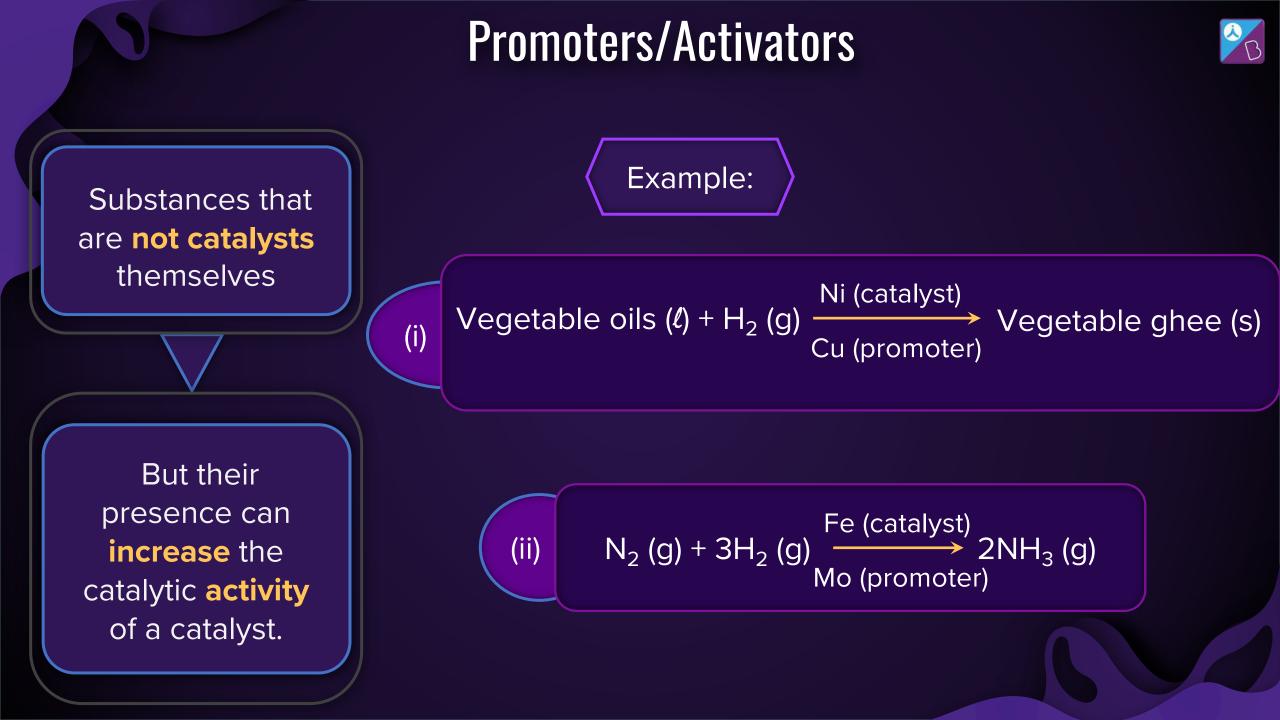
Auto Catalysis



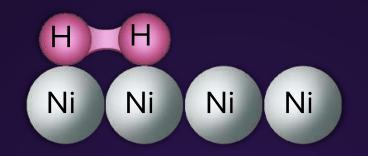
When one of the **products** of a reaction behaves as a **catalyst** for that reaction and **increases** the rate of reaction

Example:





Promoters/Activators



Covalent bond much weakened and cleaves readily Η Η Ni Ni Ni Ni Мо Мо Mo Ni Ni Ni Ni

Catalytic Poisons/Anti-Catalysts

B

Substances that are **not catalysts** themselves

But their presence decreases the activity of a catalyst Poisoning is due to **preferential adsorption** of poison on the surface of the catalyst.

Catalytic Poisons/Anti-Catalysts

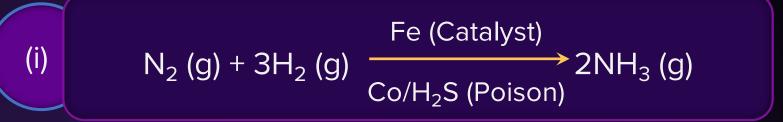
Catalyst Poisoning chemical compounds

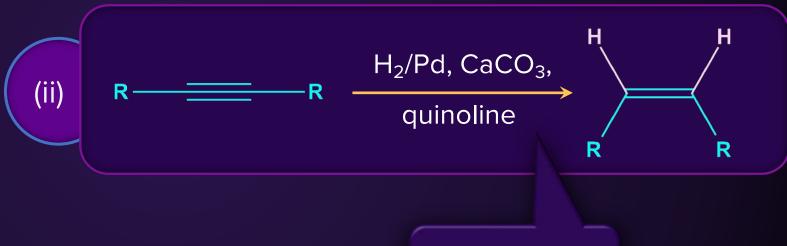
> Deposition of chemical poison on the catalyst surface

Deactivation of catalyst

Catalytic Poisons/Anti-Catalysts

Example

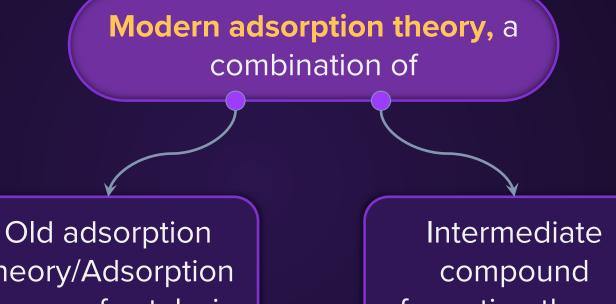




Lindlar's Catalyst



Adsorption Theory of Heterogeneous Catalysis



formation theory

theory/Adsorption theory of catalysis

Old Adsorption Theory



The **reactants** in gaseous state or in solution, are **adsorbed** on the surface of the **solid catalyst**.

The **increase** in concentration of the **reactants** on the surface **increases** the **rate** of reaction.

The **heat** of adsorption (exothermic process) is utilized in **enhancing** the **rate** of the reaction.

Intermediate Compound Formation Theory



A catalyst forms **temporary bonds** with the reactants resulting in an **intermediate complex**.

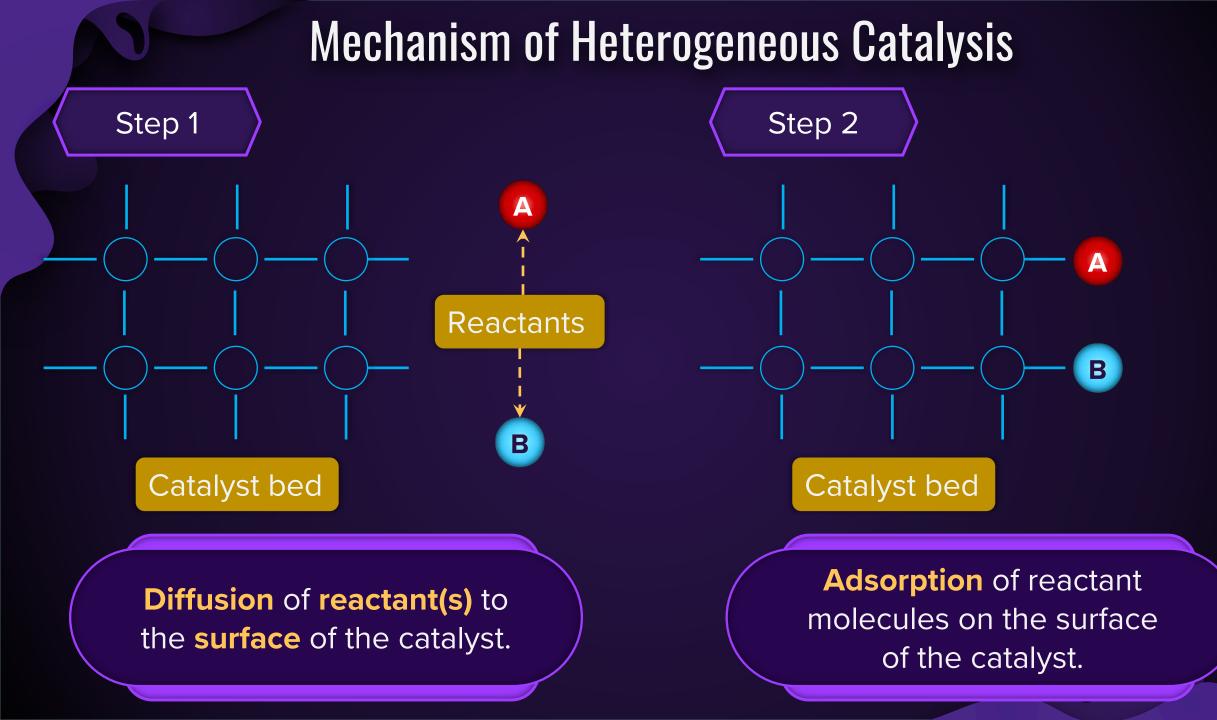
> This exists for a **short time** and decomposes to **yield products** and the catalyst.

Mechanism of Heterogeneous Catalysis

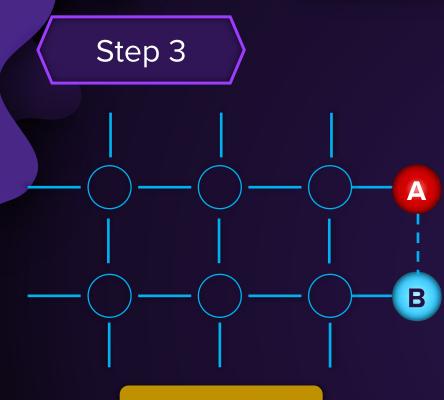
The surface of the catalyst, unlike the inner part of the bulk, has free valancies that provide the seat for chemical forces of attraction. Gas molecules are held up on the surface due to loose chemical combination.

Different molecules are **adsorbed** side by side and **react with each other** forming **new molecules**.

The **formed** product molecules may **evaporate,** leaving the surface for the **fresh reactant** molecules.

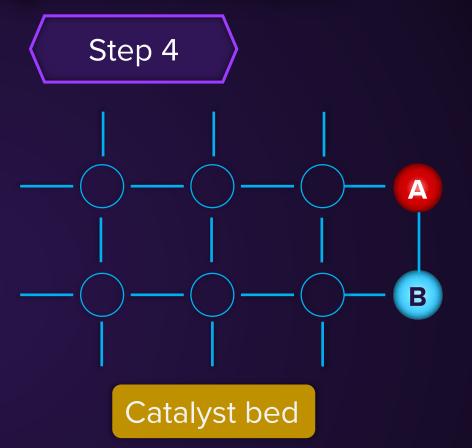


Mechanism of Heterogeneous Catalysis



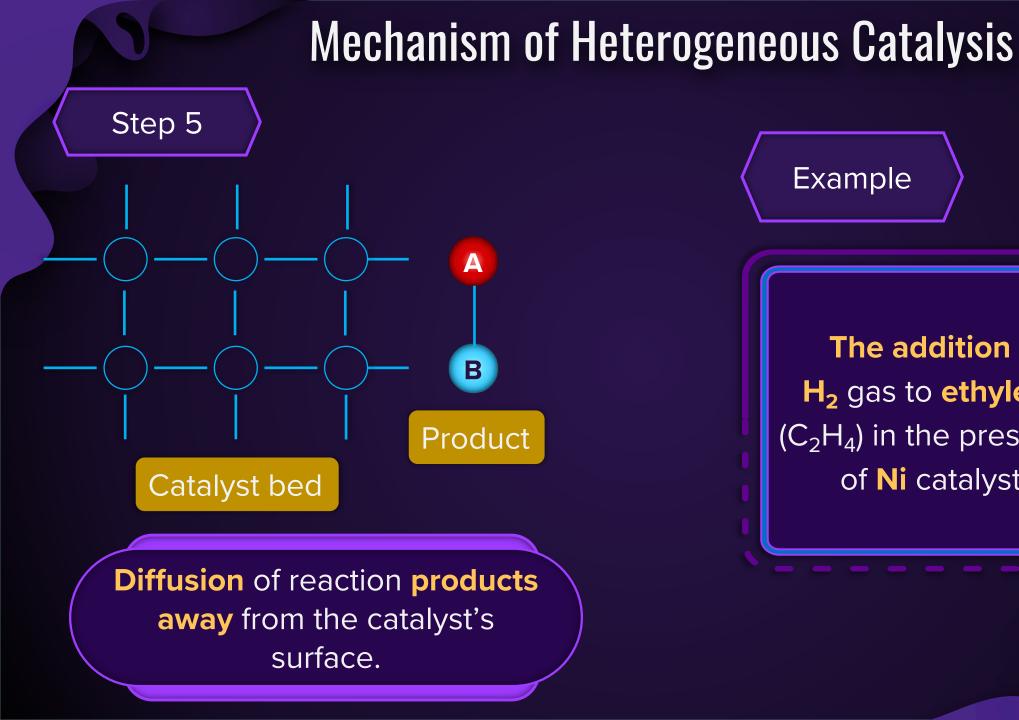
Catalyst bed

Occurrence of **chemical reaction** on the catalyst's surface through the formation of an **intermediate**.



Desorption of reaction **products** from the catalyst surface, making the **surface available again** for more reaction to occur.







The addition of H₂ gas to ethylene (C_2H_4) in the presence of Ni catalyst.



Modern Adsorption Theory

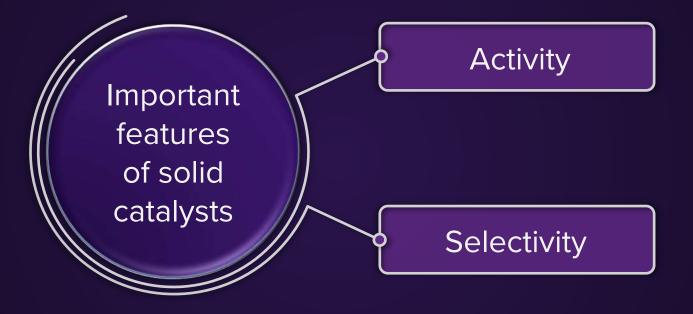


This theory **explains** why the catalyst remains **unchanged** in mass and chemical composition at the end of the reaction

It is effective even in small quantities

But does not explain the action of catalytic promoters and catalyst poisons

Important Features of Solid Catalysts





Activity



The activity of a catalyst depends upon the strength of chemisorption to a large extent. Reactants must get adsorbed reasonably strongly on to the catalyst to become active.

However, adsorption shouldn't be **so** strong that reactants are **immobilised**.

No space on surface for further reactants



The maximum activity is shown by groups **7–9** elements

$$2H_2(g) + O_2(g) \xrightarrow{Pt(s)} 2H_2O(\ell)$$

Selectivity



The ability of a catalyst to **direct** a reaction to yield a **particular product** selectively, under the **same** reaction conditions, **different products** are possible.

The action of a catalyst is **highly selective** in nature.

A substance that acts as a catalyst in **one** reaction may **fail** to catalyse **another** reaction.



Example

$$CO + H_2 \xrightarrow{\text{Ni surface}} CH_4 + H_2O$$

$$CO + H_2 \xrightarrow{Cu surface} HCHO$$

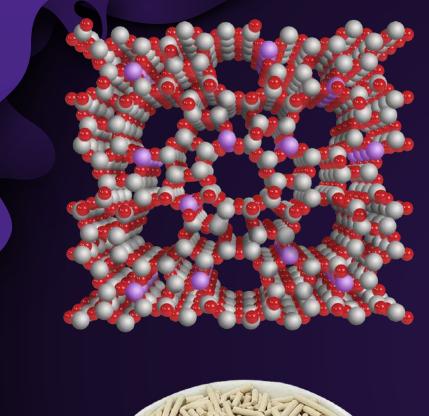
$$CO + H_2 \xrightarrow{\text{ZnO surface}} CH_3OH$$



Shape Selective Catalysis



The catalytic reaction that depends upon the **pore structure** of the catalyst and the **size** of the **reactant** and **product** molecules. Zeolites are good shape-selective catalysts because of their honeycomb-like structures.



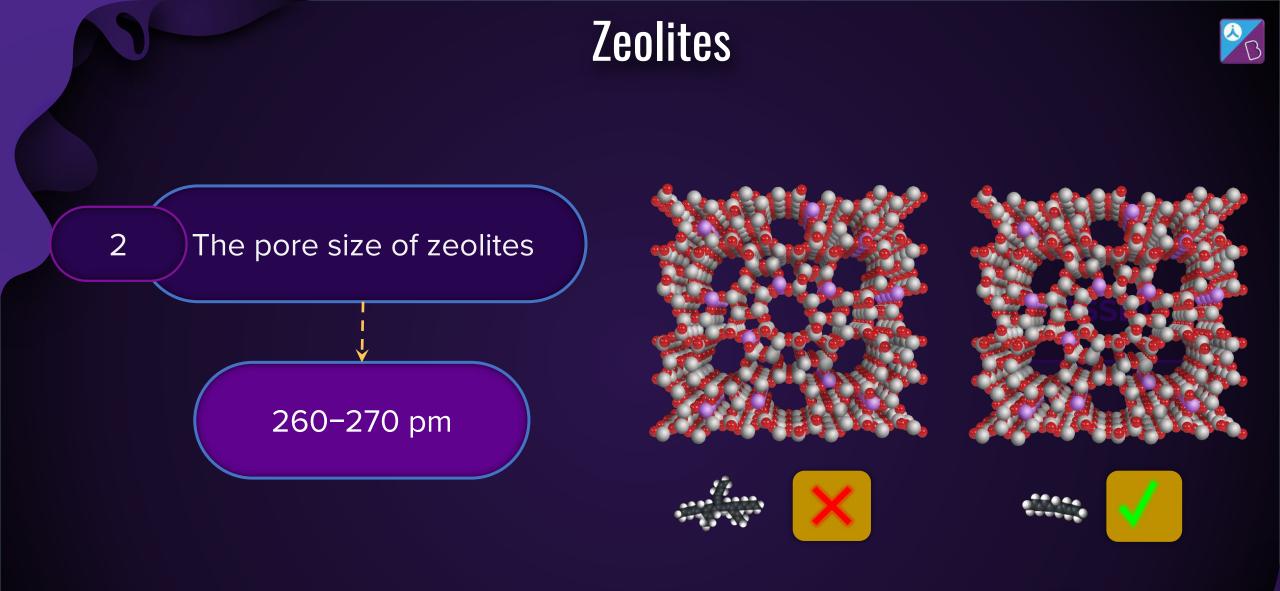
Zeolites



Microporous **aluminosilicates** with **3D** network of silicates

Some **silicon** atoms are replaced by **aluminium** atoms giving **Al-O-Si** framework





Uses of Zeolites



Used as a catalyst in petroleum industries for **cracking of hydrocarbon** and **isomerisation**



The catalyst **ZSM-5** converts **alcohol directly into gasoline** by dehydrating it to give a mixture of hydrocarbons.

R-OH -----> Hydrocarbon mixture

Enzyme Catalysis



Complex nitrogenous organic compounds which are produced by living plants and animals They are actually protein molecules of high molecular mass and form colloidal solutions in water.

Enzyme Catalysis



Numerous reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes.

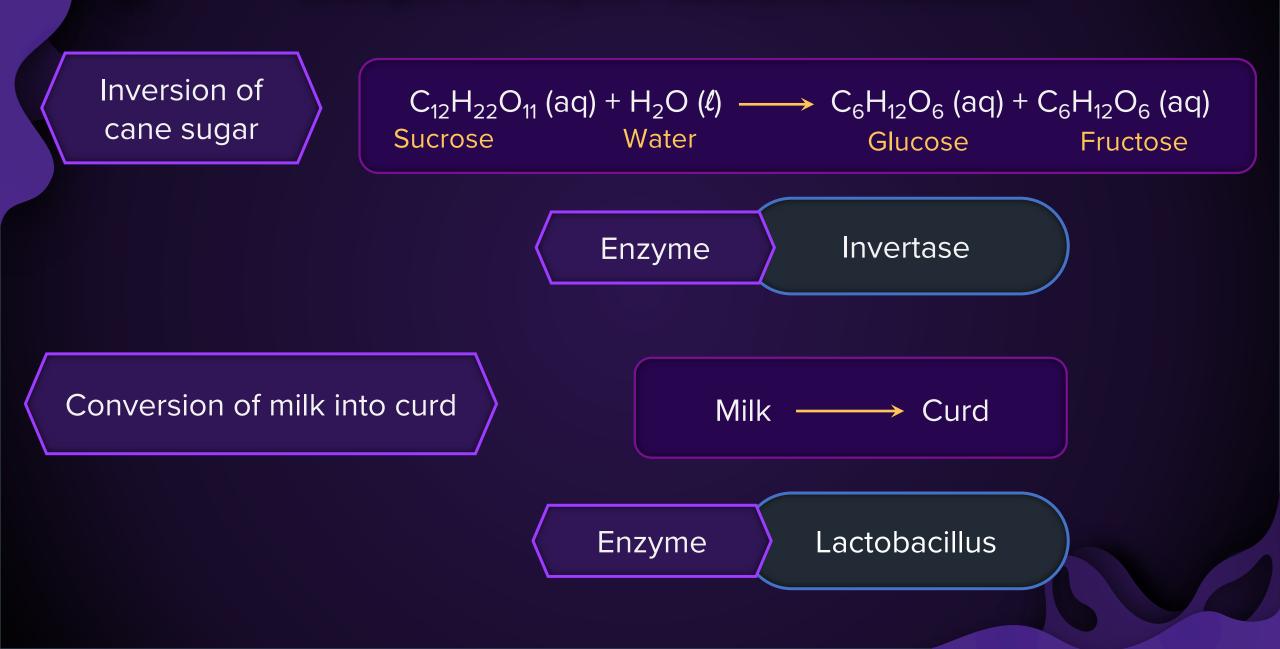
The enzymes are, thus, termed as

Biochemical catalysts

And the phenomenon is known as

Biochemical catalysis

Example of Enzyme-Catalysed Reactions



Mechanism of Enzyme Catalysis



There are a **number of cavities** present on the **surface** of enzymes. The reactant molecules that have **complementary shape** fit into these cavities just like a **key fits into a lock.**

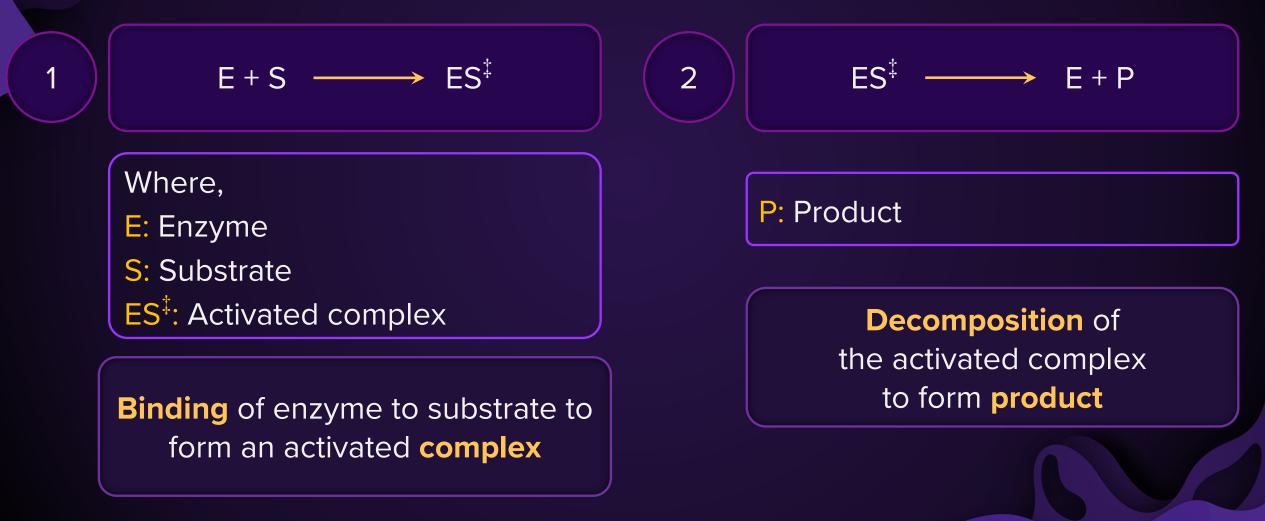
They are usually the active centers on the surface of enzyme particles.

The activated complex thus formed, decomposes into products

Steps Involved in Enzyme-Catalysed Reaction



The enzyme-catalysed reactions may be considered to proceed in **two steps**.



Characteristics of Enzyme Catalysis

2



Most efficient

One molecule of an **enzyme** may transform

1

One million molecules of the reactant per minute Highly **specific** in nature

Each enzyme is **specific** for a **given reaction**

One enzyme cannot catalyse more than one reaction

Characteristics of Enzyme Catalysis

Highly active under optimum temperature On either side of the optimum temperature, the enzyme activity decreases.

The rate of an enzyme reaction becomes maximum at a **definite** temperature.

3

This is known as **optimum** temperature.

Optimum temperature range for enzymatic activity 298-310 K

Human body temperature suitable for enzyme-catalysed reactions

310 K

Characteristics of Enzyme Catalysis

Highly active under optimum pH



Increasing activity in the presence of **co-enzymes** and **activators**

The **rate** of an enzymecatalysed reaction is **maximum** at a particular pH

4

This is known as **optimum pH**

The enzymatic activity increases in the presence of certain substances

known as **co-enzymes**

Non-protein organic molecules (example: vitamin)

pH range: 5–7

Effect of Activators on Enzyme Activity



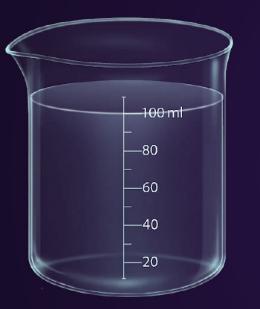
Generally, metal Activators ions Influence of 6 inhibitors and poisons Weakly The inhibitors or poisons interact Na⁺, Mn²⁺, Co²⁺, bonded with the active functional groups Cu²⁺, etc. to enzyme on the enzyme surface molecules Often reduce or completely increase Example: **destroy** the catalytic the catalytic For Amylase, activity of the enzymes activity activity increases

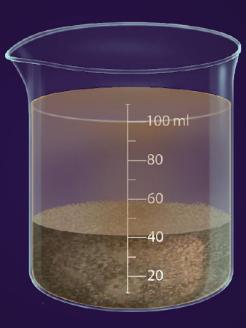
in presence of

Na⁺ ions

Types of Mixtures









Homogeneous mixture: Solution Example: Salt solution

Heterogeneous mixture: Suspension Colloid: Milk





Between the two extremes of suspensions and solutions,

we come across a large group of systems called **colloidal dispersions** or simply **colloids**

The phase that is dispersed/present in the form of colloidal particles

Dispersed

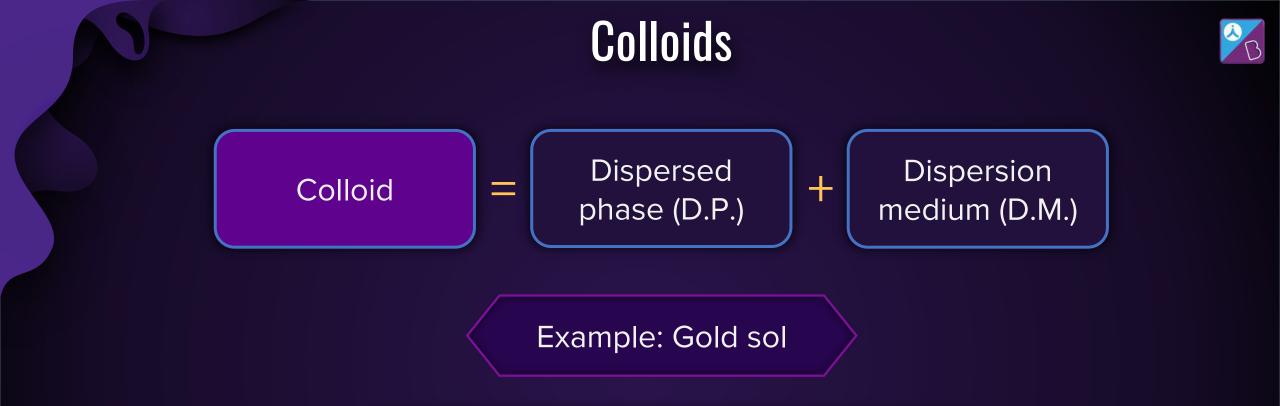
phase (D.P.)

Dispersion medium (D.M.)

Colloids consist

of two parts

A medium in which colloidal particles are dispersed



A colloid is a **heterogeneous** system in which one substance is dispersed (**dispersed phase**) as very fine particles in another substance called **dispersion medium**.

Solution vs Colloid

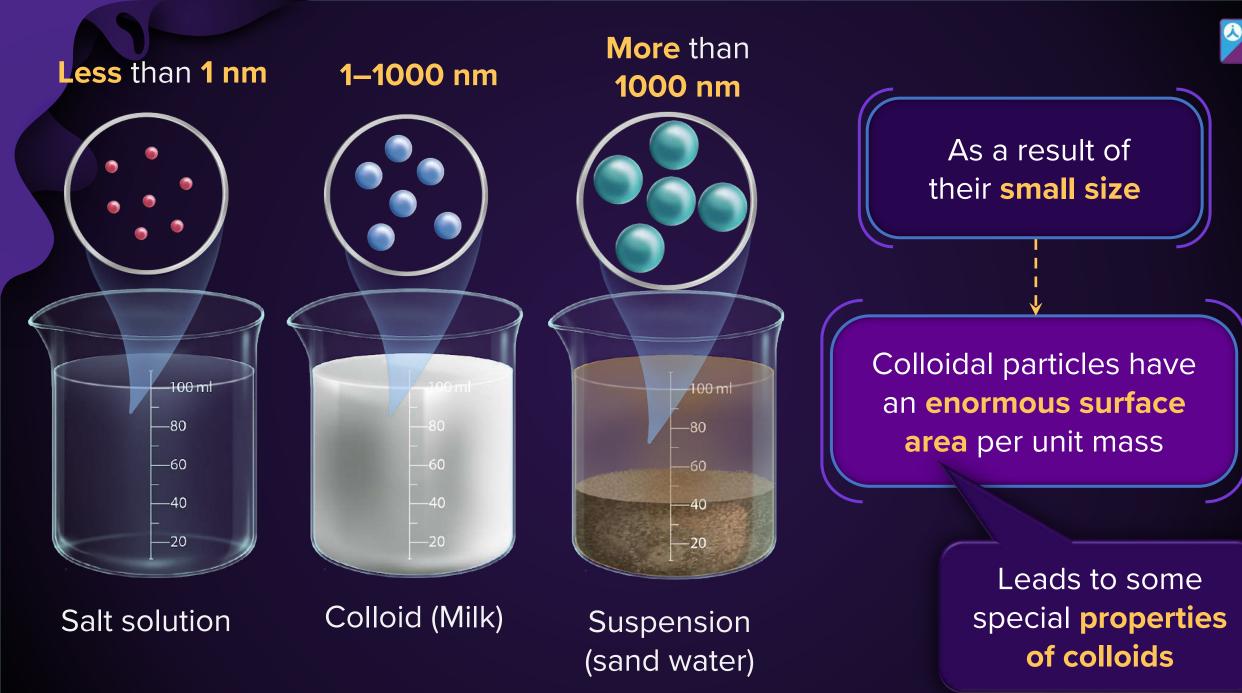
B

In solution

The constituent particles are ions or small molecules In colloid

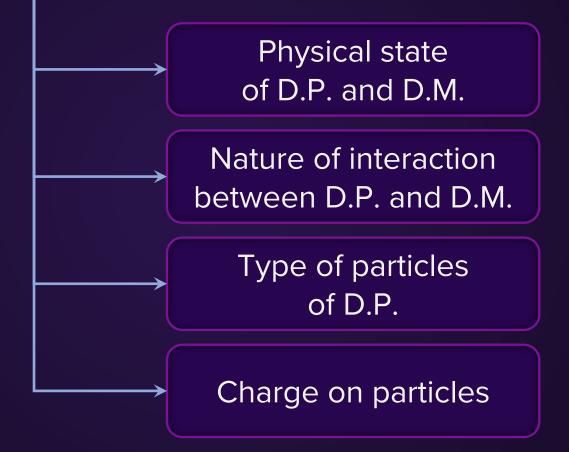
The dispersed phase may consist of particles of a **single macromolecule** or an **aggregate of many atoms, ions, or molecules**

Colloidal particles are larger than simple molecules but small enough to remain suspended.





Classification of colloids based on



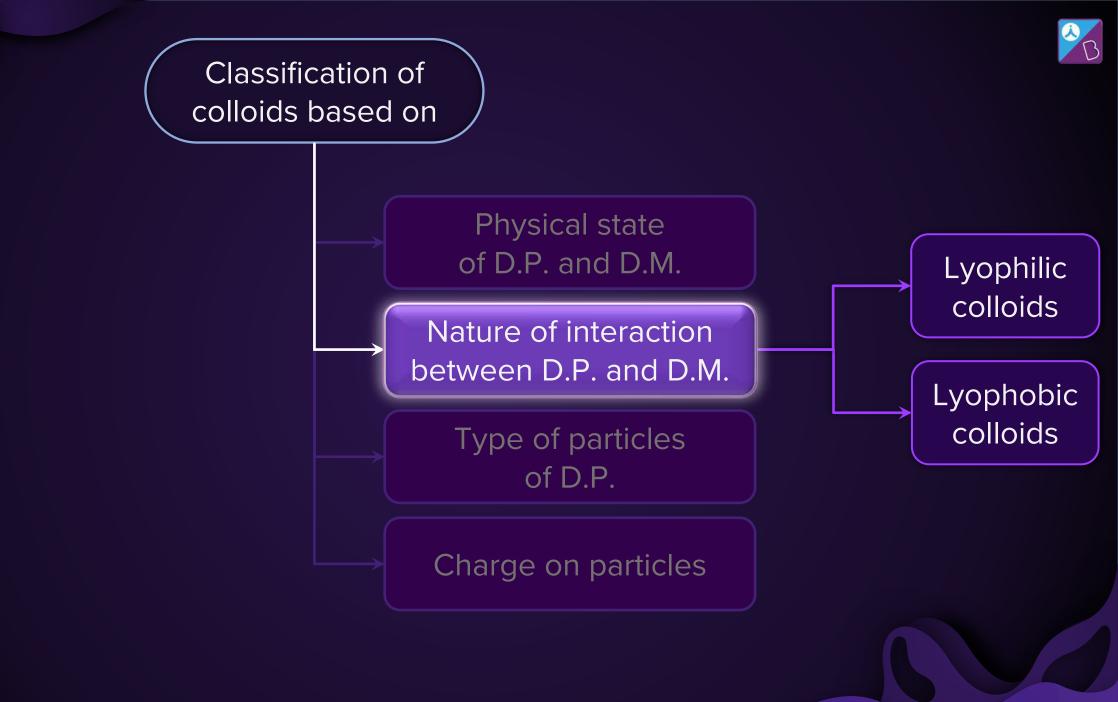
Classification of Colloids

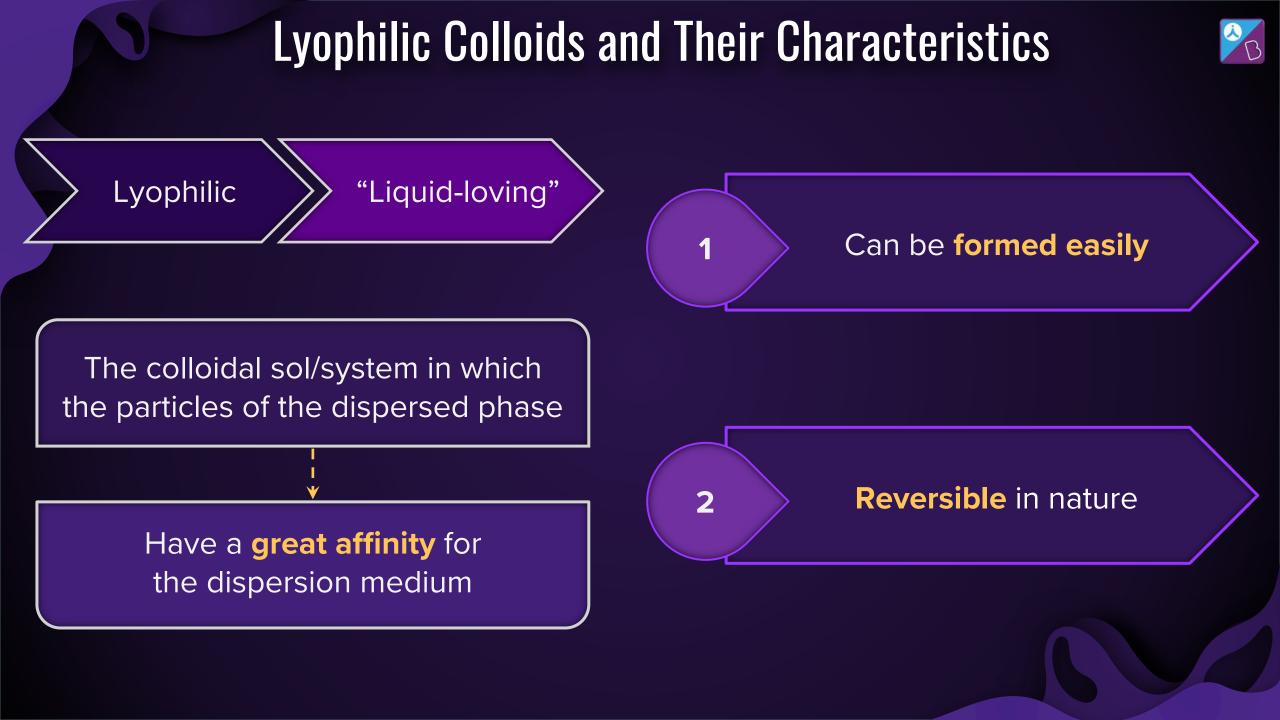


Depending upon whether the dispersed phase and the dispersion medium are **solids, liquids, or gases, eight** types of colloidal systems are possible.

The mixture of a gas with another gas is **homogeneous** system, so it's **not** a colloidal system.

Dispersed phase	Dispersion medium	Name
Solid	Solid	Solid sol
	Liquid	Sol
	Gas	Aerosol
Liquid	Solid	Gel
	Liquid	Emulsion
	Gas	Aerosol
Gas	Solid	Solid sol
	Liquid	Foam



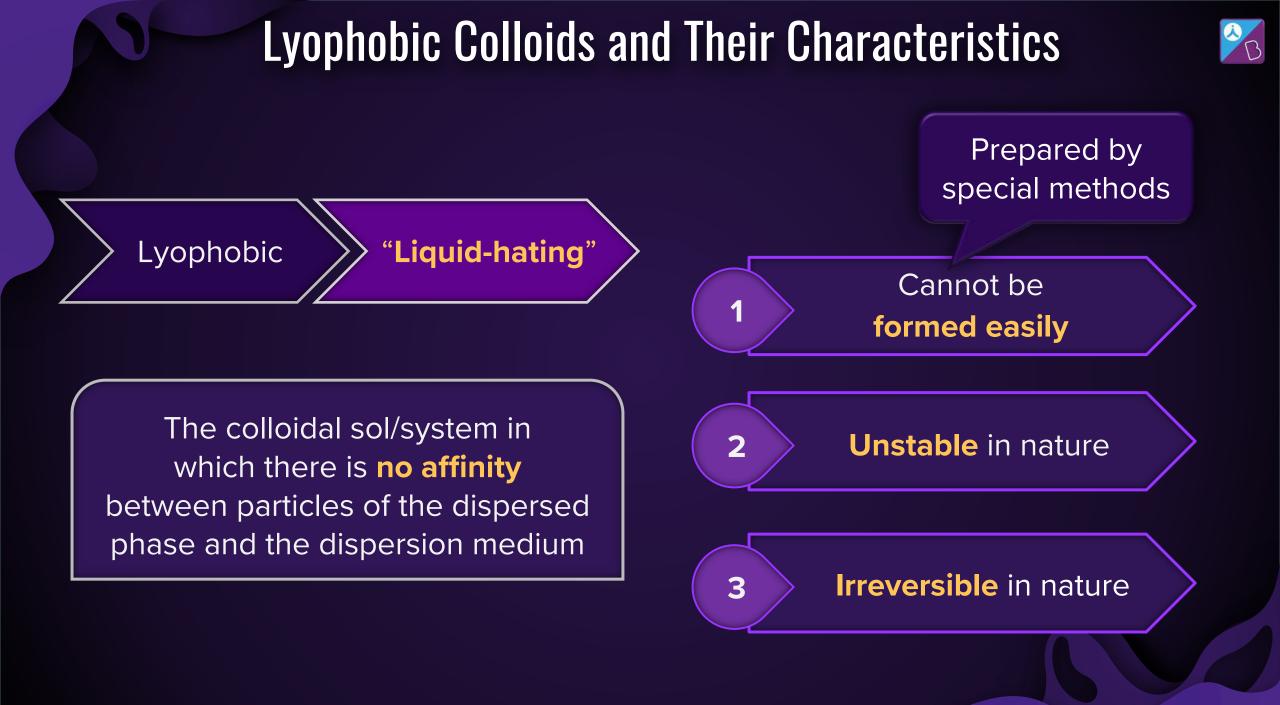


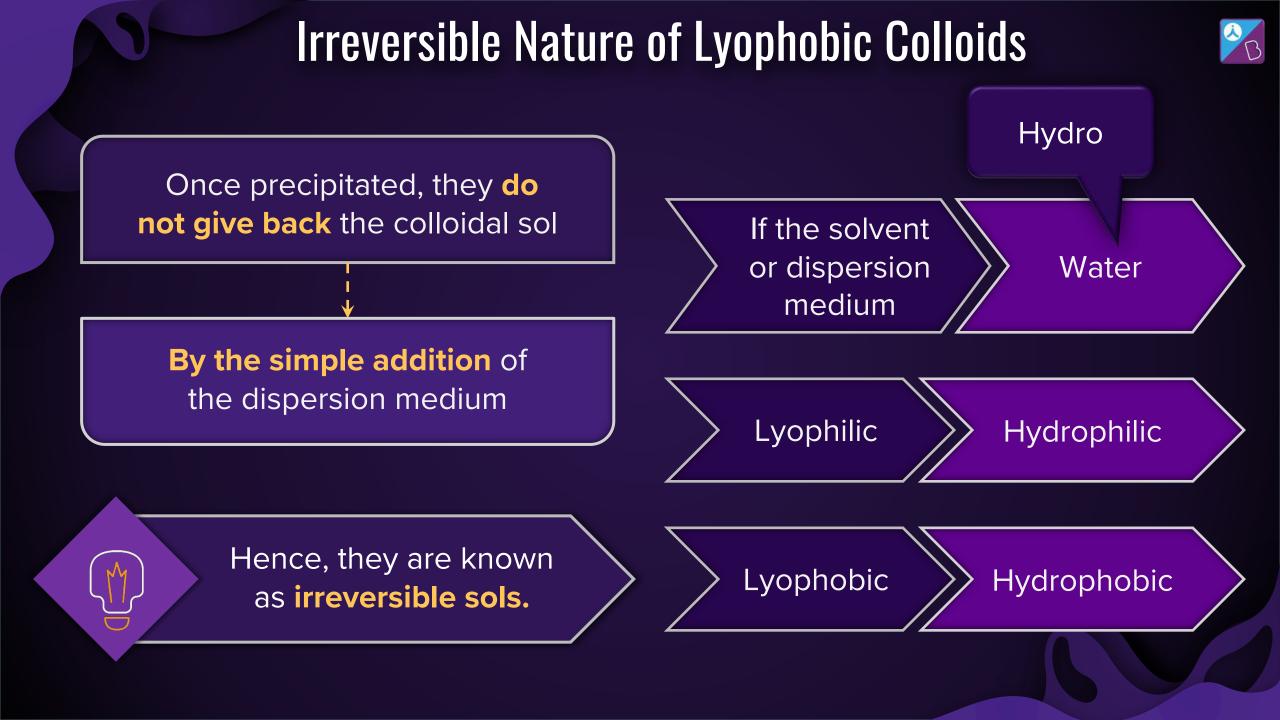
Reversible Nature of Lyophilic Colloids

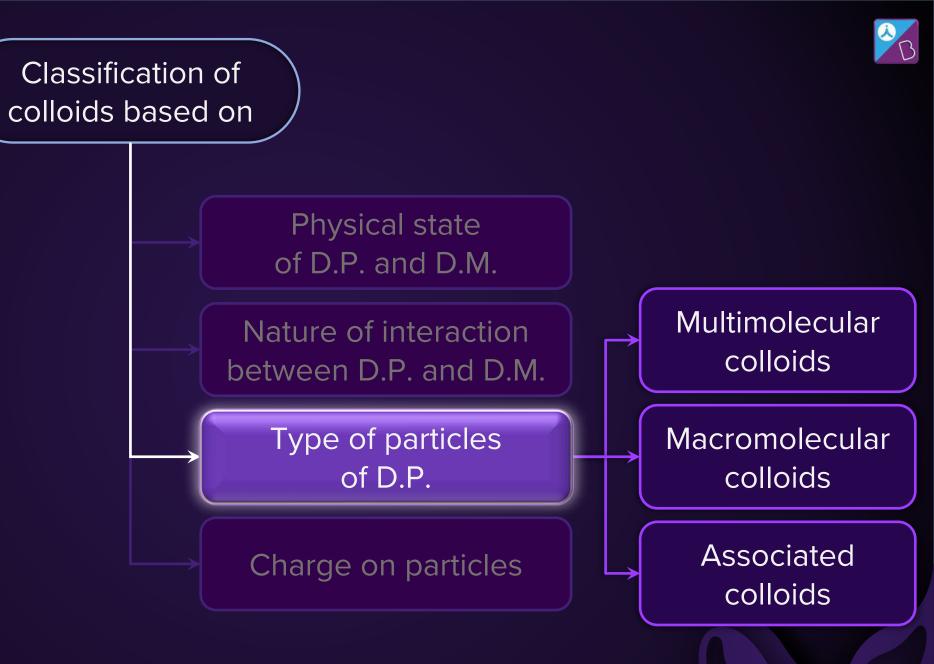
If the dispersion medium is separated from the dispersed phase, the sol can be reconstituted by simply remixing with the dispersion medium.

Hence, they are known as **reversible sols.**









Multimolecular Colloids

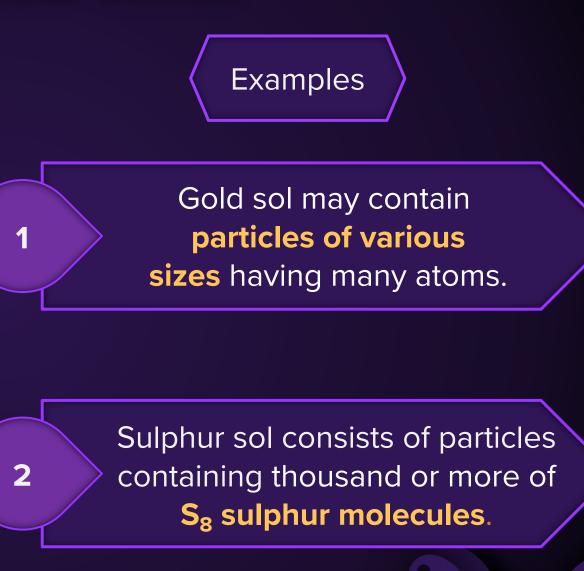


On dissolution,

A large number of atoms or smaller molecules of a substance **aggregate together**.

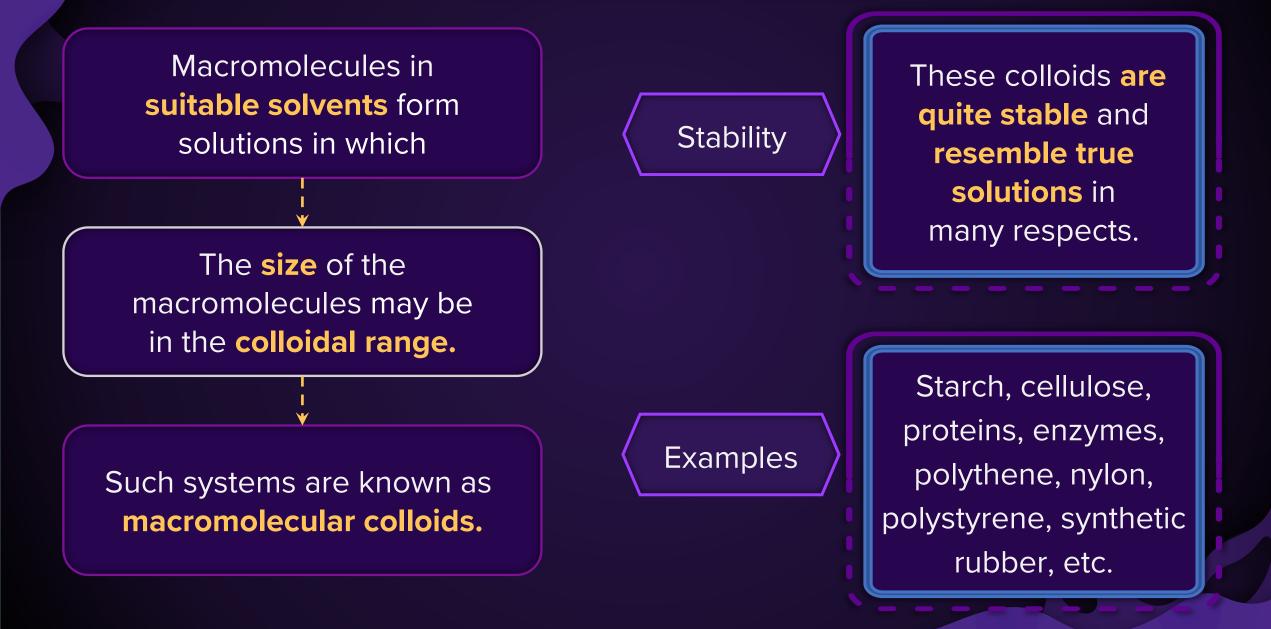
They **form** species having **size in the colloidal range** (1–1000 nm).

Such species are known as **multimolecular colloids**.



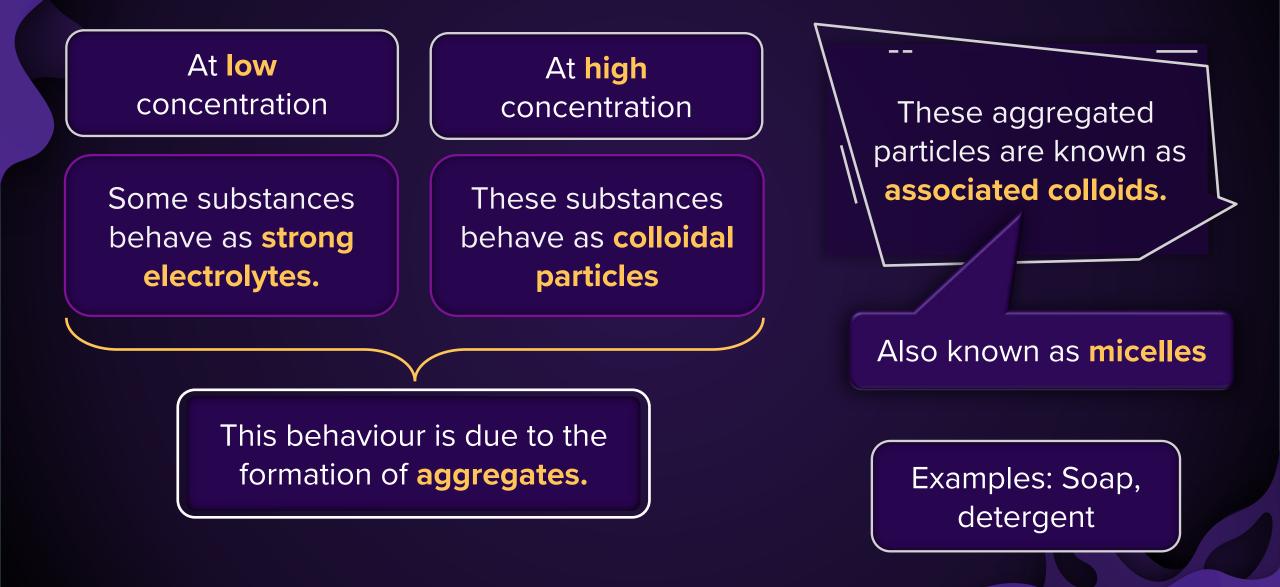
Macromolecular Colloids





Associated Colloids





Micelles



Micelles are relatively small, spherical structures composed of a few to some thousand molecules.

These molecules **attract one another** to form a larger aggregate which falls in the colloidal range.



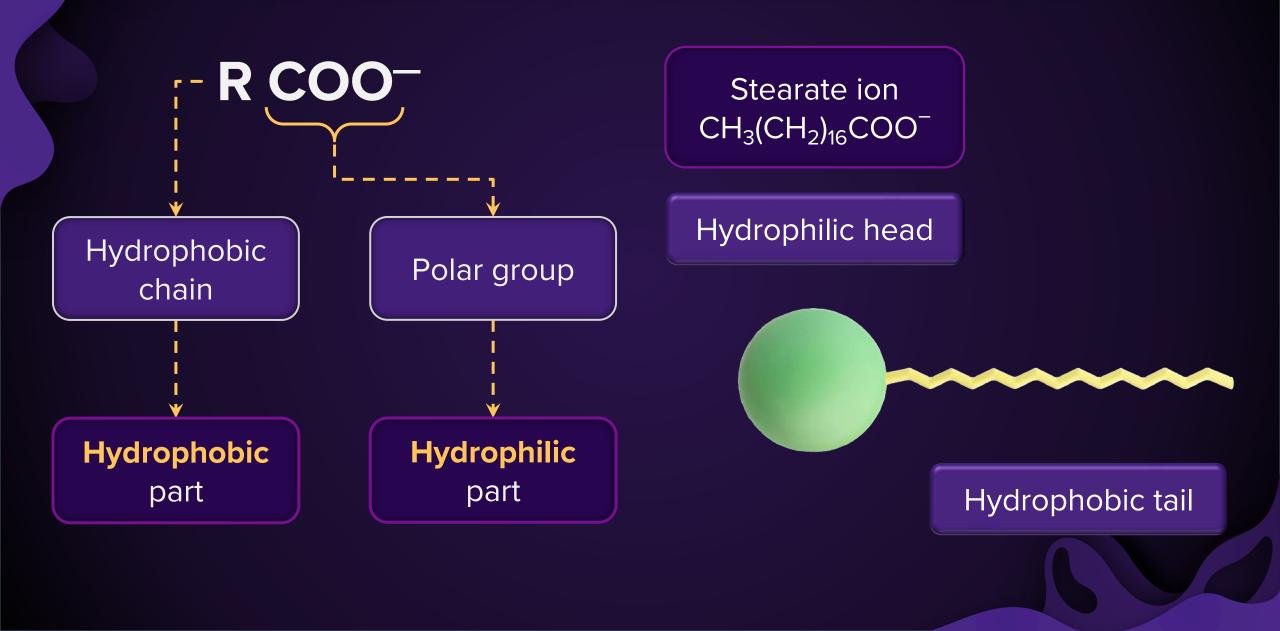
Soap is a sodium salt of a higher fatty acid which is represented as

 $\mathsf{RCOO}^-\mathsf{Na}^+$

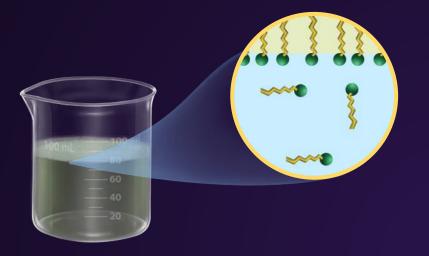
Examples: Sodium stearate $CH_3(CH_2)_{16}COO^-Na^+$

Hydrophilic and Hydrophobic Ends of a Soap Ion





Mechanism of Micelle Formation



When sodium stearate ${CH_3(CH_2)_{16}COO^-Na^+}$ is **dissolved** in water, it **dissociates** into RCOO⁻ and Na⁺ ions. Where R = CH_3(CH_2)_{16} So, RCOO⁻ arranges itself in such a way that COO⁻ can be close to water and the hydrocarbon chain can stay away from it by staying at the surface.

Mechanism of Micelle Formation



But at higher concentration, these are **pulled into the bulk** of the solution and they aggregate in a **spherical form.** The spherical form has the hydrocarbon chains pointing towards the centre.

The **COO**⁻ part remains **outward** on the surface of the sphere.

Mechanism of Micelle Formation



This aggregated form is known as **micelle,** which may contain 100 such ions. Critical micelle concentration (CMC)

It is the **concentration above which** micelle formation takes place.

Kraft temperature (T_k)

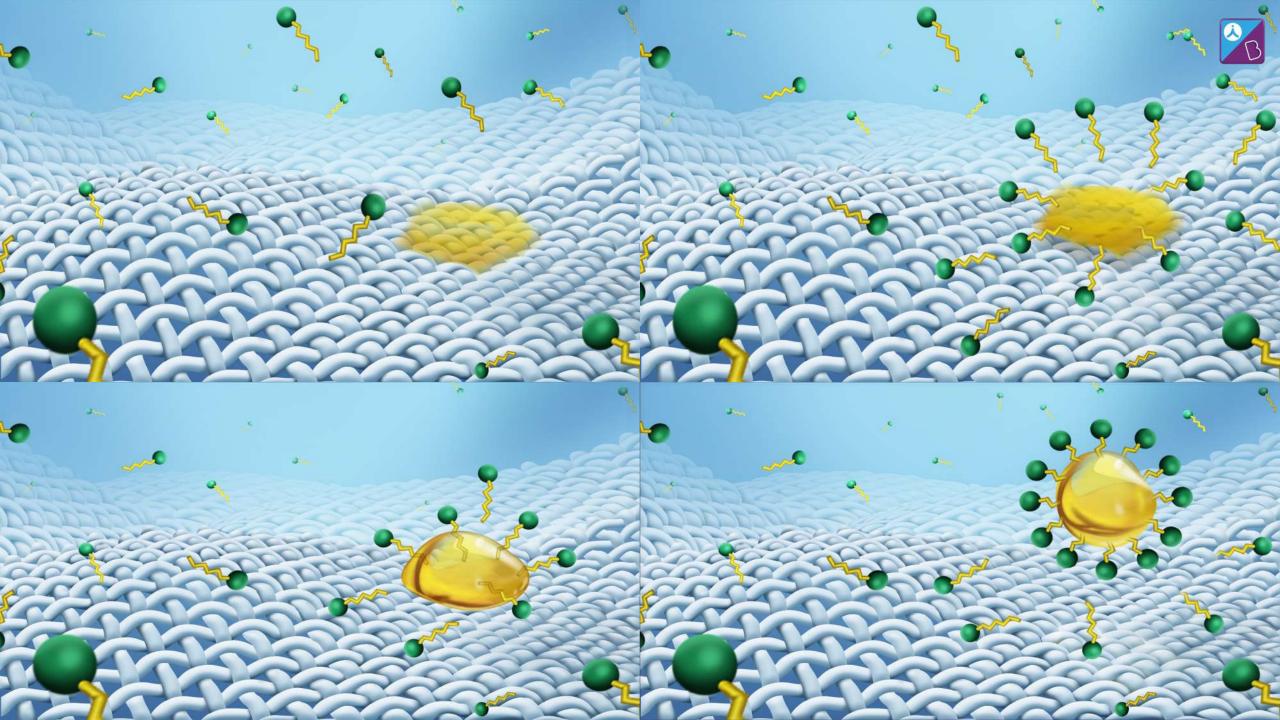
The **formation** of micelles takes place only **above** a **particular temperature.**

The Cleansing Action of Detergents

Sodium lauryl sulphate ${CH_3(CH_2)_{11}SO_4^-Na^+}$

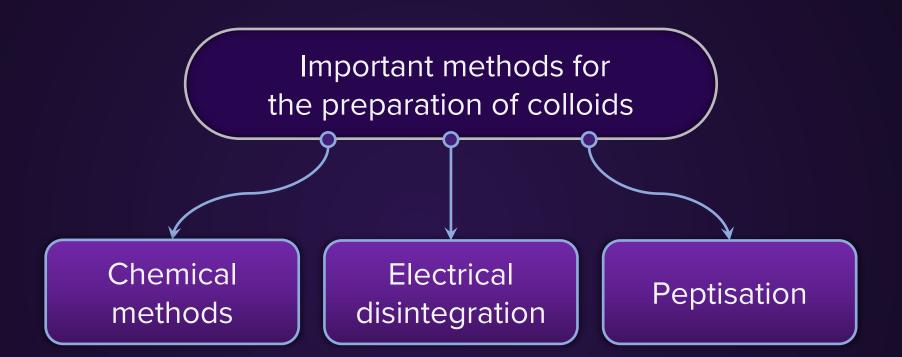
The **polar** group is **–SO**⁻ along with the long hydrocarbon chain.

So, the **mechanism** of micelle formation in detergents is the **same** as that of soaps.



Preparation of Colloids

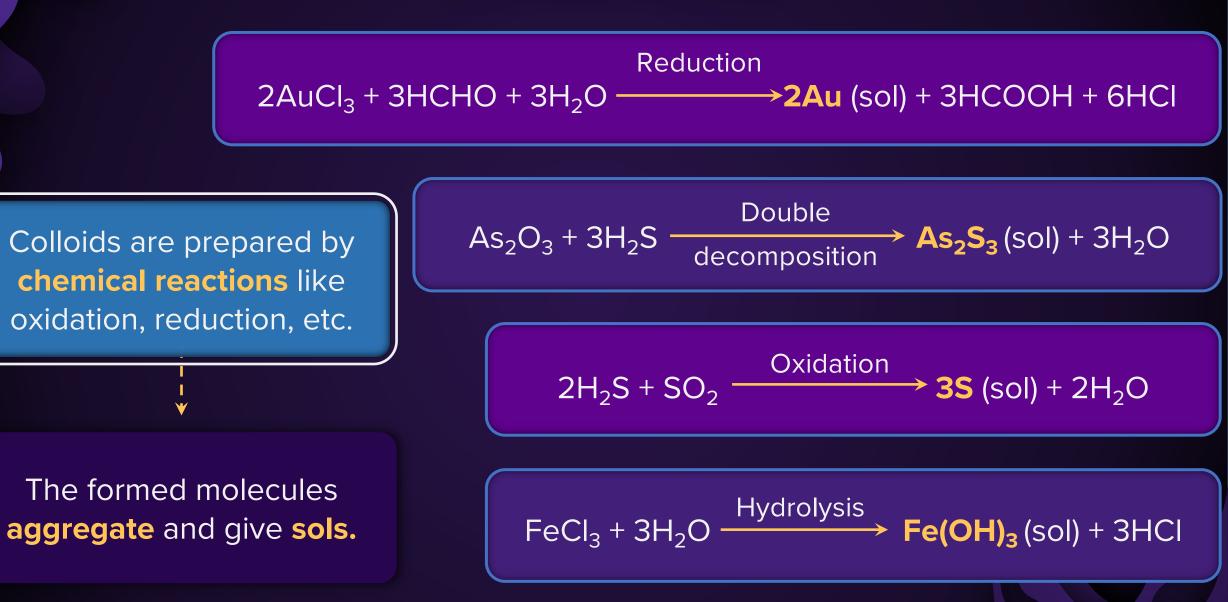






Chemical Methods





Electrical Disintegration

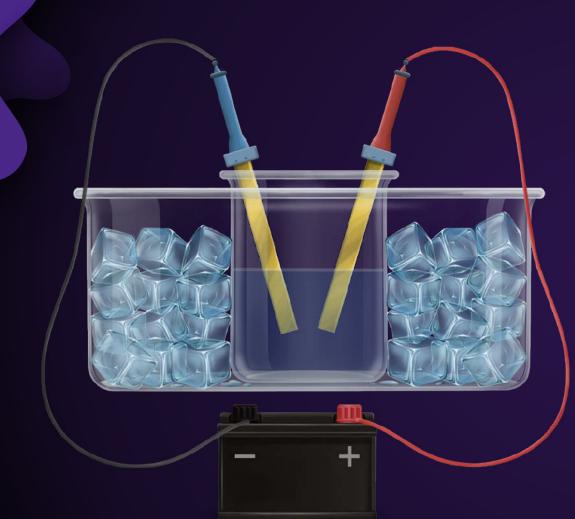


The process involves both **dispersion and condensation.**

It is also known as Bredig's arc method.

The colloidal **sols of metals** such as **gold, silver, platinum**, etc. can be prepared by this method

Mechanism of Bredig's Arc Method



An electric arc is struck between metal electrodes immersed in the dispersion medium.

The intense heat produced vapourises the metal.

It then **condenses** to form particles of colloidal size.

Peptisation

Example

Freshly precipitated

Fe(OH)₃ is shaken

with aqueous solution

of FeCl₃

Peptising

agent



The process of converting a precipitate into colloidal sol by shaking with dispersion medium in the presence of a small amount of electrolyte

> Peptising agent

Generally, it is used to convert a **freshly prepared precipitate** into a **colloidal sol.**

Peptisation



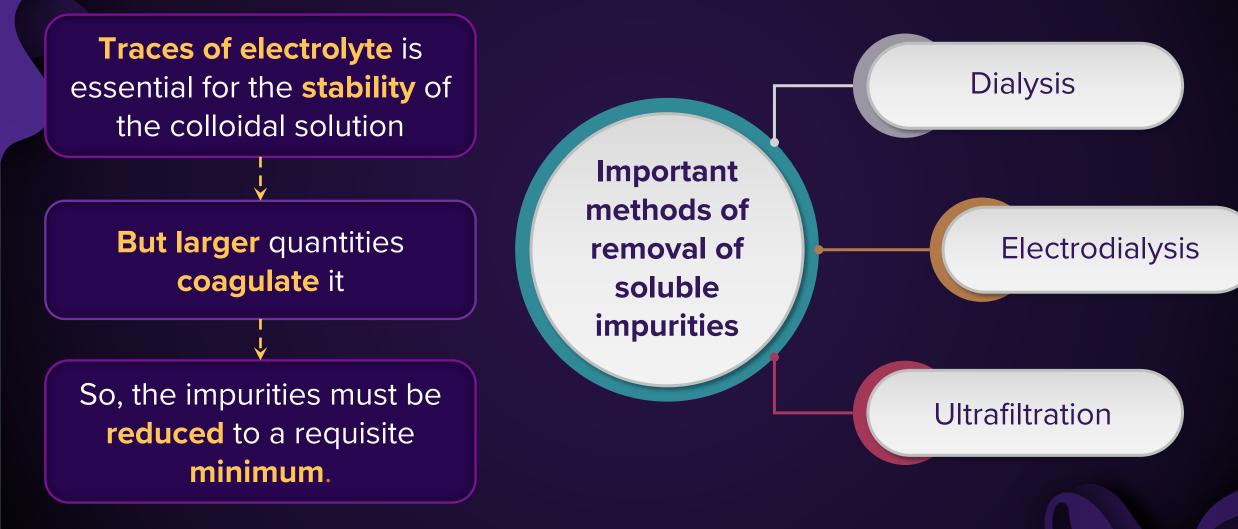
Colloidal sol formation



The precipitate adsorbs electrolyte ions on its surface, this causes the development of positive or negative charge on precipitates, which ultimately break up into smaller particles of colloidal size

Purification of Colloidal Solution









Process of **removing a dissolved substance** from a colloidal solution by means of **diffusion** through a **suitable membrane**

Animal membrane (bladder) or parchment paper or cellophane sheet

Membranes

Since particles (ions or smaller molecules) in a **true solution** can **pass through** the membrane but **not the colloidal** particles

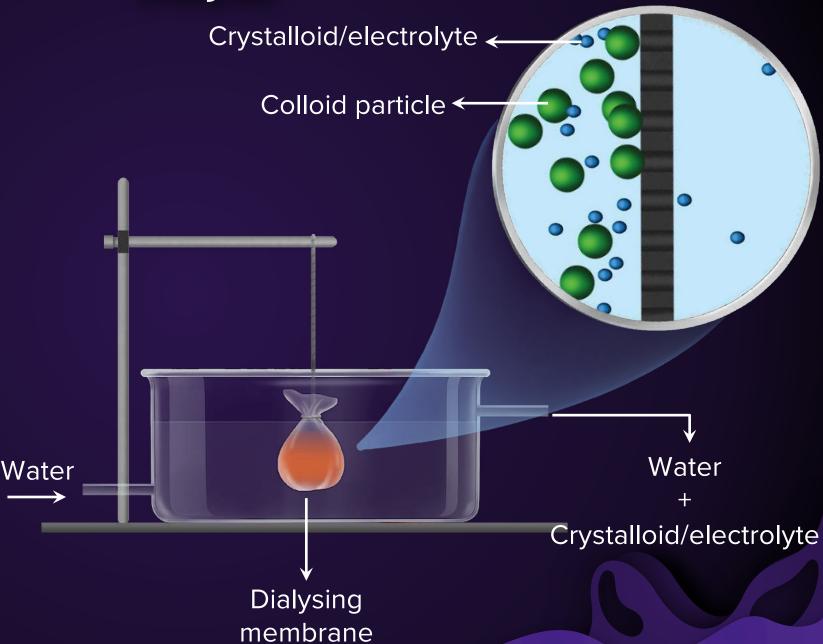
Membranes can be used for **dialysis**

Dialyser



The apparatus used for dialysis process is called as **dialyser**.

The molecules or ions in colloidal solution diffuse through dialysing membrane in running water and pure colloidal solution is left behind.



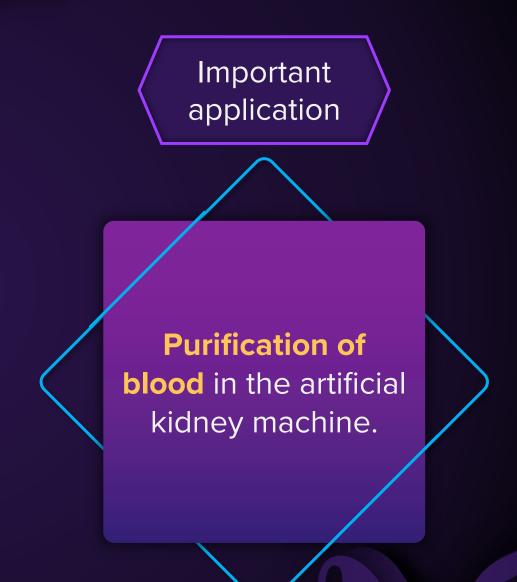
Electrodialysis

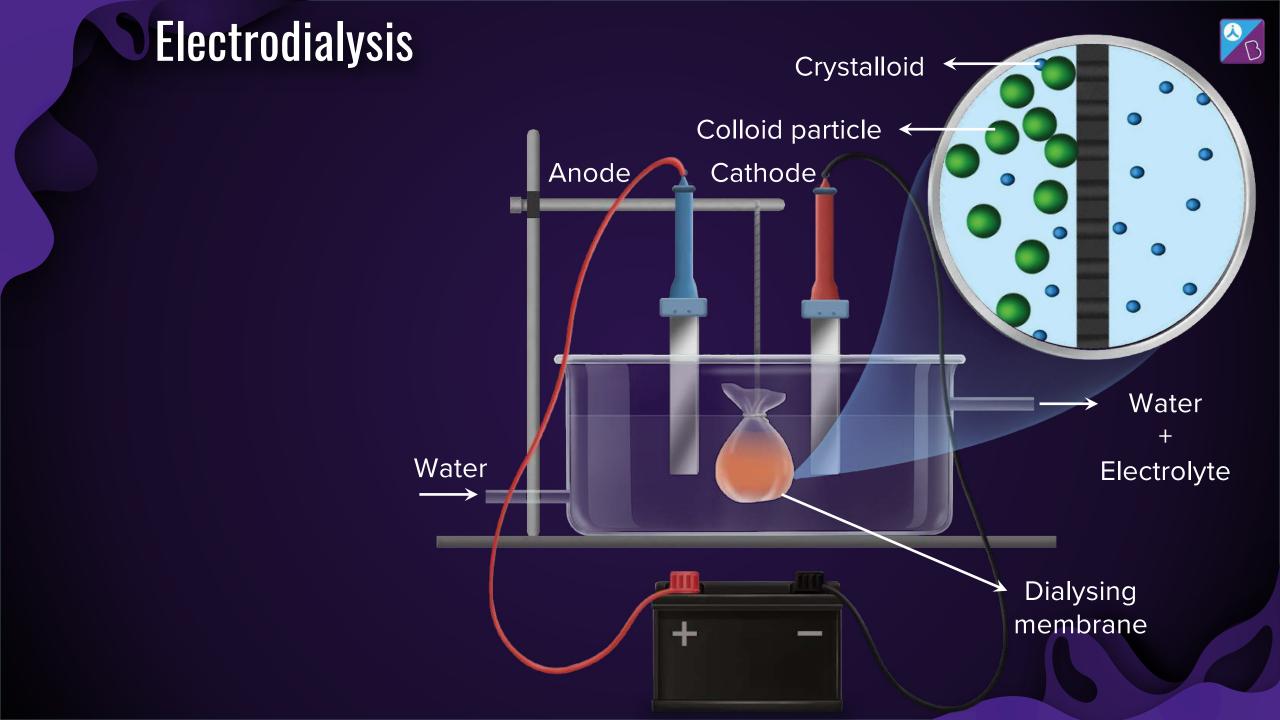


Similar to dialysis ----> But faster

If the dissolved substance in the impure colloidal solution is **only an electrolyte**

The process can be made **faster** by **applying** an **electric field**





Ultrafiltration



The process of **separating** colloidal particles from solvent and soluble solutes by **specially prepared filters.**

> Sol particles pass through ordinary filters

The filter should be permeable to all substances except colloidal particles

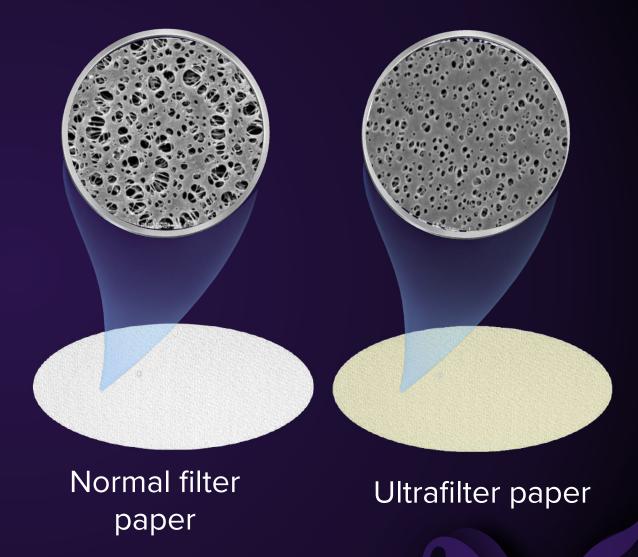
Ultrafilter paper is used for this purpose

Preparation of Ultrafilter Paper

Prepared by **soaking** the filter paper in a **collodion** solution

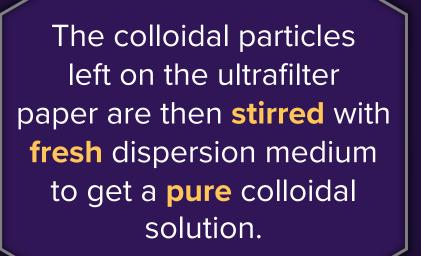
Hardening it by formaldehyde and then drying it

The usual collodion is a **4% solution of nitrocellulose** in a mixture of **alcohol** and **ether**.





Ultrafiltration



Properties of colloidal solution



Colligative properties

Tyndall effect

Colour

Brownian movement

Charge on colloidal particles

Electrophoresis

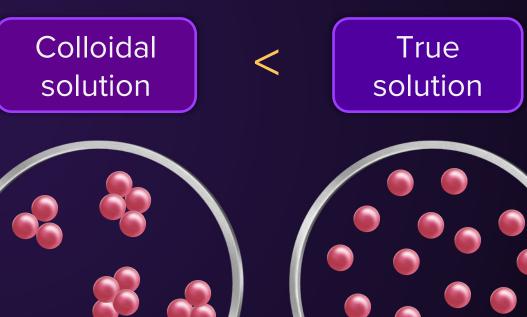
Coagulation or precipitation

Colligative Properties



At the same concentration

Therefore, the colligative property values of



Colloidal particles are **bigger aggregates**.

The **number of particles,** per unit volume, in a colloidal solution is **small** compared to a true solution.

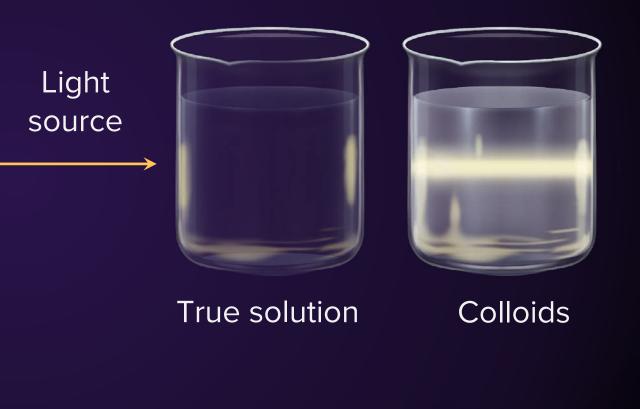
Tyndall Effect

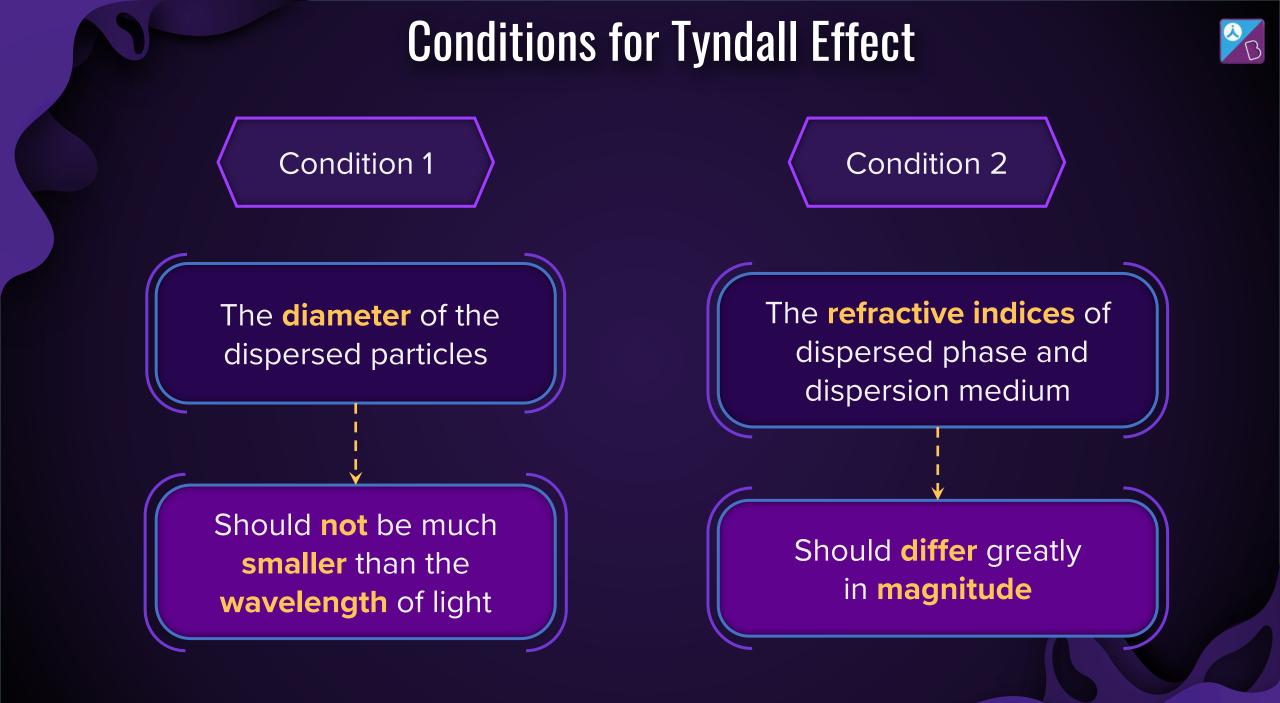


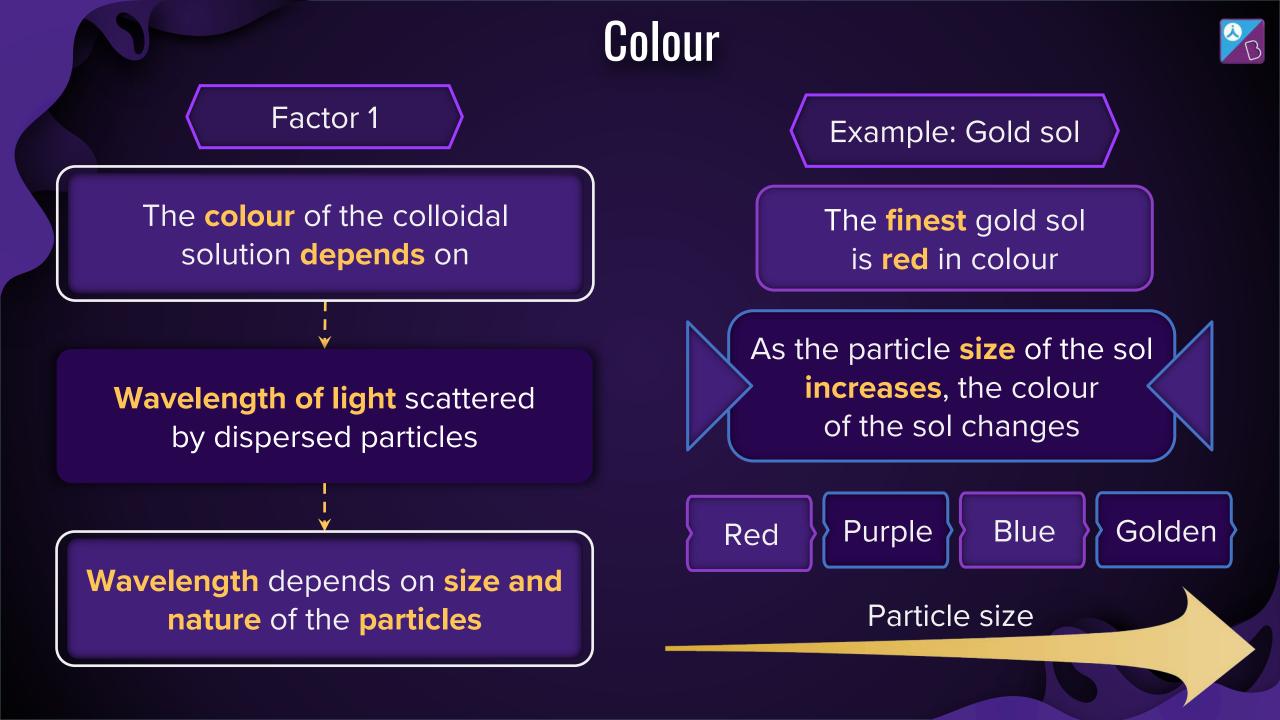
If a strong **beam** of light is **passed** through a **colloidal sol** placed in a **dark** place

Path of the beam gets illuminated due to the scattering of light by colloidal particles.

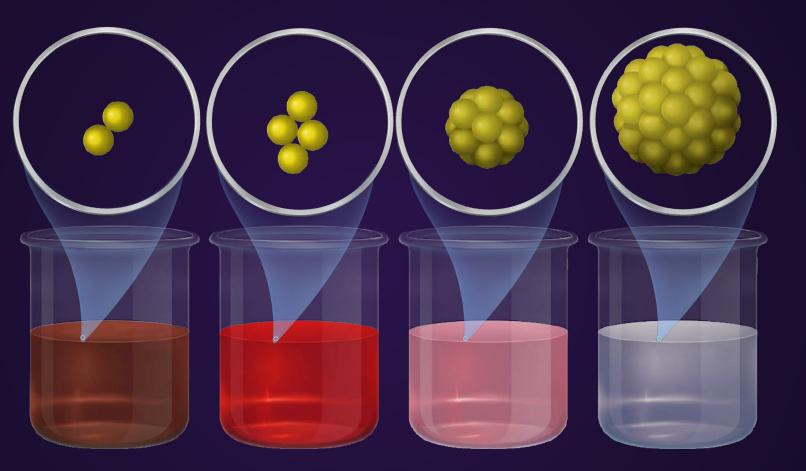
This phenomenon is called as **Tyndall effect**





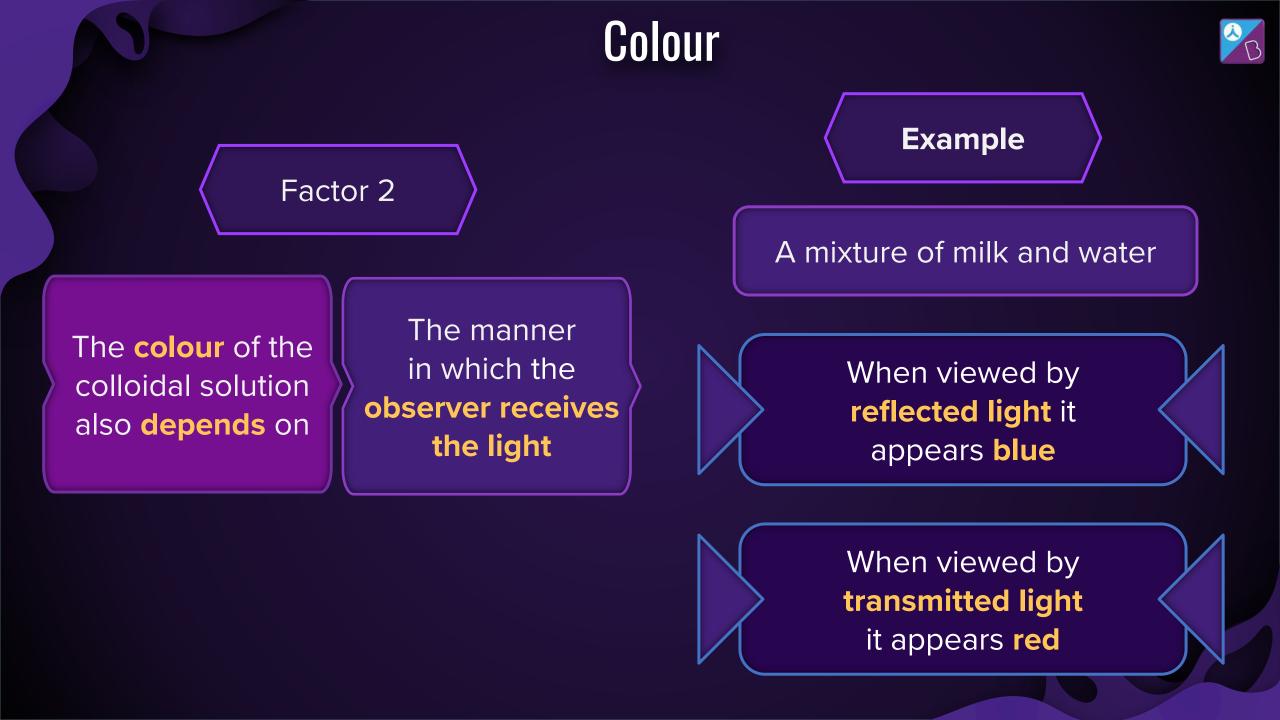


Effect of Particle Size on Colour



Size of colloidal particles





Brownian Movement



When viewed under an ultramicroscope, colloidal particles appear to be in a continuous zig-zag motion.

> Known as Brownian movement

The Brownian movement takes place

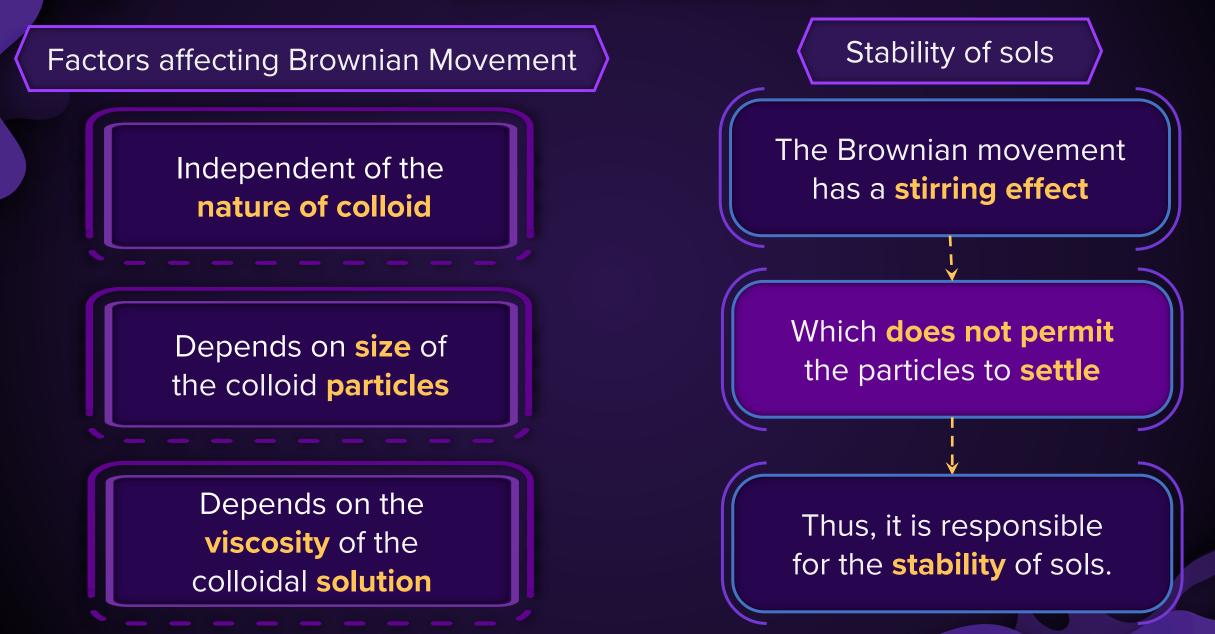
Due to the **unbalanced bombardment** of the

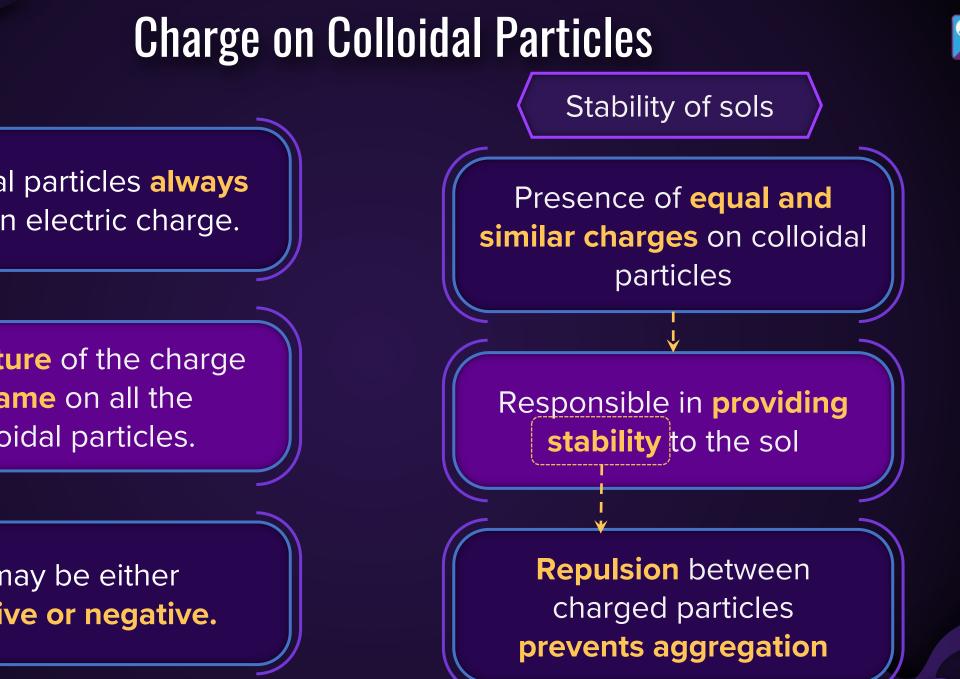
particles

By the molecules of the dispersion medium

Brownian Movement







Colloidal particles **always** carry an electric charge.

The **nature** of the charge is **same** on all the colloidal particles.

It may be either positive or negative.

Common Charged Sols



S. No.	Positively charged sols	Negatively charged sols
1	Hydrated metallic oxides (Examples: Al ₂ O ₃ .xH ₂ O, Fe ₂ O ₃ .xH ₂ O, etc.)	<mark>Metals</mark> (Examples: Cu, Ag, Au sols)
2	Basic dye stuffs (Examples: Methylene blue sol)	<mark>Metallic sulphides</mark> (Examples: As ₂ S ₃ , Sb ₂ S ₃ , CdS, etc.)
3	Haemoglobin (blood)	Acid dye stuffs (Examples: Eosin, congo red sols)
4	Oxides (Example: TiO ₂ sol)	Sols of starch, gum, gelatin, clay, charcoal, etc.

Possible Reasons for Charge on Colloidal Particles





1

2

3

Electron capture by sol particles during electro dispersion of metals

Preferential adsorption of ions from solution

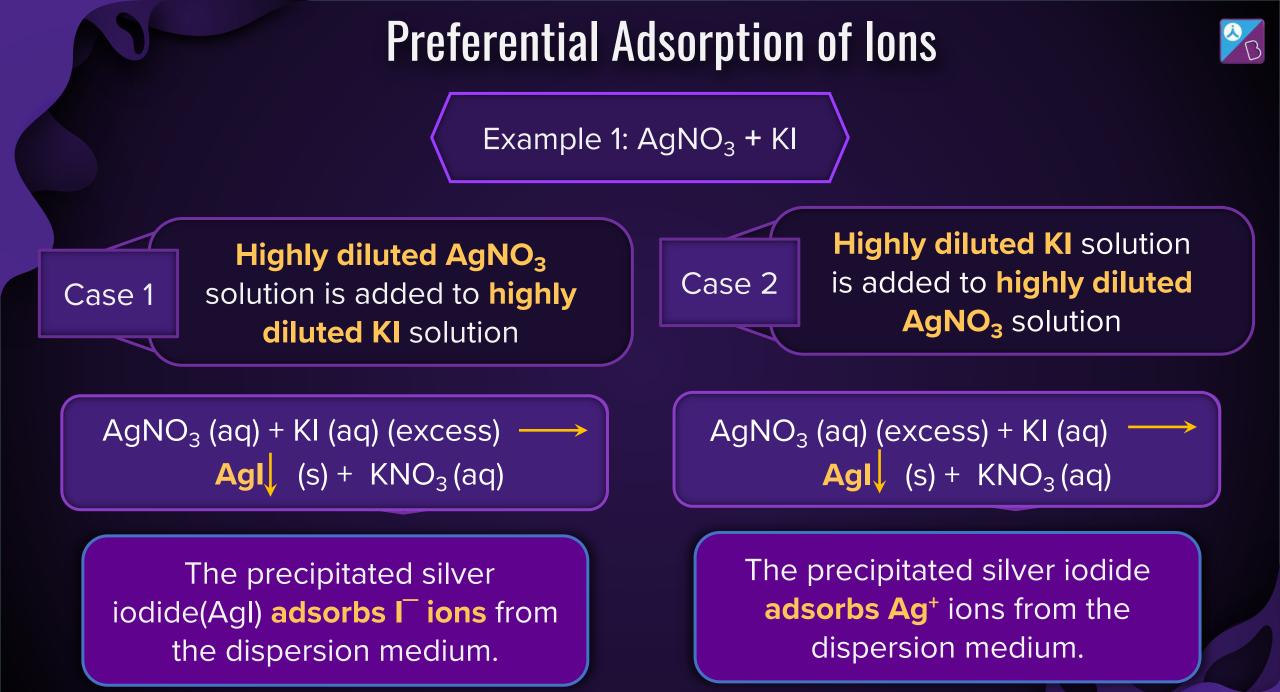
Formation of **electrical double layer**

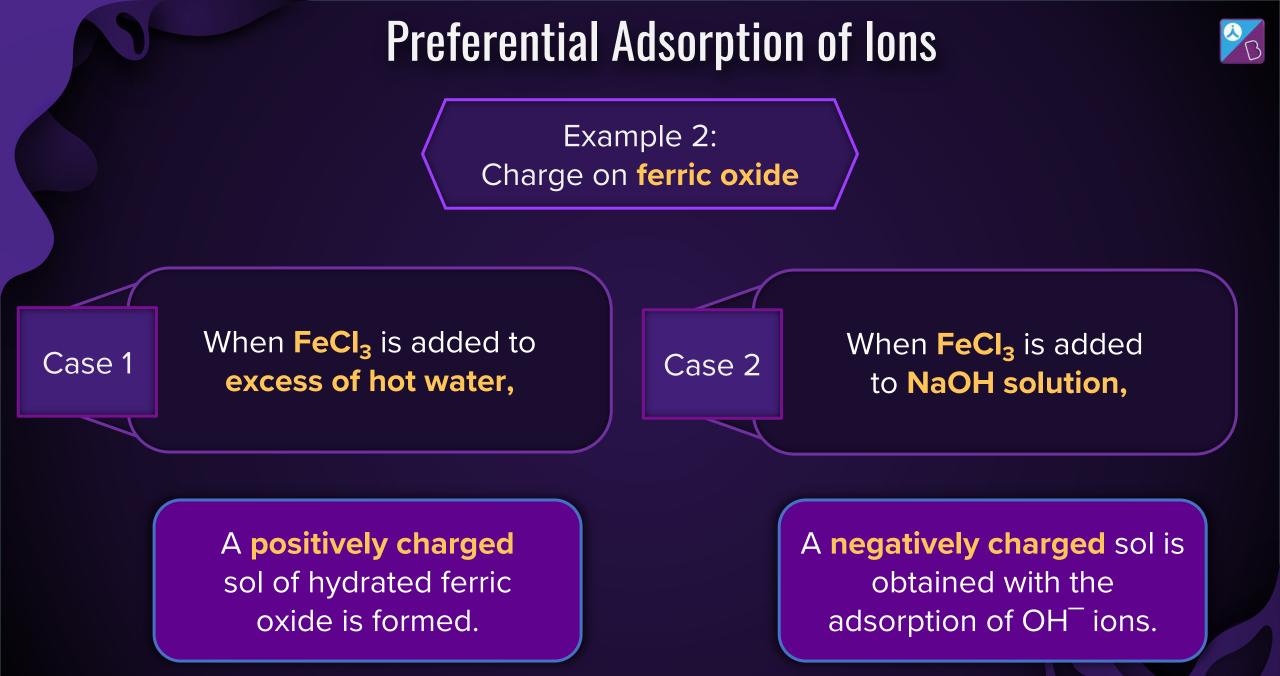
Preferential Adsorption of Ions



When **two or more ions** are present in the dispersion medium

Preferential adsorption of the ion common to colloidal particle usually takes place





Interactions Between Oppositely Charged Ions



By selective adsorption of a common ion on the surface, a colloidal particle acquires a positive or a negative charge.

This charged layer attracts counter ions from the medium to form a second layer.

 $AgI/I^{-}K^{+}$





Selective adsorption of I⁻ions

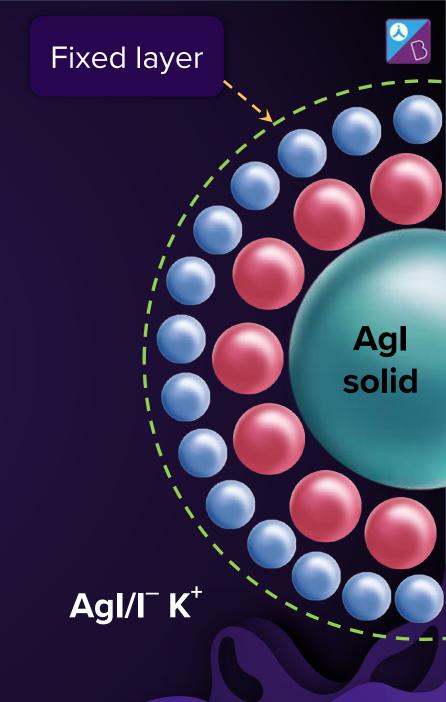


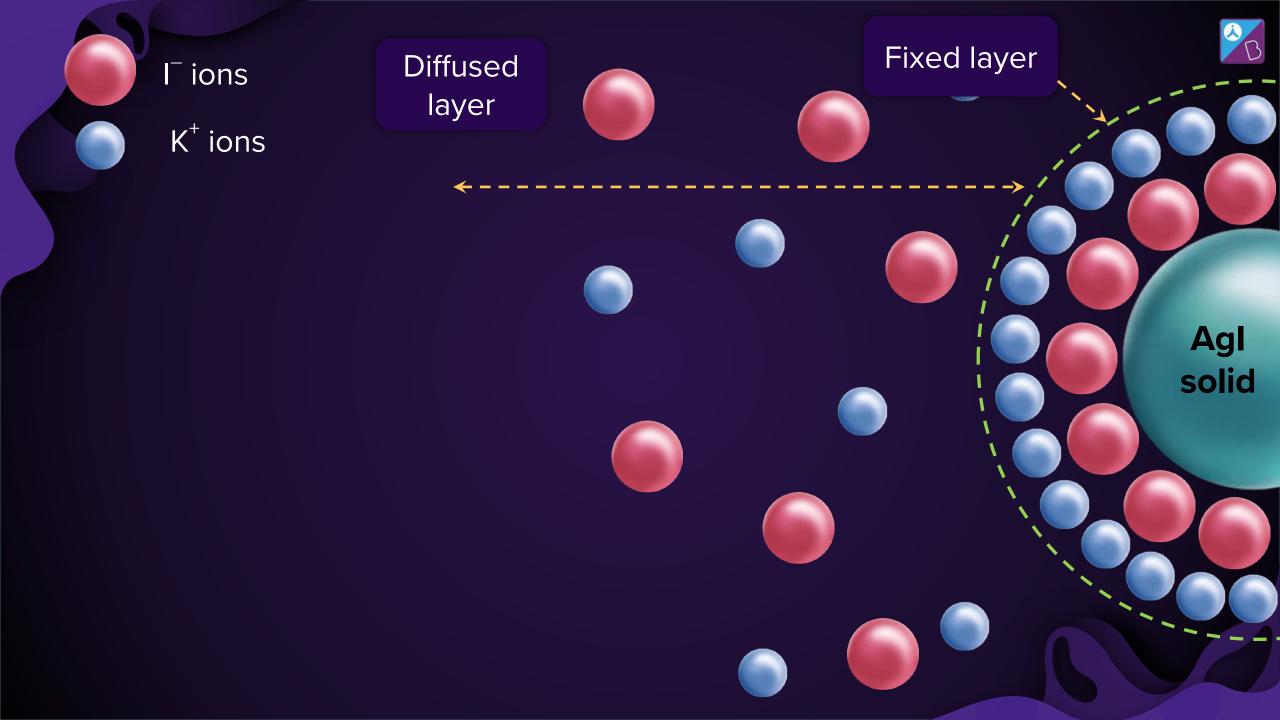


Agl/l⁻



Formation of layer of counter (K^{+}) ions

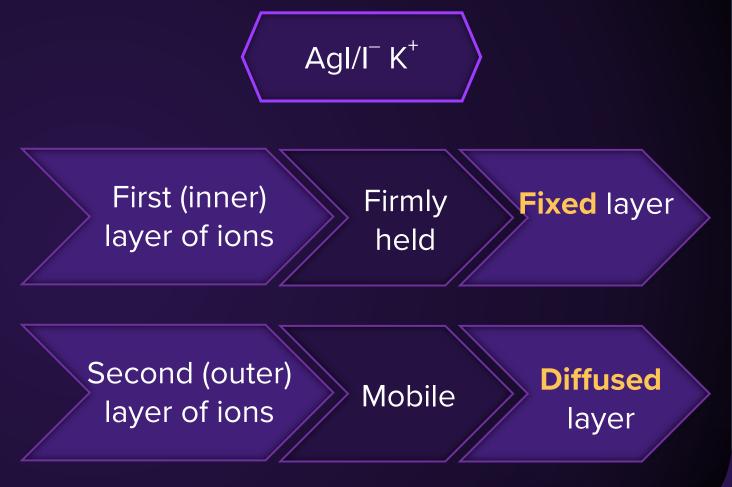




Helmholtz Electrical Double Layer



The combination of the **two layers of opposite charges** around the colloidal particle is known as **Helmholtz electrical double layer.**

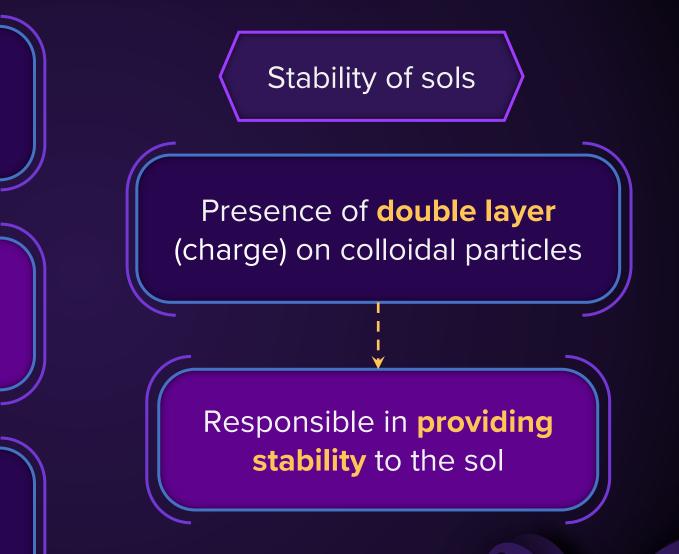


Helmholtz Electrical Double Layer



Result in **potential difference** between the layers

Called electrokinetic potential or zeta potential





Electrophoresis



The movement of colloidal particles under an applied potential is known as electrophoresis.

It confirms the existence of charge on colloidal particles.

Before electric potential is applied

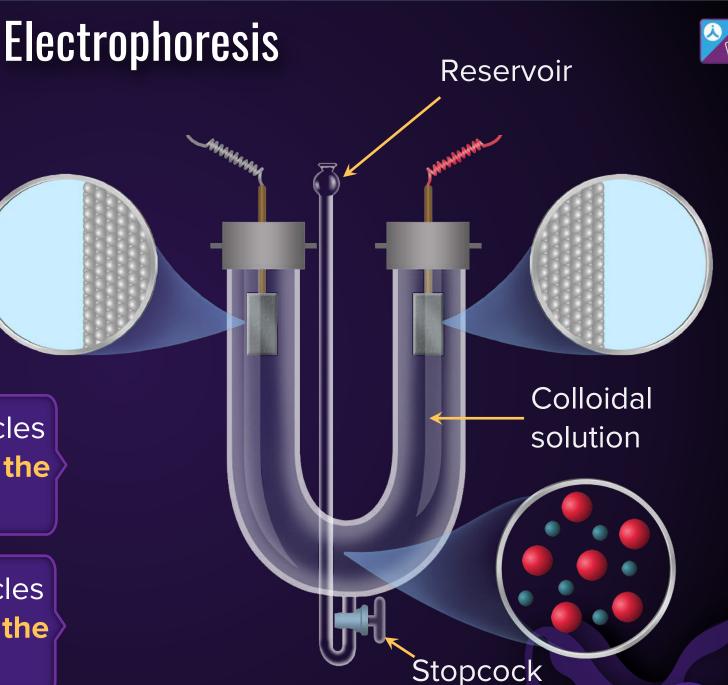
Colloidal particle

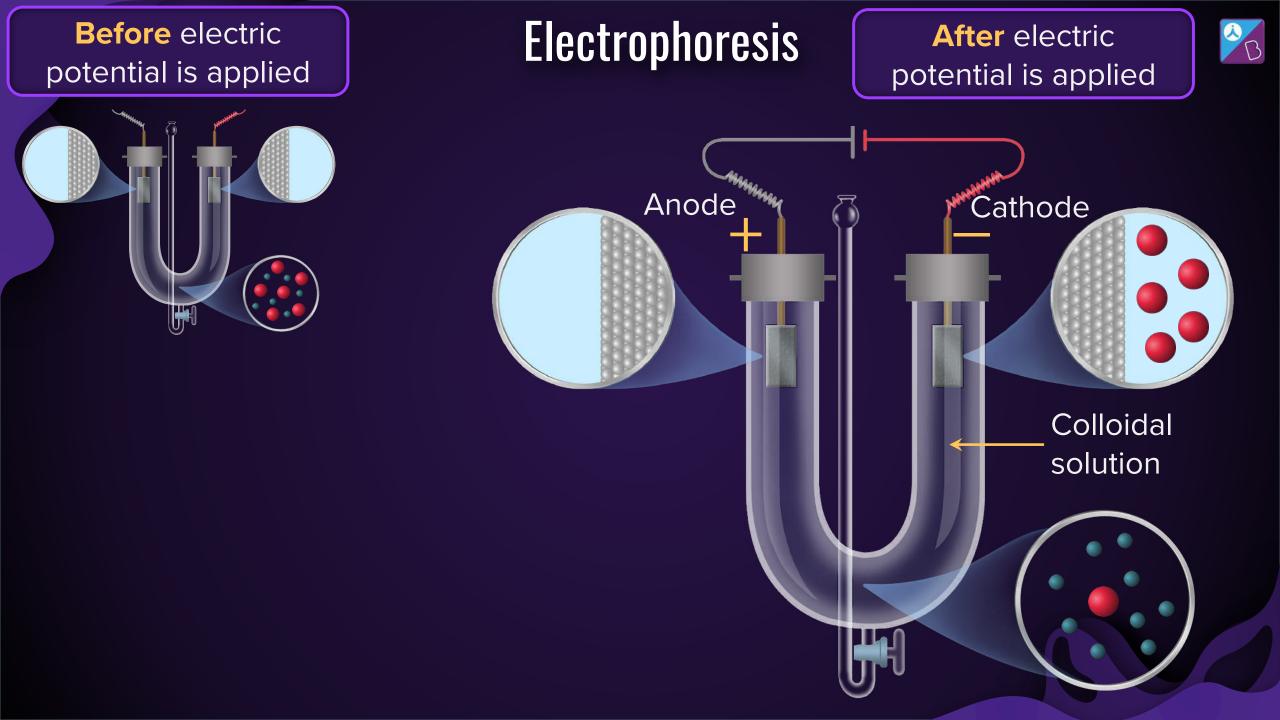
Dispersion medium particle

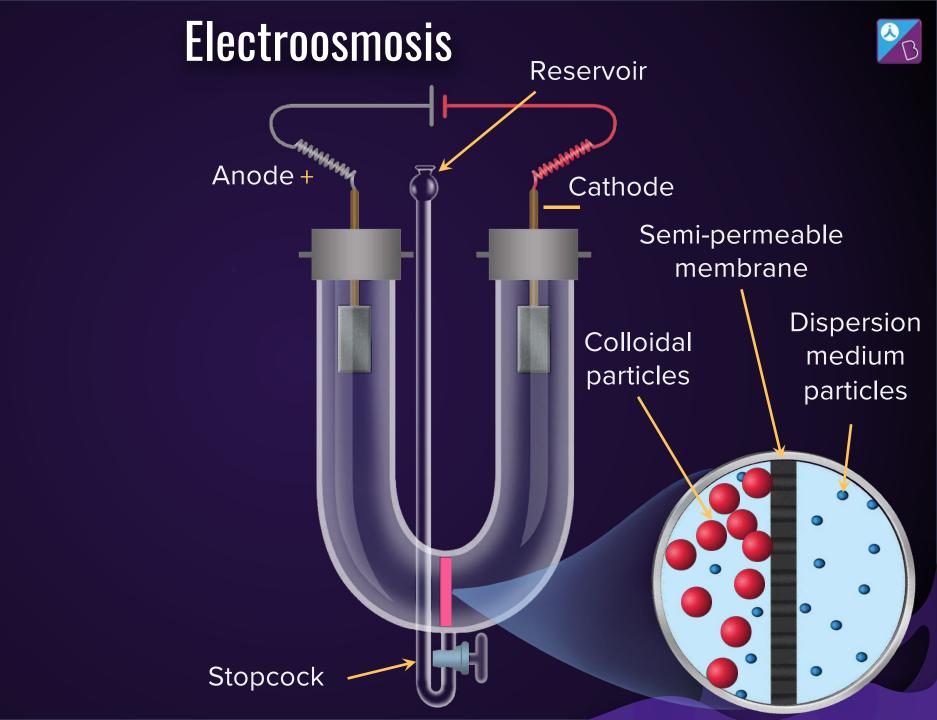
If colloidal sol is **positively** charged

Colloidal particles move **towards the** cathode.

If colloidal sol is negatively charged Colloidal particles move **towards the** anode.







Coagulation or Precipitation



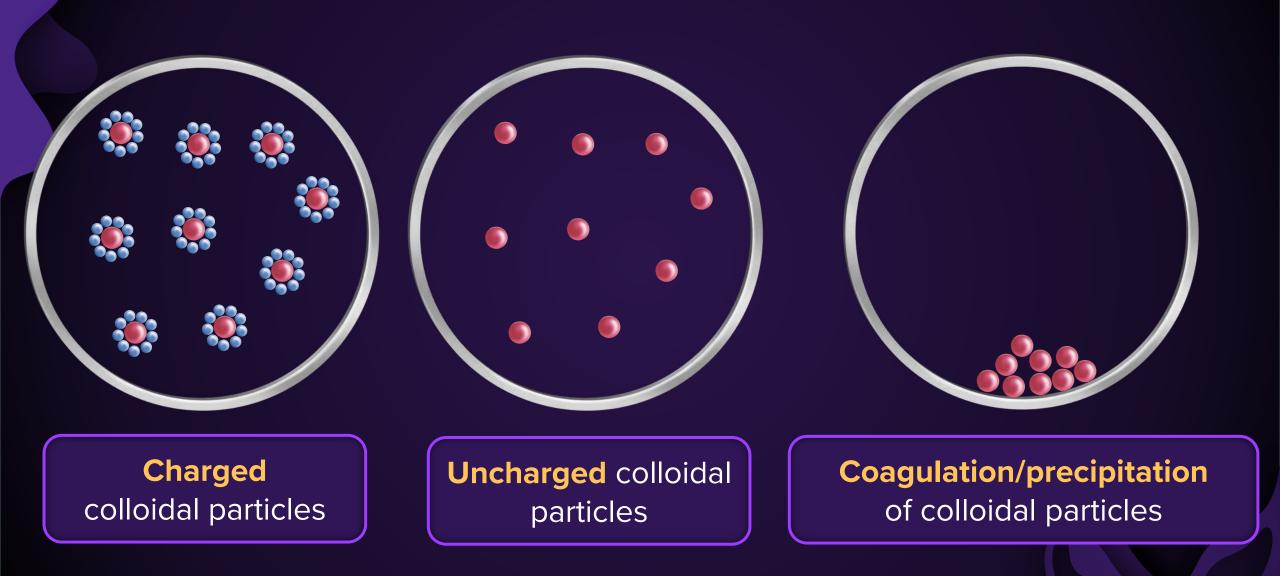
Sols are **stable** due to the presence of **charge** on particles.

If **removed**, the **uncharged** particles come close and form **aggregates**. This process of **aggregation** of colloidal particles

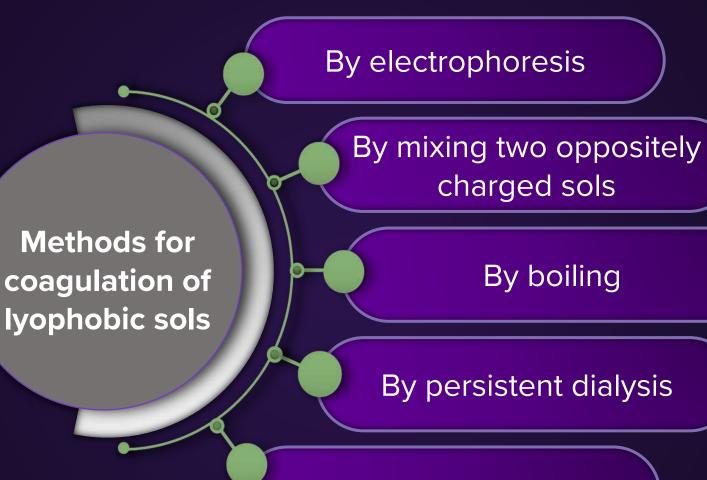
Into an **insoluble precipitate** is known as **coagulation or precipitation** of the sol.

Coagulation or Precipitation









By addition of electrolytes

Coagulation by Electrophoresis



The **charged** colloidal particles move towards **oppositely charged** electrodes.

They get **discharged** and **precipitated**.

Coagulation by Mixing Two Oppositely Charged Sols



Oppositely charged sols, when **mixed** in **appropriate amounts**

This type of coagulation is known as **mutual coagulation**.

Neutralise their charges and get partially or completely precipitated Example: Mixing of hydrated ferric oxide (positive sol) and arsenous sulphide (negative sol) brings them to their precipitated forms.

Coagulation by Boiling

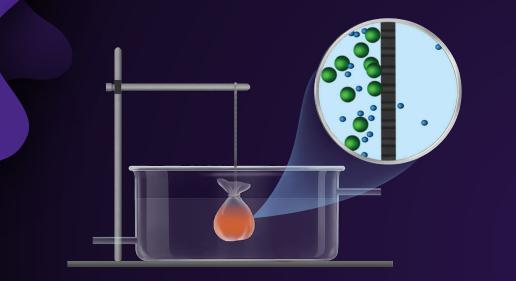


When a sol is **boiled**, the adsorbed layer is **disturbed**.

Due to **increased collisions** with the molecules of dispersion medium The increased collisions **reduce** the **charge** on the particles. The particles settle down in the form of a precipitate.

Coagulation by Persistent Dialysis





On **prolonged** dialysis, if **traces** of the electrolyte present in the sol are **removed completely**

The colloid becomes **unstable** and **ultimately coagulates**.



Coagulation by Addition of Electrolytes



Coagulating Colloid particles neutralise (flocculating) by interacting with ions oppositely charged ions. Leads to their coagulation The colloidal particles are precipitated. A negative ion causes the precipitation of positively charged sol and vice versa.

When **excess** of an electrolyte is added

Hardy-Schulze Rule



Generally,

valency of the flocculating ion added

Greater is its power to cause coagulation

Greater the

Coagulating (or flocculating)

power

For **positively charged** sols,

Order of coagulating power of anions (coagulating ions)

 $[Fe(CN_6)]^{4-} > PO_4^{3-} > SO_4^{2-} > CI^{-}$

For **negatively charged** sols,

Order of coagulating power of cations (coagulating ions)

 $AI^{3+} > Ba^{2+} > Na^+$

Coagulating or Flocculating Value

The minimum concentration of an electrolyte in millimoles required to cause coagulation of one litre of colloidal solution

Coagulating value

Millimoles of electrolyte

Volume of sol in litre

Expressed in millimoles litre⁻¹

Coagulating or Flocculating Value





Increase in charge on the coagulating ion



Stability of Lyophilic Sols



Lyophilic sols are **more stable** than lyophobic sols.

Reasons for stability

Charge on colloidal particles

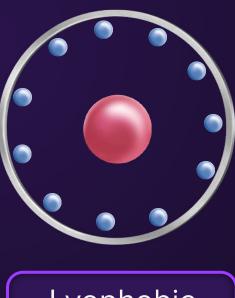
Solvation of

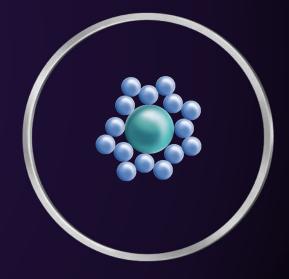
2

colloidal particles

Solvent particleLyophilic sol particle

Lyophobic sol particle



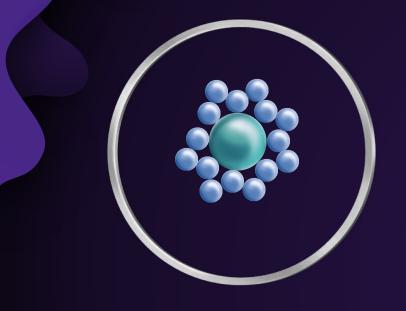


Lyophobic colloid



Coagulation of Lyophilic Sols









By adding suitable solvent

Example: Alcohol and acetone are added to hydrophilic sol.

Protection of Lyophobic Colloids

SB

Since lyophilic sols are more stable than lyophobic sols

Lyophilic sols have a unique property to protect lyophobic sols. Lyophilic particles **form**

a layer around

lyophobic particles.

When lyophilic sol is

added to lyophobic sol

Lyophilic sols used for this purpose are known as **protective colloids.** Lyophilic particles protect lyophobic sol from electrolytes.

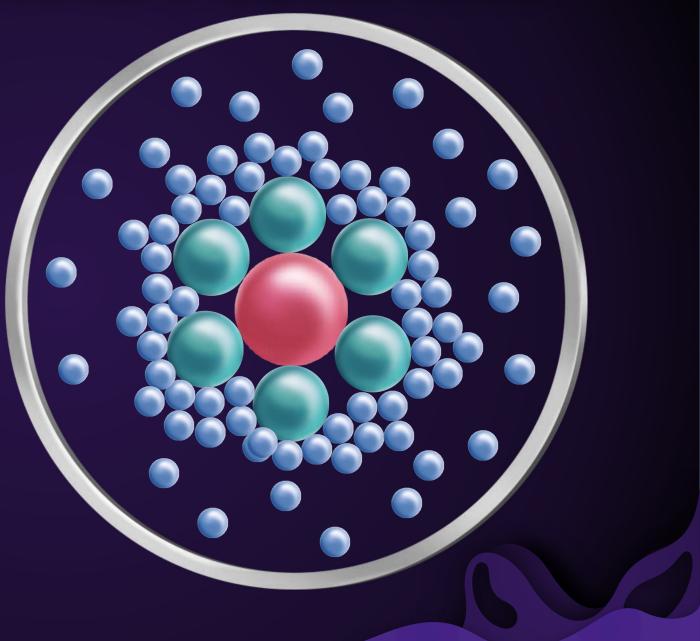
Solvent particle

Lyophilic sol particle

Lyophobic sol particle

Protection of Lyophobic Colloids





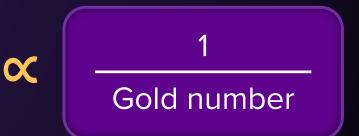
Gold Number



It is the minimum weight in milligrams of a protective colloid required to prevent the coagulation of 10 mL of a standard gold sol when 1 mL of a 10% NaCl solution is added to the sol

Smaller the gold number, greater will be protecting power of the protective colloid.

Protecting power of protective colloid



Emulsion



Liquid-liquid colloidal system Dispersion of finely divided droplets in another liquid If a mixture of two immiscible or partially miscible liquids is shaken

> A coarse dispersion of one liquid in the other is obtained.

It is called an emulsion.

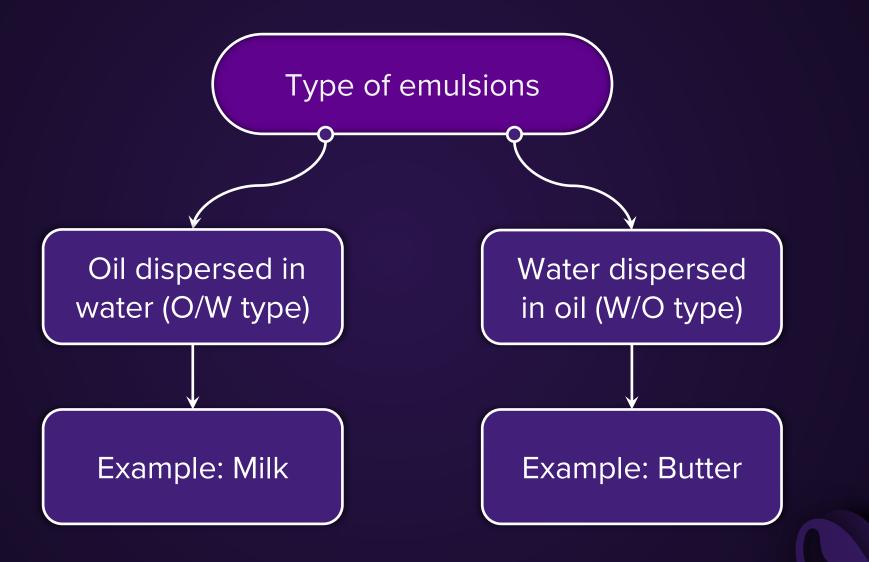
Preparation of Emulsion





Type of Emulsions





Emulsions





A third component known as emulsifying agent is added for stabilisation.

It forms an **interfacial film** between suspended particles and the medium.

Demulsification



It is the **separation** of an emulsion into its **constituent liquids**.

It can be achieved by freezing, heating, centrifugation, etc.



Fog or Mist

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Colloids Around Us

Applications of Colloids

B

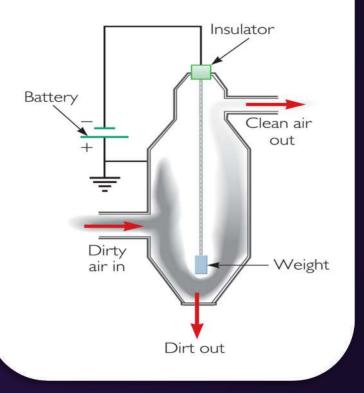
Smoke



Smoke is a colloidal solution of **solid particles**.

Such as carbon, arsenic compounds, dust, etc.

Schematic Diagram of an Electrostatic Precipitator



Cottrell Smoke Precipitator

Electrical Precipitation of Smoke



Smoke is **led through** a chamber containing **weight (plate)**

The smoke particles, on coming in **contact** with the plate

Having a **charge opposite** to that carried by smoke particles

Lose their charge and get precipitated