

## Surface Chemistry

### Absorption

- Surface phenomenon (in a solid/liquid)
- Substance adsorbed → adsorbate
- Substance on which it is adsorbed → adsorbent
- Spontaneous, exothermic, lowers entropy
- Reverse of adsorption → desorption
- Adsorption of gases on metal surface → occlusion

### Types

#### Physisorption

- Molecules held by weak Vander Waal's forces
- Low heat of adsorption (20-40 kJ/mole)
- Forms multilayered layers
- Reversible
- Non specific

#### Chemisorption

- Molecules held by strong chemical bonds

### Factors

- Surface area  $\propto$  adsorption
- nature of gas:  
critical temp of gas  $\propto$  Vander Waal's force  $\propto$  adsorption
- pressure: Le Chatelier principle - pressure  $\propto$  adsorption

### Colloidal state

A heterogeneous system, particle size between 1 nm to 1000 nm

### Classification

Based on the affinity of dispersed phase particles for the dispersion medium

Based on the type of particles of the dispersed phase

### Lyophilic Colloids

- (Intrinsic colloids)
- Have greater affinity.  
e.g.: Gum, starch, gelatin, rubber etc.
  - Reversible Soln
  - Highly stable due to high hydration in solution

### Multimolecular Colloids

- formed by association of large number of molecules by weak Vander Waal's force
- Lyophobic, Gold Sol  
Pt-sol, S-sol

### Macromolecular Colloids

- All molecular larger in size, e.g.: Polymer enzymes etc.

### Properties

- Colloidal solutions are heterogeneous, stable, filterable, low colligative properties, Tyndall effect (scattering of light), Brownian movement (Zig-zag movement), Electrophoresis, Electroosmosis, Coagulation or Flocculation, Hardy Schulze Rule

- \* High heat of adsorption ( $40 - 450 \text{ kJ/mol}$ )
- Specific
- Forms unimolecular layer.
- Irreversible

**Adsorption Isotherm**  
The curve showing the variation of the amount of adsorbate at a particular temp with pressure/concentration

**Friedelich adsorption isotherm :-**  
plot of  $\frac{x_m}{m}$  vs.  $P$  at constant  $T$  i.e.  $\frac{x_m}{m} \propto P$

**Langmuir adsorption isotherm**  
plot of  $\frac{P}{(x/m)}$  vs.  $P$  assuming formation of monolayer of adsorbate

### Emulsions

Dispersed phase and dispersion medium are liquids (immiscible).

Emulsifiers → stabilize them, e.g. soaps

### Types

Oil in water (O/w): milk  
Water in oil (W/o): cream, butter

### Properties

- All colloidal properties
- Demulsification by heating, centrifugation or adding electrolyte or chemical destruction of emulsifying agent

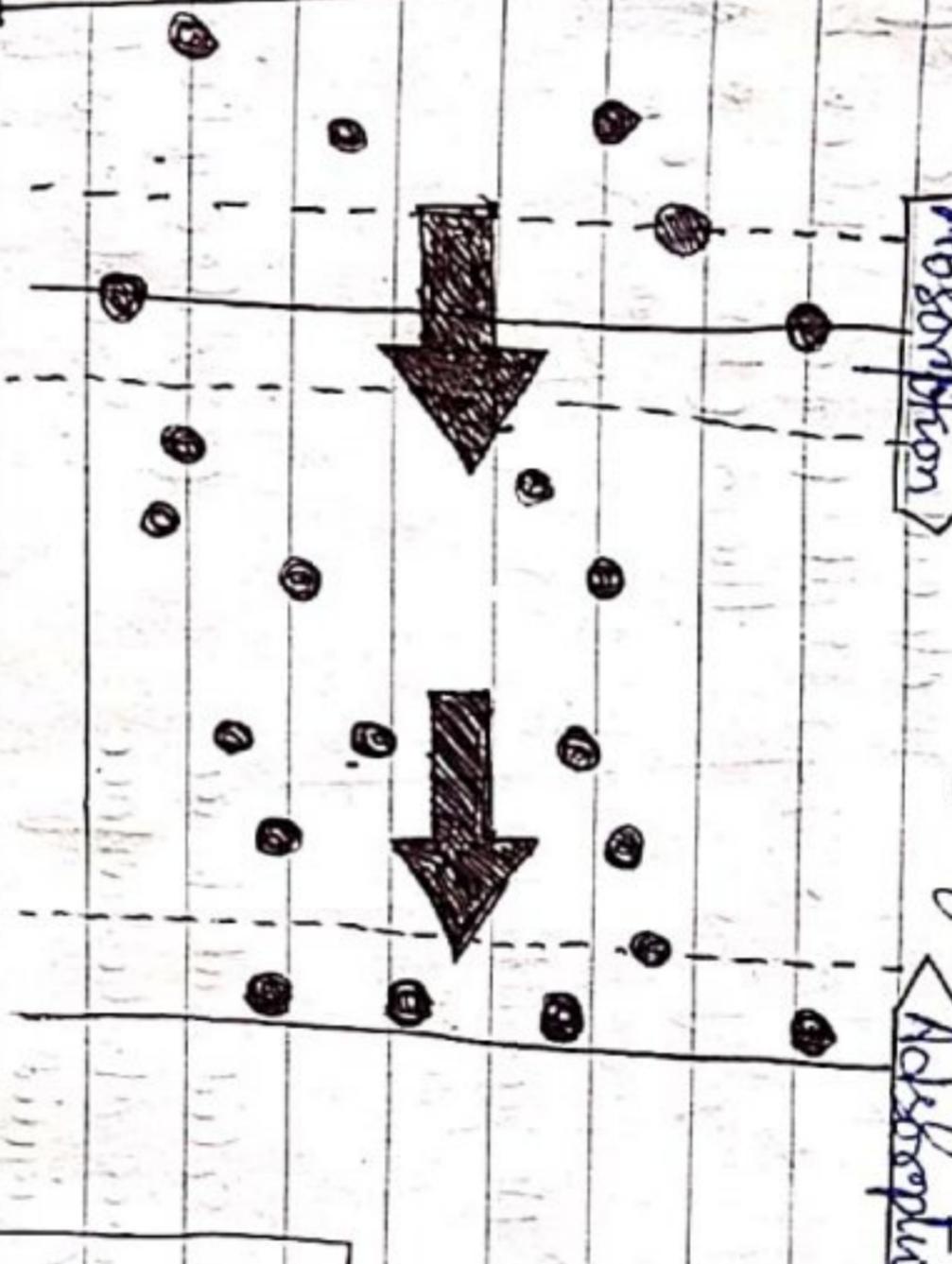
(Extrinsic Colloids)  
Very little or no affinity  
e.g. Metals and their sulphides etc.

- Irreversible solutions  
Unstable → easily precipitated
- Need stabiliser for preservation

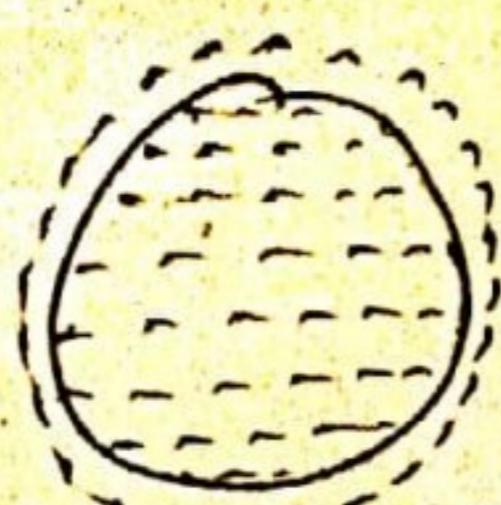
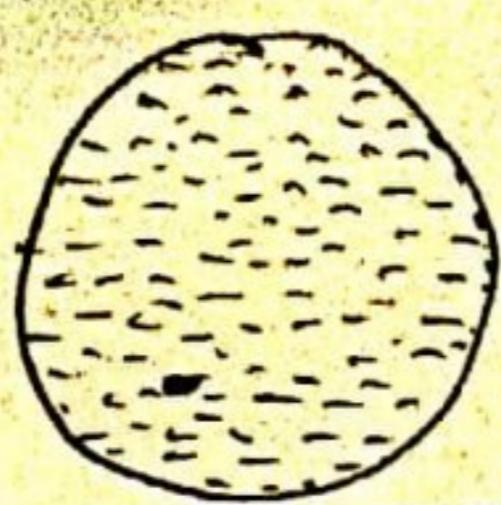
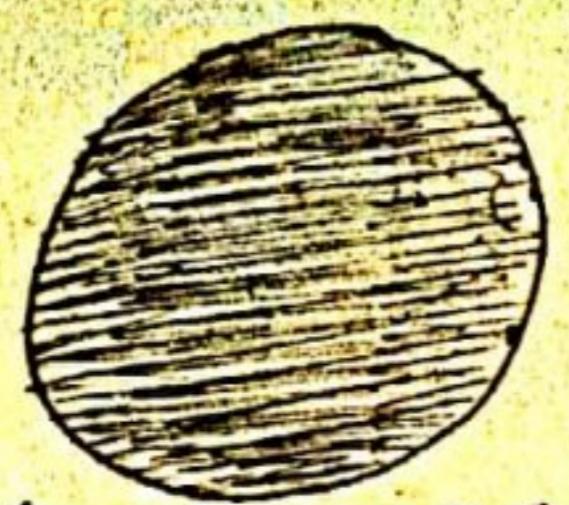
### Associated Colloids

Behave as strong electrolytes at low concentration and at high concentration exhibit colloidal properties due to formation of aggregated particles, known as "Micelles", due to migration above "Krafft temp." forming the critical micelle concentration.

(CMC). Have non polar hydrophobic chain R (tail) and hydrophilic COO<sup>-</sup> (head). e.g.: Sodium stearate ( $\text{C}_{17}\text{H}_{35}\text{COONa}$ )



**CQ**  
(b) When animal charcoal is added to the solution of an organic dye say methylene blue & the solution is well shaken, then the filterate turns colorless. This is because the molecules of the dye are adsorbed on the surface of charcoal.



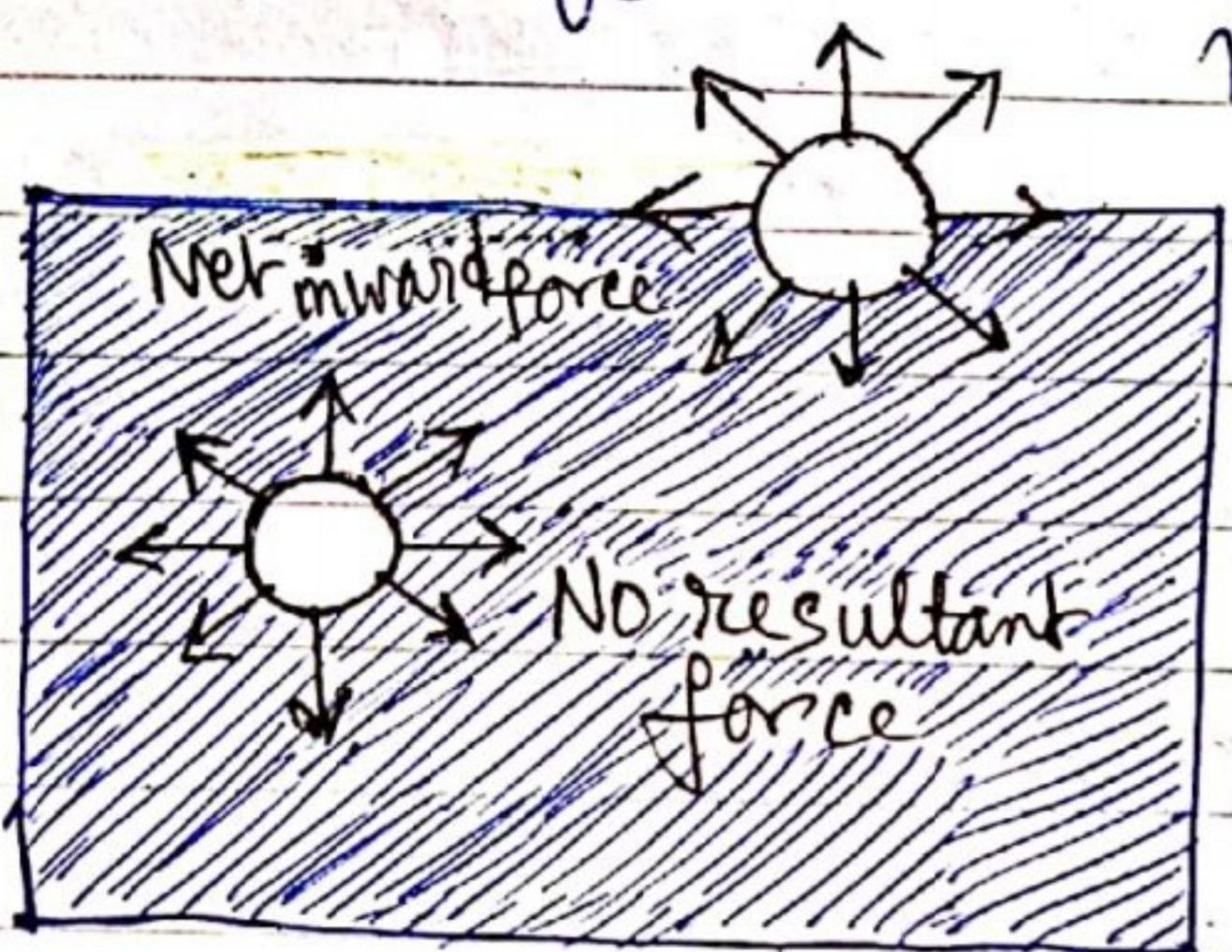
~~Absorption~~

~~Absorption~~

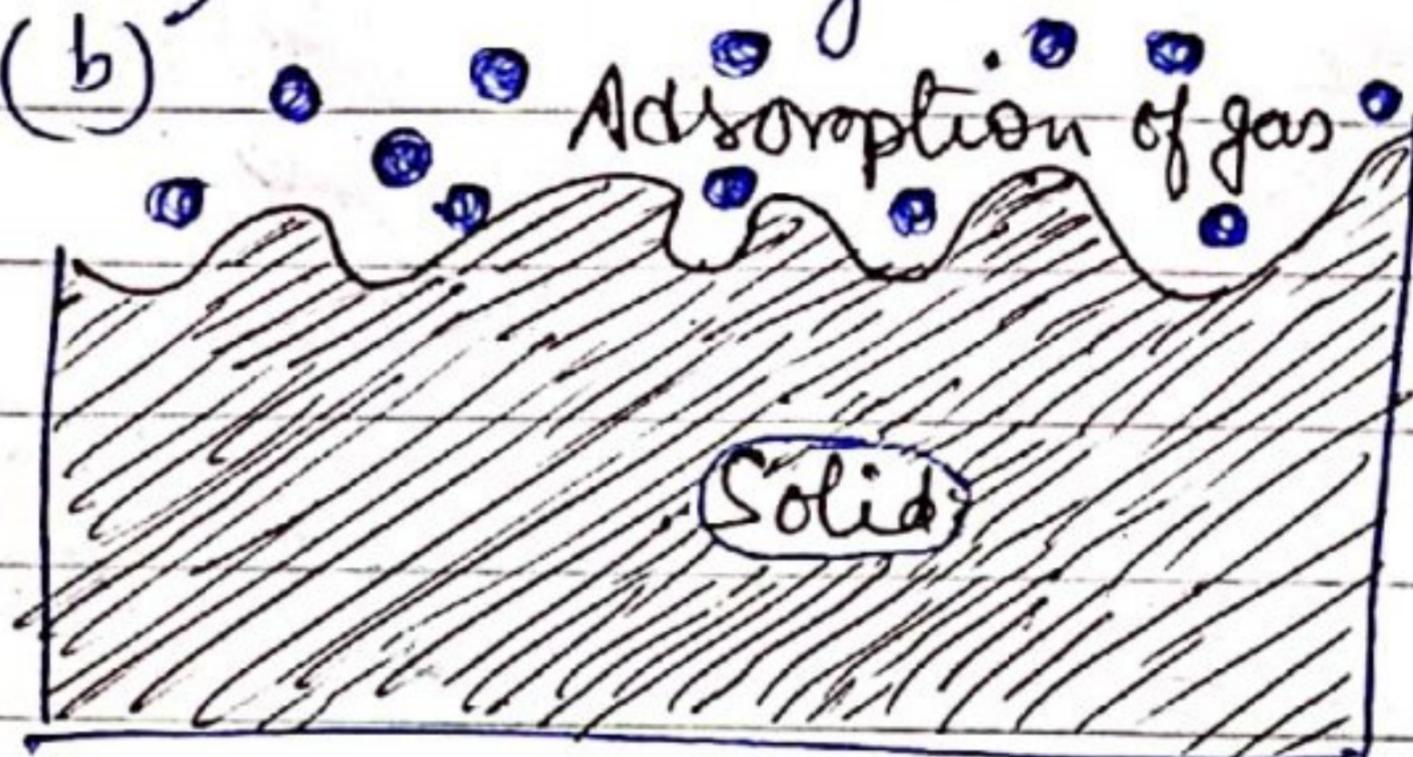
Sorption

### Mechanism of adsorption

1. Adsorption is due to unbalanced molecular forces or Vander Waals force.
2. It arises because of the unbalanced forces on the surface of the solids and liquids (a). As a result, the surface of the solid/liquid tends to satisfy their residual forces by attracting & retaining the molecules of other species (a gas or dissolved substance) when brought in contact with them (b).



(a) A liquid or solid substance inward forces at the surface of solid/liquid.



(b) Adsorption of a gas at the solid surface.

17/8/19

During adsorption, there is always ( $\downarrow$ ) in the residual forces of surface i.e. there is ( $\downarrow$ ) in surface energy which appears as heat. Therefore, (i) Adsorption is an exothermic process.

$$\Delta H = -ve.$$

(Enthalpy decrease)

(ii) Free movement becomes restricted

$$\Delta S = -ve \text{ (Entropy decreases)}$$

(iii) Adsorption process is spontaneous

$$\Delta G = -ve \text{ (Gibb's free energy decrease)}$$

a) On the basis of Gibb's Duhem equation:

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

can be  $-ve$  if  $\Delta H$  has sufficiently high negative value as  $-T\Delta S$  is  $+ve$ .

b) As the adsorption proceeds  $\Delta H$  becomes less & less negative ultimately  $\Delta H$  becomes equal to  $T\Delta S$  &  $\Delta G$  becomes zero. At this stage equilibrium has reached.

## Absorption

It's a BULK phenomenon,  
substances get penetrate  
(or adsorbed) through the  
bulk.

Unified distribution throughout  
the bulk.

Absorption takes place with  
uniform rate through the  
process.

## Adsorption

It's a Surface phenomenon,  
substances get accumulate  
on the surface only.

It is not distributed uniformly.

It initially takes place faster & then  
gradually decreases.

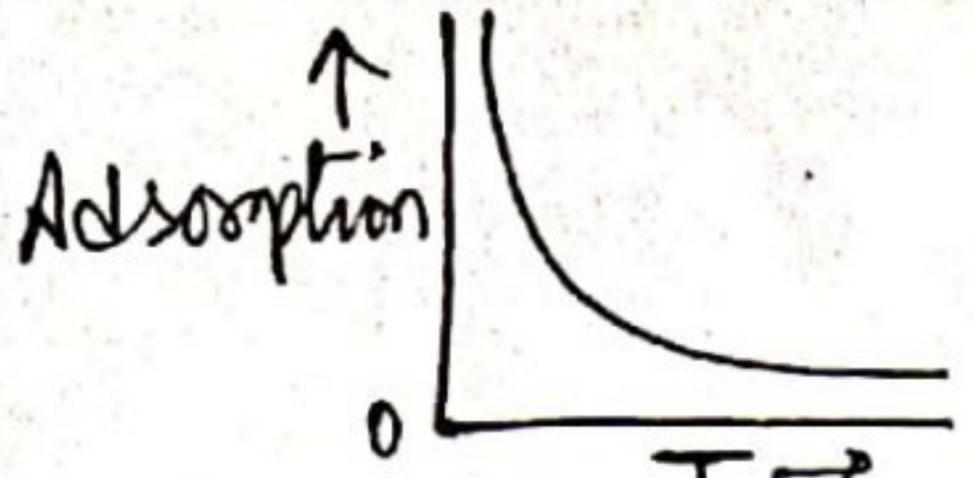
There are two types of adsorption — physisorption (or physical adsorption) and chemisorption (or chemical adsorption).

## Physisorption

- ① The forces operating here are weak Van der Waal's forces.
- ② Heat of adsorption is low about  $20 - 40 \text{ kJ/mole}$ .
- ③ Usually occurs at low temp. and  $\downarrow$  with  $\uparrow$  in Temp.
- ④ It is reversible.
- ⑤ It forms multimolecular layers.
- ⑥ It is not specific in nature.

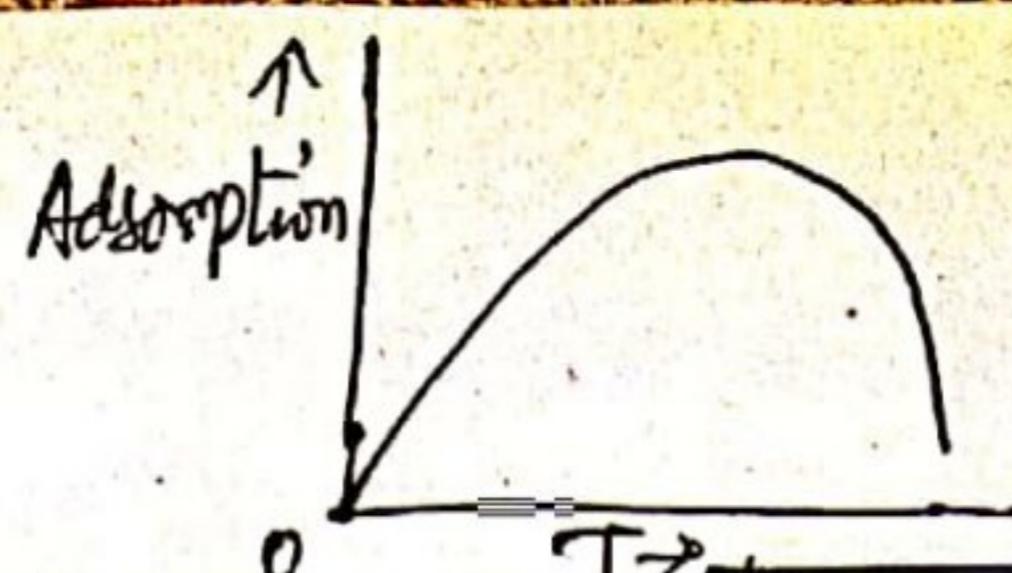
## Chemisorption

- ① The forces operating here are similar to those of a chemical bond.
- ② Heat of adsorption is high about  $40 - 400 \text{ kJ/mole}$ .
- ③ It occurs at high temp.
- ④ It is irreversible.
- ⑤ It forms monomolecular layer.
- ⑥ It is highly specific in nature & occurs only when there is bond formation between adsorbate and adsorbent molecules.



### Physisorption

- (7) Extent of adsorption is directly related to the ease of liquification of the gas.
- (8) It doesn't involve appreciable activation energy ( $E_a$ ). In most cases, the activation energy required is almost nil.



### Chemisorption

- (7) There is no correlation between extent of adsorption and ease of liquification of the gas.

- (8) It generally requires appreciable ( $E_a$ ) since a chemical rxn is to take place.

## Factors affecting adsorption of Gases on Solids

### Surface area of the Adsorbent - (or solid)

Greater the surface area, greater is the extent of adsorption. Activated charcoal, silica gel and alumina are regarded as good adsorbents because of their porous nature and large surface areas. Finely divided transition metals like Co, Ni, Pt act as good adsorbents.

Extent of adsorption  $\propto$  surface area of adsorbent  
directly proportional to adsorption.

### Activation of the Adsorbent

The process of increasing the surface area of an adsorbent and making it a better adsorbent is called activation. Such adsorbent is called activated adsorbent which can be carried in a number of ways.

- a) some adsorbents are activated by strong heating
- b) the adsorbent is sub-divided into small/fine pieces to increase the surface area.

✳ → But chemisorption first increases with temp but after a particular extent decreases with increase in temp.

### • Nature of gas:

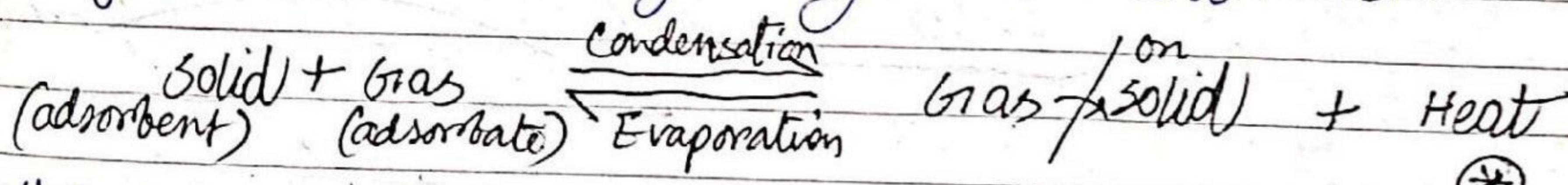
The amount of gas adsorbed by a solid depends on the nature of gas. In general, easily liquefiable gases (i.e. with higher critical temp.) are readily adsorbed at Van Der Waal's forces are stronger near the critical temp. [at,  $T_c \uparrow \propto$  rate of adsorption]

Ex- Under given conditions of temp. and pressure, gases like  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are adsorbed to greater extent than the gases like  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ .  $\text{CO}_2 < \text{NH}_3$  [due to intermediate moderating adsorption] it bonds.

### ④ Extent of Adsorption of gas & Ease of liquefaction of gas & critical temp. of gas

In chemical adsorption, a gas adsorbed on the solid only if it forms chemical bonds.

• Effect of Pressure of the gas: Physical adsorption of a gas on a solid is generally reversible. Thus:



When pressure increases, more gas is adsorbed as the vol. of the gas decreases (by Chatelier's Principle).

The effect of pressure on chemisorption is negligible.

### ⑤ What is adsorption isotherm?

A) The variation in the amount of gas adsorbed by the adsorbent with pressure at const temp. can be expressed by means of a curve known (as) adsorption isotherm, or at const temp., the plot of graph  $w/m$  vs. pressure is known as isotherm.

$\frac{w}{m}$  - Extent or amount of gas adsorbed in which  
 $w$  = the mass of adsorbate  
 $m$  = Mass of the adsorbent

$$P \propto T$$

$$\begin{array}{r} 273 \\ 195 \\ 78 \end{array}$$

### Freundlich adsorption Isotherm

When  
 $T = \text{constant}$

(i) It is clear from the figure that

the extent of adsorption ( $x_m$ )

$\uparrow$  with pressure and

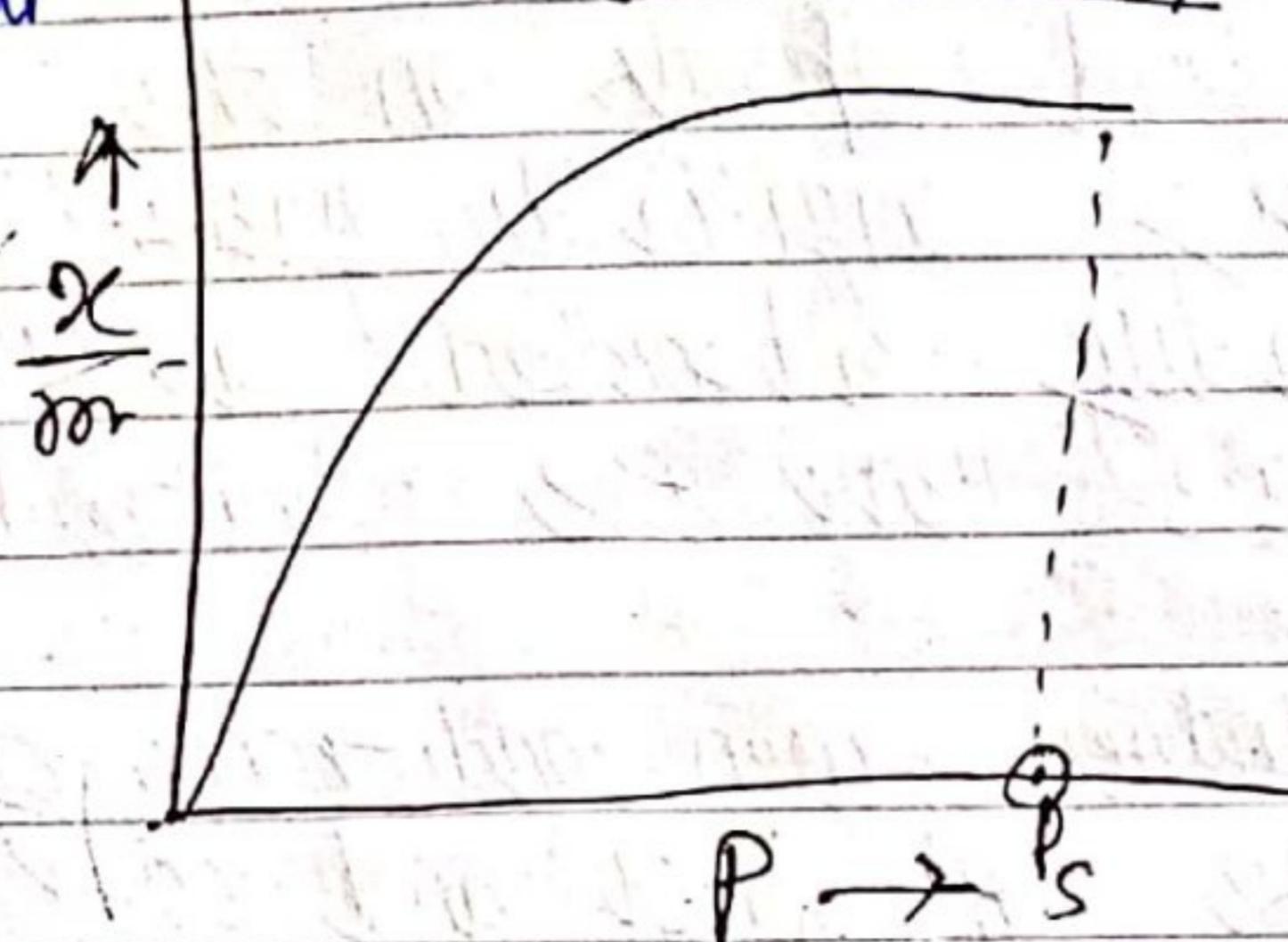
becomes maximum

corresponding to pressure

$P_s$  called Equilibrium

pressure (Saturation

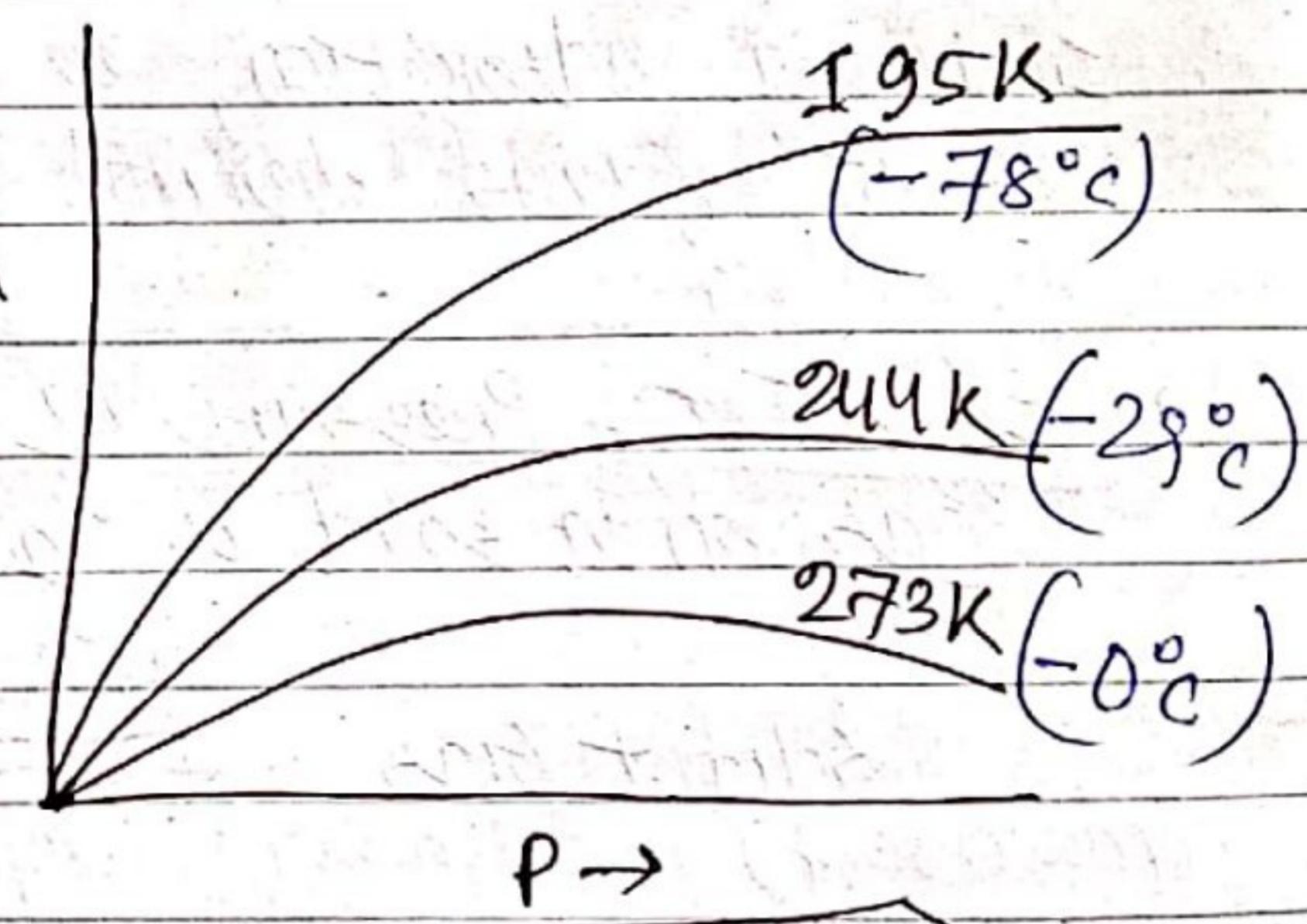
pressure).



### Adsorption Isotherm

(ii) Since adsorption is a reversible process, desorption also takes place simultaneously.

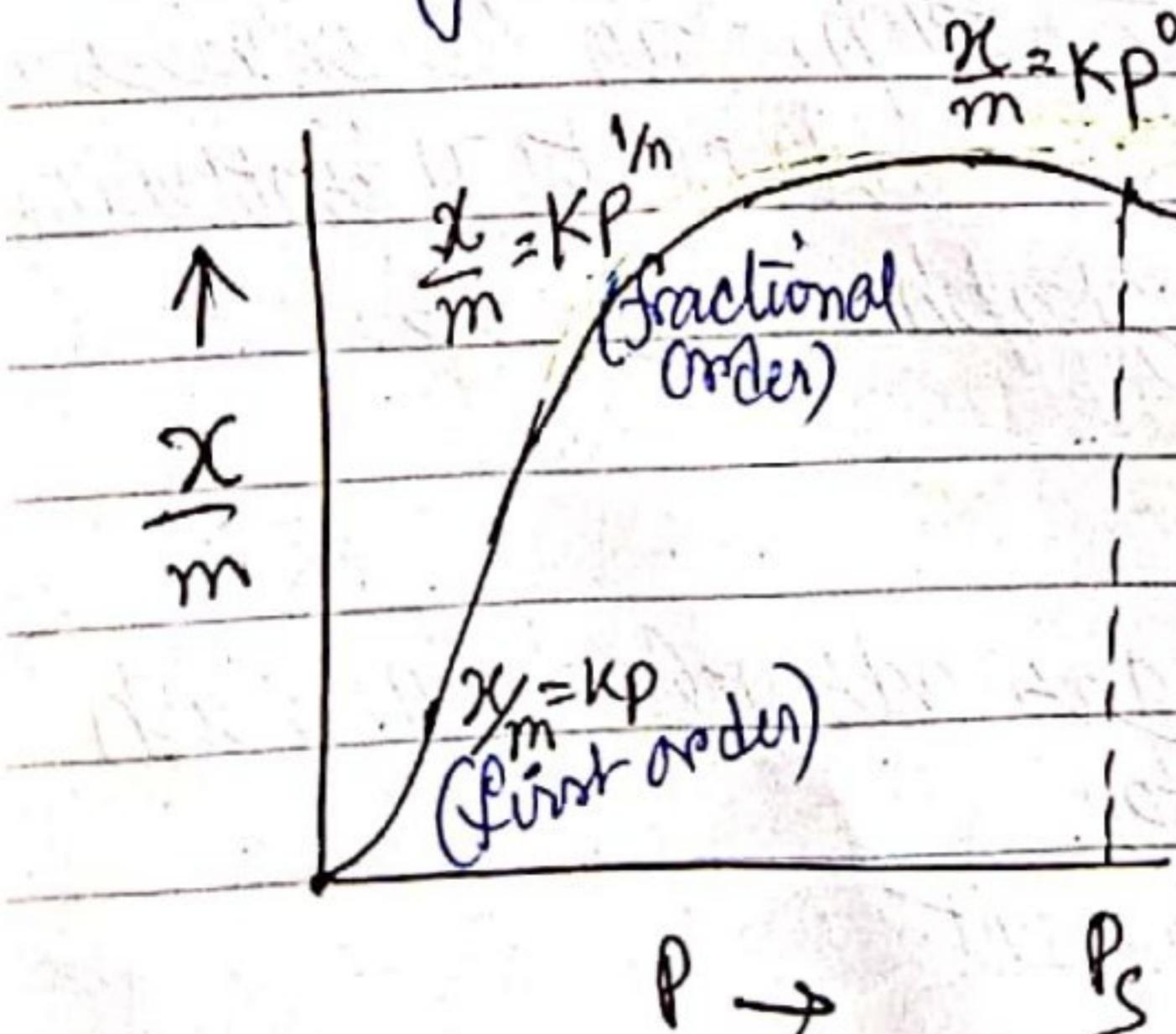
(iii) At  $P_s$ , the amount of gas adsorbed becomes equal to the amount of gas desorbed so that the extent of adsorption becomes constant even though the pressure is increased.



### Adsorption Isotherm

(iv) However at fixed pressure there is a decrease in physical adsorption with increase in temp.

(v) The variation of extent of adsorption ( $x_m$ ) with pressure ( $P$ ) was given mathematically by Freundlich,



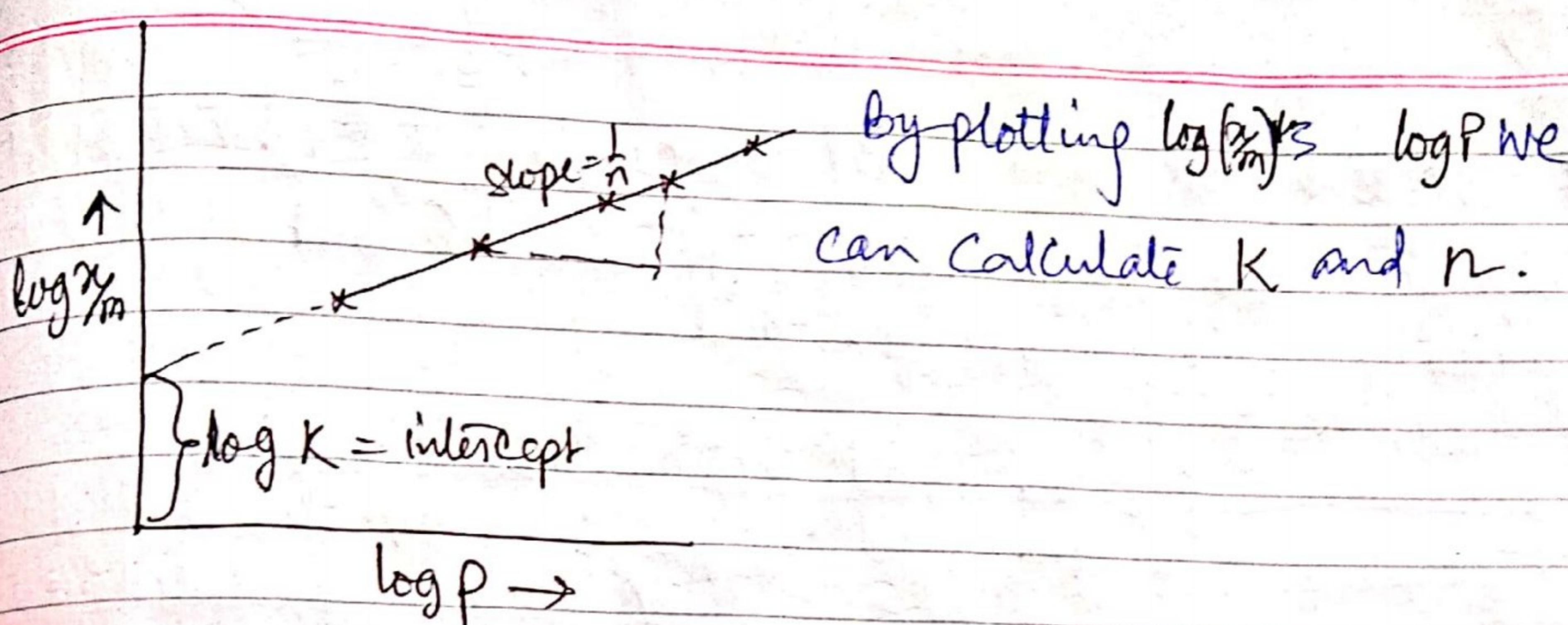
• At low pressure Extent of adsorption is directly proportional to pressure

$$x_m \propto p \Rightarrow \frac{x}{m} = Kp$$

• At intermediate range of pressure

$$\frac{x}{m} \propto p^{1/n} \quad \text{or} \quad x_m = Kp^{1/n}$$

$$\log x_m = \log K + \frac{1}{n} \log K_p$$



- At high pressure  $\frac{x}{m} = \text{constant}$ , or  $\frac{x}{m} \propto P^0$   
At high pressure  $\frac{x}{m}$  becomes (independent) of pressure.

### Langmuir Adsorption Isotherm

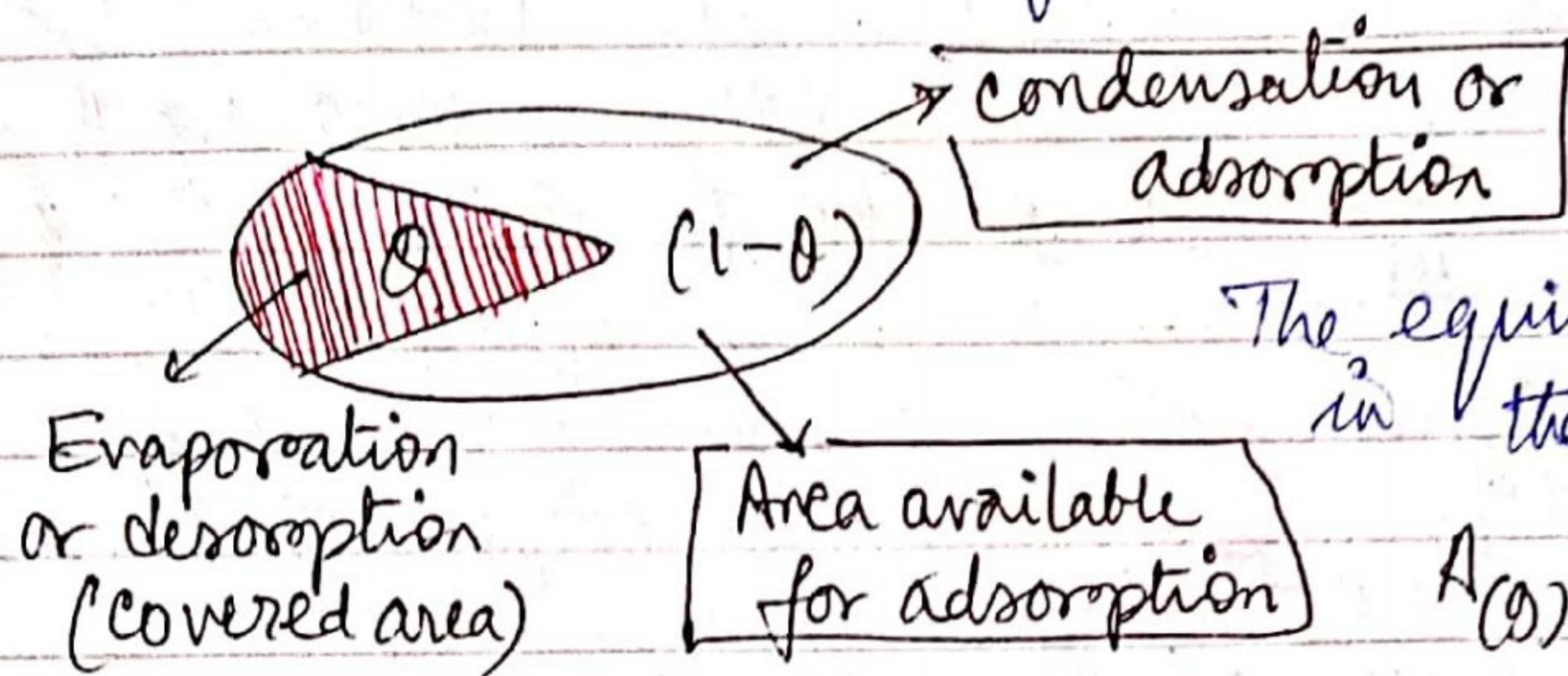
- Langmuir derived an adsorption isotherm on theoretical considerations based on kinetic theory of gases.
- A solid surface contains a fixed number of adsorption sites.
- Each site <sup>such</sup> adsorbs a single molecule. Thus, layer of the adsorbed gas was only one molecule thick, i.e. unimolecular. Since such type of adsorption is obtained in the case of chemisorption.
- Langmuir adsorption isotherm works particularly well for Chemisorption.
- Absorption is considered as an equilibrium process comprising of vaporization and condensation occurring simultaneously at a given temp.
- Rate of evaporation is proportional to the area of the surface covered by the adsorbed gas.

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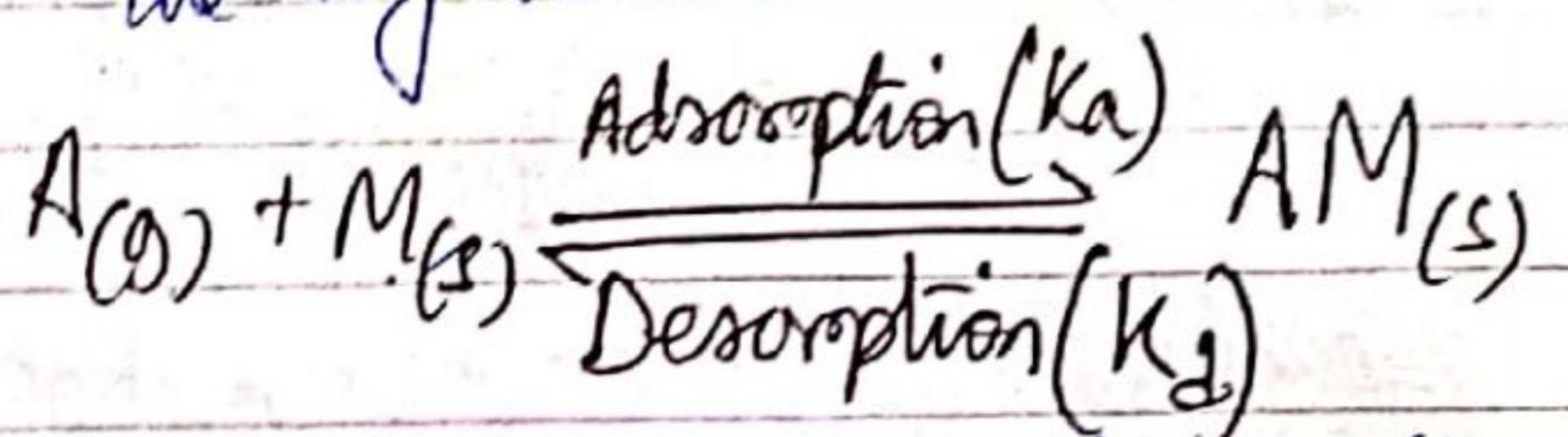
## Derivation of Langmuir Adsorption Isotherm

Let gas A is adsorbed over the surface of metal M having Total "n" sites available for adsorption. Fraction " $\theta$ " out of 'n' sites is occupied by gas molecules and

$$\theta = \frac{\text{No. of adsorption sites occupied}}{\text{No. of adsorption sites available}}$$



The equilibrium is established in the system :



and rate of adsorption ( $R_a$ )  $\propto$  Pressure of gas ( $P$ )  $\times$  No. of sites available for adsorption  
[ $n(1-\theta)$ ] - (i)

and rate of desorption ( $R_d$ )  $\propto$  no. of adsorbed molecules ( $n\theta$ ) - (ii)

$$R_a = k_a \times P \times n(1-\theta) \quad - \quad (i)$$

$$R_d = k_d n\theta \quad - \quad - \quad (ii)$$

At equilibrium  $R_a = R_d$

$$k_a P \times (1-\theta) = k_d \times \theta$$

$$\therefore k_a P (1-\theta) = k_d \theta$$

is a new constant  $\left(\frac{k_a}{k_d}\right) = \frac{\theta}{P(1-\theta)}$

$$\therefore K = \frac{\theta}{P(1-\theta)}$$

$$\frac{1-\theta}{\theta} = \frac{1}{K_p P}$$

$$\frac{1}{\theta} - 1 = \frac{1}{K_p P}$$

$$\frac{1}{\theta} = 1 + \frac{1}{K_p P}$$

$$\frac{x}{m} \propto \left[ \theta = \frac{K_p P}{1 + K_p P} \right] - \textcircled{iii}$$

### Limitations of Langmuir adsorption isotherm

- ① It doesn't consider T.
- ② In it only monolayered adsorption is assumed.
- ③ It doesn't explain all types of isotherms.

### Absorption from solution

- Extent of adsorption  $\uparrow$  with  $\uparrow$  in concentration of solute in solution.
- Extent of adsorption  $\downarrow$  with  $\uparrow$  in temp.
- Extent of adsorption  $\uparrow$  with  $\uparrow$  in surface area of adsorbent

### Absorption Isotherm

$$x_m = K C^m \Rightarrow \log x_m = \log K + \frac{1}{n} \log C$$

From the graph between  $\log(x_m)$  and  $\log C$ , K and n can be calculated.

### Catalysis

- A substance which influences the rate of rxn without being consumed in the rxn is called catalyst and the phenomenon is called Catalysis. Catalyst causes  $\downarrow$  in  $E_a$ .

Q 5.6 What do you understand by activation of adsorbent?  
How is it achieved?



Catalyst

+ve catalyst  
If a catalyst  
↑ the rate of rxn

-ve catalyst  
If a catalyst  
↓ the rate of rxn

Autocatalyst  
When one of the products act as catalyst

Induced Catalyst  
One of the reactants act as catalyst

Key points:

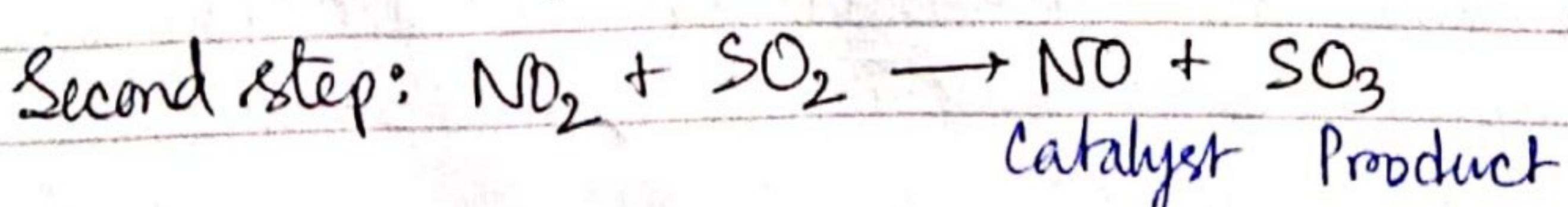
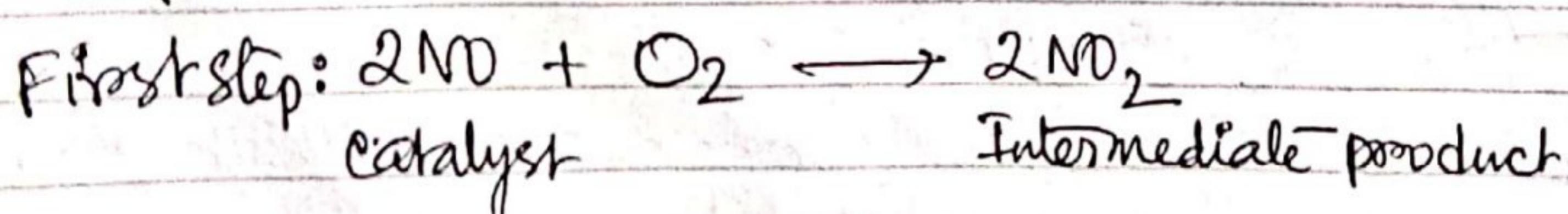
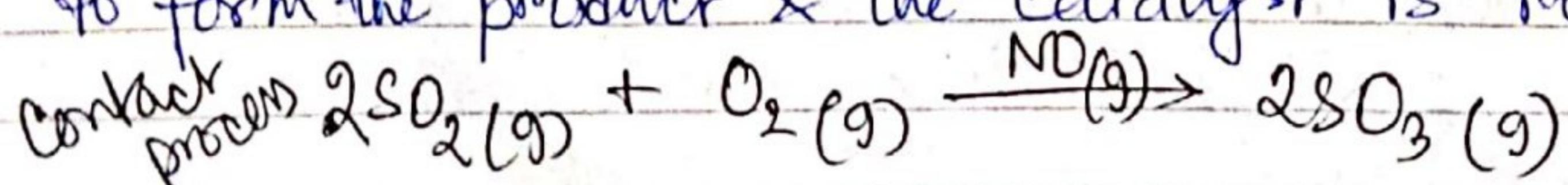
- Catalyst doesn't shift the equilibrium
- Catalysts are highly specific in nature
- Catalysts don't change  $\Delta E$  of rxns.
- $\Delta E = E_p - E_r$  = energy difference between products & reactants

□ Homogeneous Catalyst: When the catalyst is present in the same phase as the reactants and products it is called homogeneous catalyst and process is called homogeneous catalytic rxn.

Mechanism

- First catalyst combines with reactant to form an intermediate.

- Intermediate either decomposes or combines with other reactant to form the product & the catalyst is regenerated.

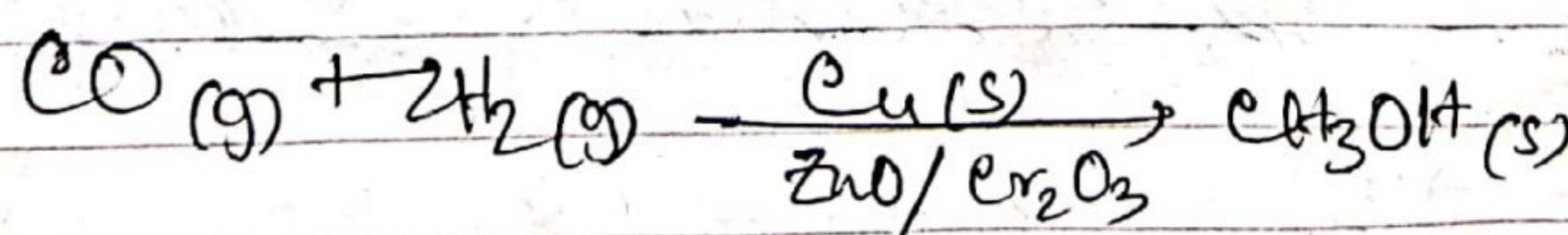
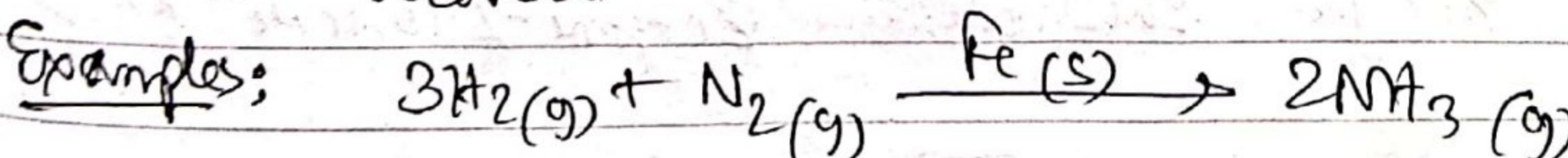
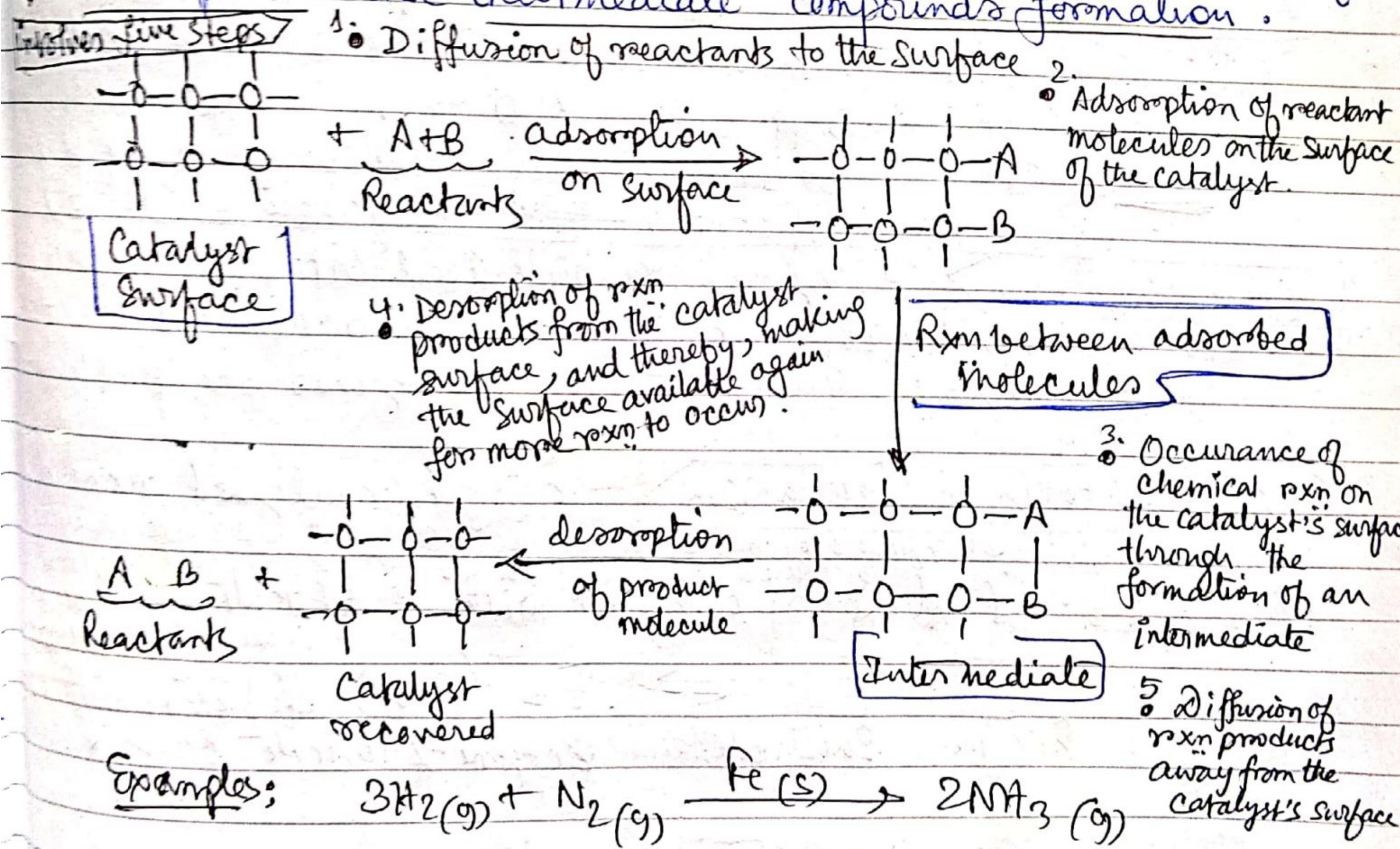


## Examples:

Process	Product	Catalyst
1. $2SO_2 + O_2 \rightarrow 2SO_3$	$SO_3(g)$	$NO(g)$
2. Oxidation of $CO(g)$	$CO_2(g)$	$NO(g)$
3. Inversion of sucrose solution	glucose & fructose	$H^+(aq)$
4. Hydrolysis of ester	acid & alcohol	$H^+(aq)$

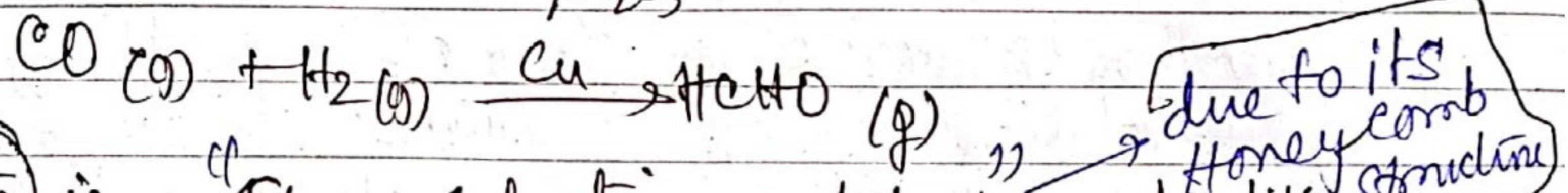
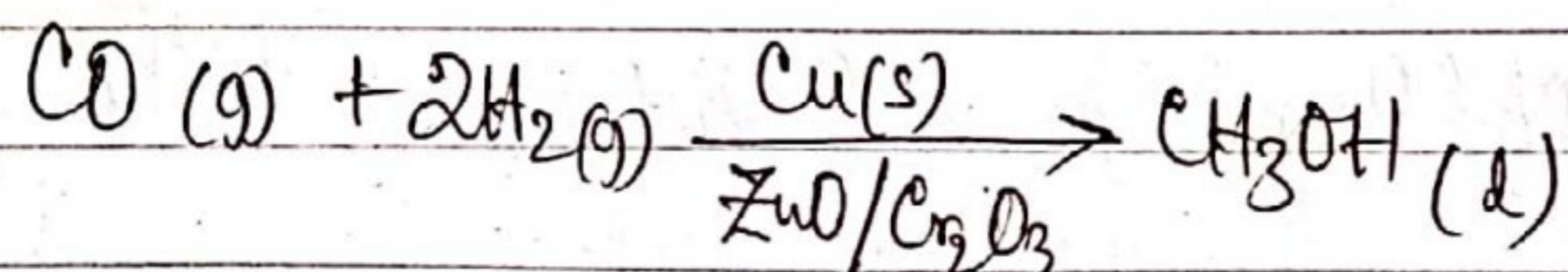
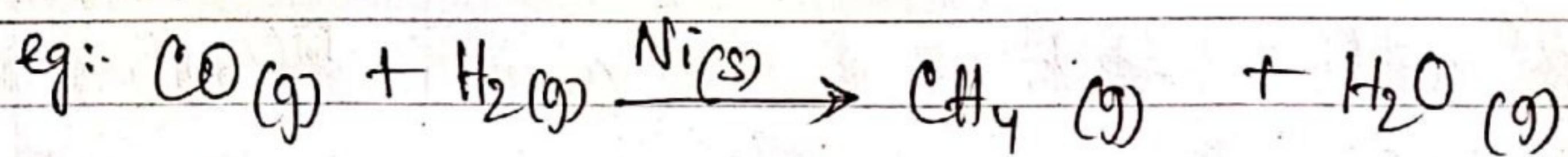
**Heterogeneous Catalyst** When the catalyst is in different phases from the reactants, it is called heterogeneous catalyst.

**Mechanism** Modern adsorption theory is a combination of adsorption and intermediate compounds formation.



**Activity** Activity is the ability of catalyst to accelerate chemical rxns. It can be as high as  $10^{10}$  times in certain rxns.

**Selectivity** :- The ability of a catalyst to direct a rxn to give a particular product is called Selectivity.



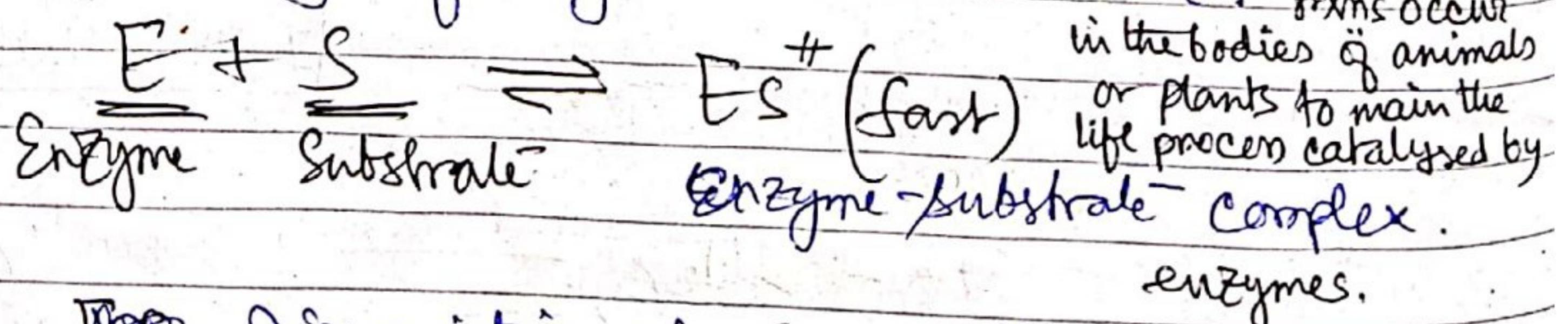
**Zeolite** is a shape selective catalyst due to its honeycomb like structure. Catalytic rxn that depends upon the pore structure of the catalyst and the size of the reactant & product molecules.

ZSM-5 is used in petroleum industry. Ca<sup>++</sup>. The rxn selectivity of ZSM-5 depends upon the size of the cavities, pores and distribution of pores in structure. Pore size in zeolite varies from 260 pm to 740 pm.

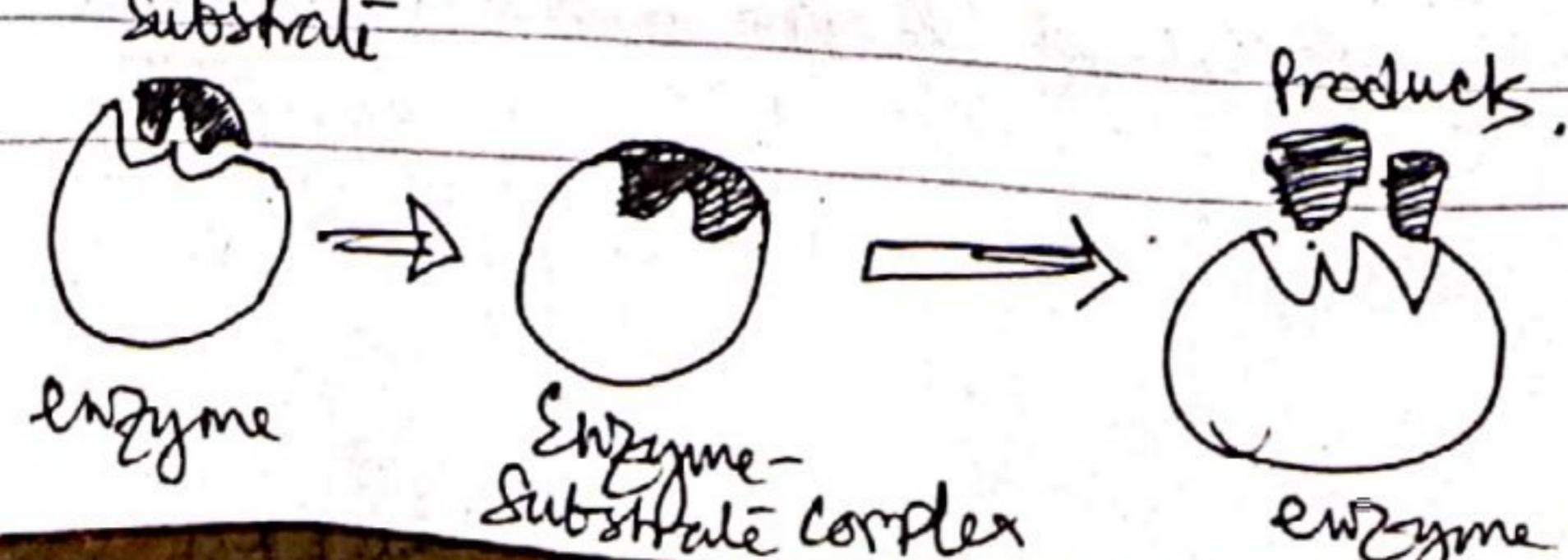
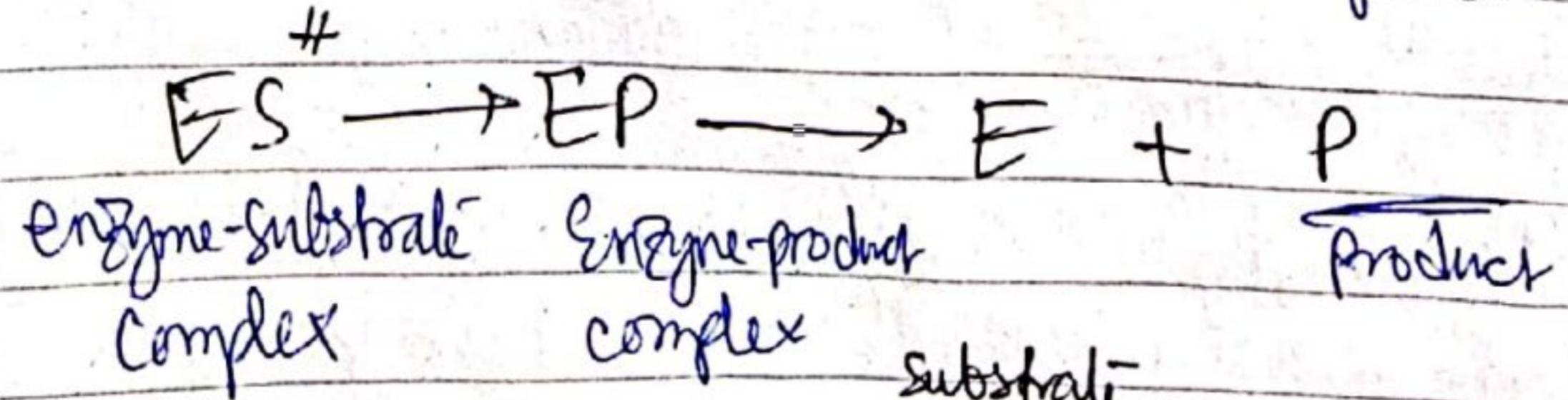
In ZSM-5, alcohols are processed in the pores to the petrol or gasoline. Alcohols  $\xrightarrow{\text{ZSM-5}}$  Gasoline (Petrol)

**Enzyme catalysis** Enzymes are biological catalysts produced by living cells which catalyse the biochemical rxns in living organisms. Chemically all enzymes are proteins.

**Enzyme Catalysis mechanism** :- Enzyme Catalysed rxns are highly specific. Enzymes are complex nitrogenous organic compds which are produced by living plants & animals. Numerous rxns occur in the bodies of animals or plants to maintain life processes catalysed by enzyme-substrate complex.



**Step II** : ~~Dissociation~~ Dissociation of ES complex.

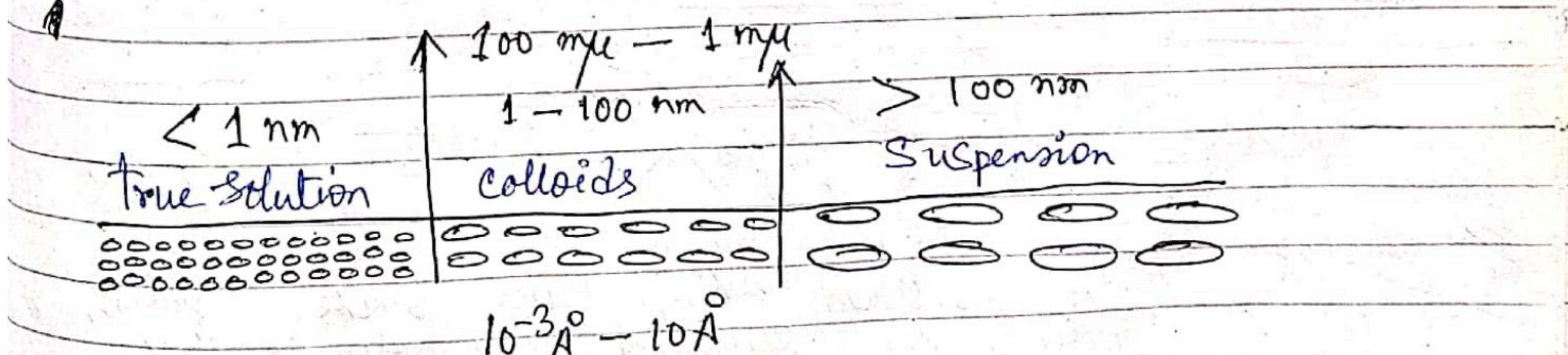


## Characteristics of Enzyme Catalysis

- ① High efficiency
- ② Highly specific nature
- ③ Highly active under optimum temp.
- ④ Highly active under optimum pH.

Enzyme	Source	Enzymatic rxn
Invertase	Yeast	Sucrose $\rightarrow$ glucose + fructose
Urease	Soybean	Urea $\rightarrow$ CO <sub>2</sub> + NH <sub>3</sub>
Pepsin	Stomach	Proteins $\rightarrow$ amino acid
Amylase	Saliva	Starch $\rightarrow$ glucose

Properties	True solutions	colloidal solutions	suspensions
size	< 1 nm	1 nm - 100 nm	> 100 nm
visibility	Invisible even under ultramicroscope	visible only under microscope	visible & even by naked eyes
diffusion	Diffuse rapidly	Diffuse slowly	Don't diffuse
Filtration	not possible not possible	not possible possible	possible possible
scattering of light	no scattering	Takes place (Tyndall effect)	Don't show Tyndall effect



$$1 \mu = 10^{-6} \text{ m} = 10^3 \text{ nm} = 10^4 \text{ Å}$$

$$1 \text{ m}\mu = 10^{-9} \text{ m} = 1 \text{ nm} = 10 \text{ Å}$$

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

Colloidal System > The colloid is not a substance it is a state of matter like — solid, liquid & gas. Colloidal system is a two phase system.

• Dispersed phase It is a discontinuous phase which is a cluster of particles within the colloidal range suspended in a dispersion medium.

■ Type of solutions: Depending on the size of the dispersed phase, solutions are divided into three classes.

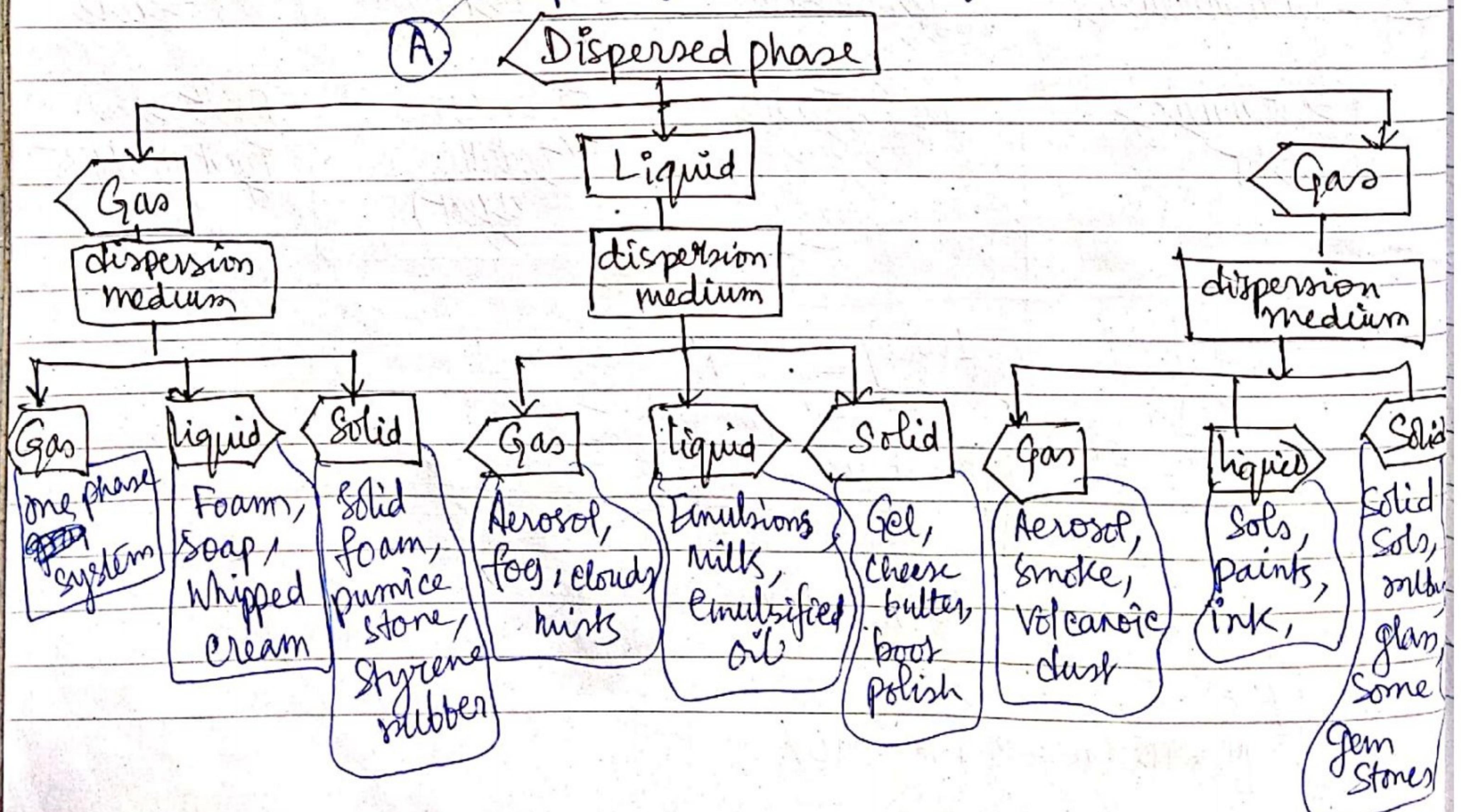
- ① True Solution (Molecular solution)
- ② Colloidal Solution (Colloidal dispersion)
- ③ Suspension (Coarse dispersion)

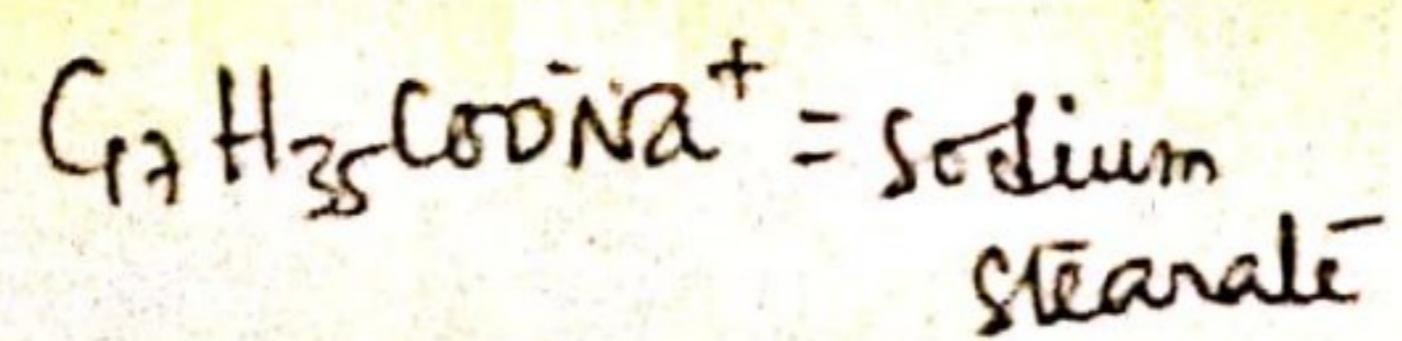
### Classification of colloids

A. Based on the physical state of dispersed phase and dispersion medium.

B. Based on the nature of interaction between two phases

C. Based on the type of particles of the dispersed phase.





~~Q/B/19~~  
 Depending on the nature of interaction between dispersed phase and dispersion medium, colloidal system are divided into 2 classes:-

Property	Lyophilic colloids (Solvent attracting)	Lyophobic colloids (Solvent repelling)
Interaction	Strong interaction between dispersed phase & medium.	Weak interaction between dispersed phase & medium
Preparation	Easy by heating/warming	Special method required
Reversibility	Reversible	Irreversible
Stability	More stable	Less stable
Viscosity	Higher than medium	Same as medium
Surface Tension	Lower than medium	Same as medium
Action of electrolyte	Not easily precipitated	Coagulation takes place
Hydration	Extensive	No hydration
Examples	Gum, gelatin, starch, protein, rubber etc.	Solutions of metal like - Ag, Au, metal sulphides like - As <sub>2</sub> S <sub>3</sub> etc.

If DM is water then named as hydrophilic & hydrophobic sols.

c. depending upon the type of particles of dispersed phase,

- Multimolecular colloids.
- Macromolecular colloids.
- Associated colloids or micelles.

#### ► Multimolecular Colloids:

These sols consist of aggregates of atoms or small atoms with diameter  $< 1 \text{ nm}$  & these molecules held together with Vander Waal's forces e.g., gold sol, Sulphur (S<sub>8</sub>) molecules.

#### ► Macromolecular Colloids:

In these colloids, the dispersed particles are themselves large molecules (usually polymers). Most lyophilic sols belong to this category.

► Micelles There are certain colloids which behave as normally strong electrolytes, at low concentrations, but exhibit colloidal properties at higher concentration due to the formation of

(ii) These colloids are better known as surface active agents (or surfactants). Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid & a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents & dispersants.

aggregated particles. These are known as micelles or associated colloids.

- The formation of micelles takes place only above a particular temp. called as Krafft temp. ( $T_k$ ) and above a particular concentration called as (CMC) Critical Micelle Concentration eg CMC of Soap is  $10^{-4}$  to  $10^{-3}$  mol/litre and the no. of molecules that constitute one micelle is called aggregation number
- Lamellar micelles: At concen higher than CMC they form extended parallel sheets known as Lamellar micelles, resemble biological membranes.
- In concentrated solutions, micelles take the form of long cylinders packed in hexagonal arrays and are called lyotropic mesomorphs.

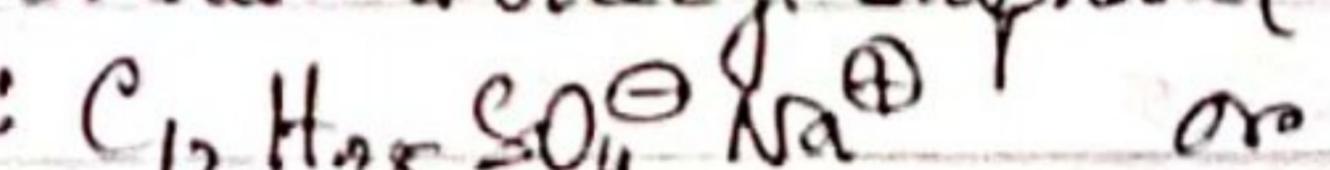
### Mechanism of micelle formation

Surfactants are usually organic compds that're amphiphilic meaning they contain both hydrophobic groups (their tails) and hydrophylic groups (their heads). They can be ionic as well as non-ionic. The ionic are soaps & detergent.

#### Ionic Surfactants

- Anionic surfactants: They contain anionic functional groups at their head such as - Sulphate, Sulphonate, phosphate and carboxylates.

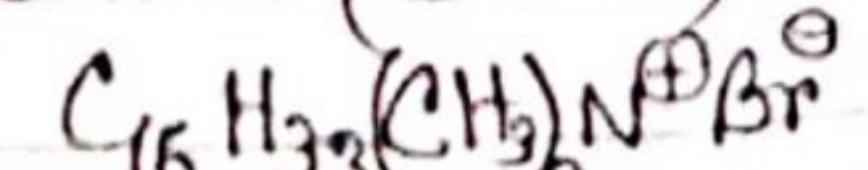
Sodium Dodecyl Sulphate (SDS)



Sodium Lauryl Sulphate (Detergent)

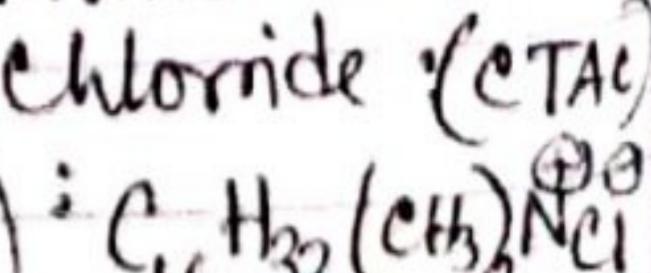
- Cationic surfactants: contain cationic functional groups at their head, such as -

Cetyl Trimethyl Ammonium Bromide (CTAB):



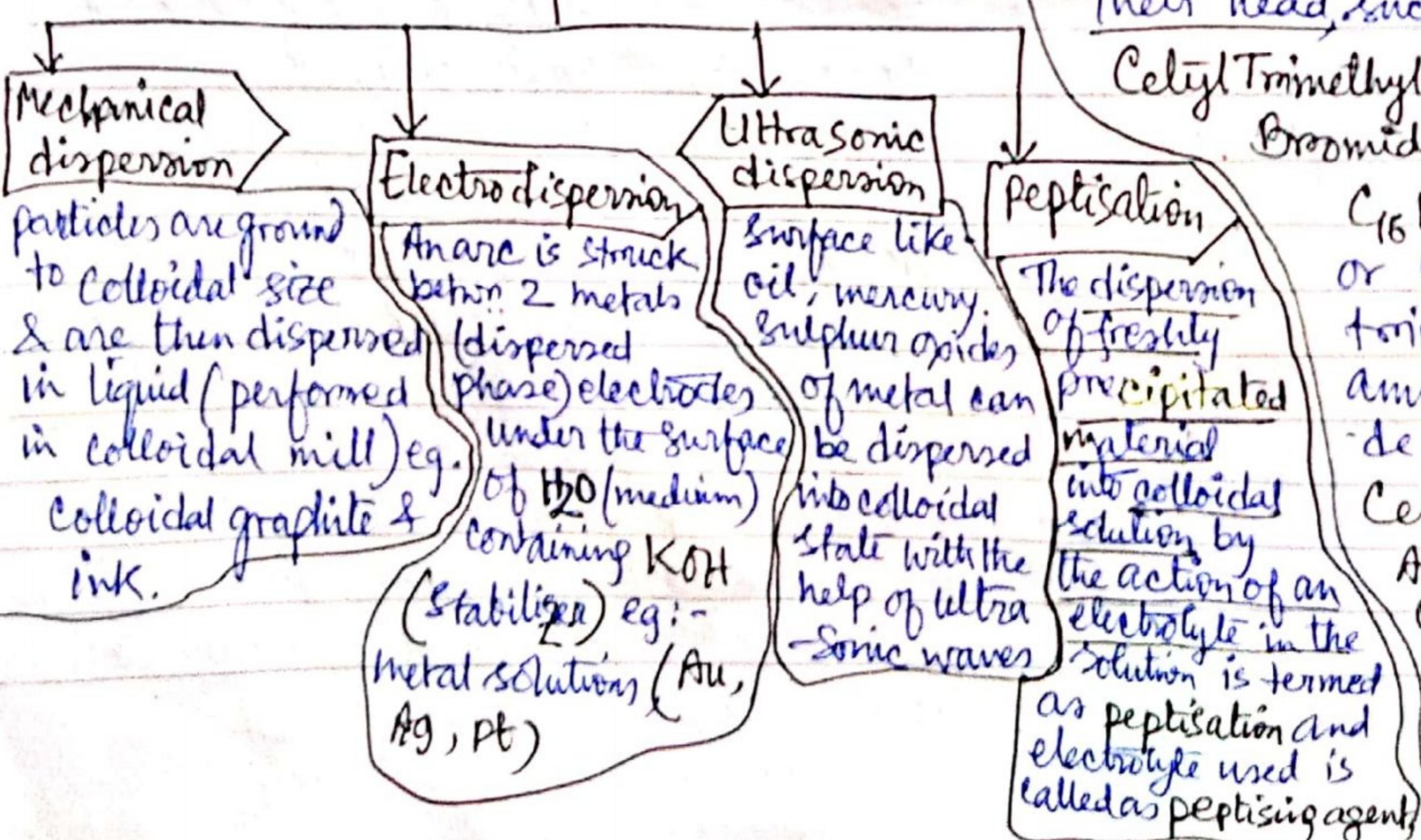
or Hexadecyl trimethyl ammonium bromide.

Cetyl Trimethyl Ammonium Chloride (CTAC)



### Preparation of aqueous Colloidal solns

#### I. Dispersion method



## Condensation method

In these methods small ions or molecules are induced to combine together to form aggregates of colloidal size either by chemical or physical methods.

**Exchange solvents**: No. of substances at those colloidal soln can be prepared by taking the solution of the substance of one solvent & pouring it into another solvent in which the substance is less soluble e.g. Alcoholic solution of sulphur.

By change of physical state

Sols of substances like Hg and Sulphur are prepared by passing their vapours through a cold water container.

or stability such as

Flocculation

sol of

Sulphur

Chemical methods

Reduction

sol of Pt, Ag etc.

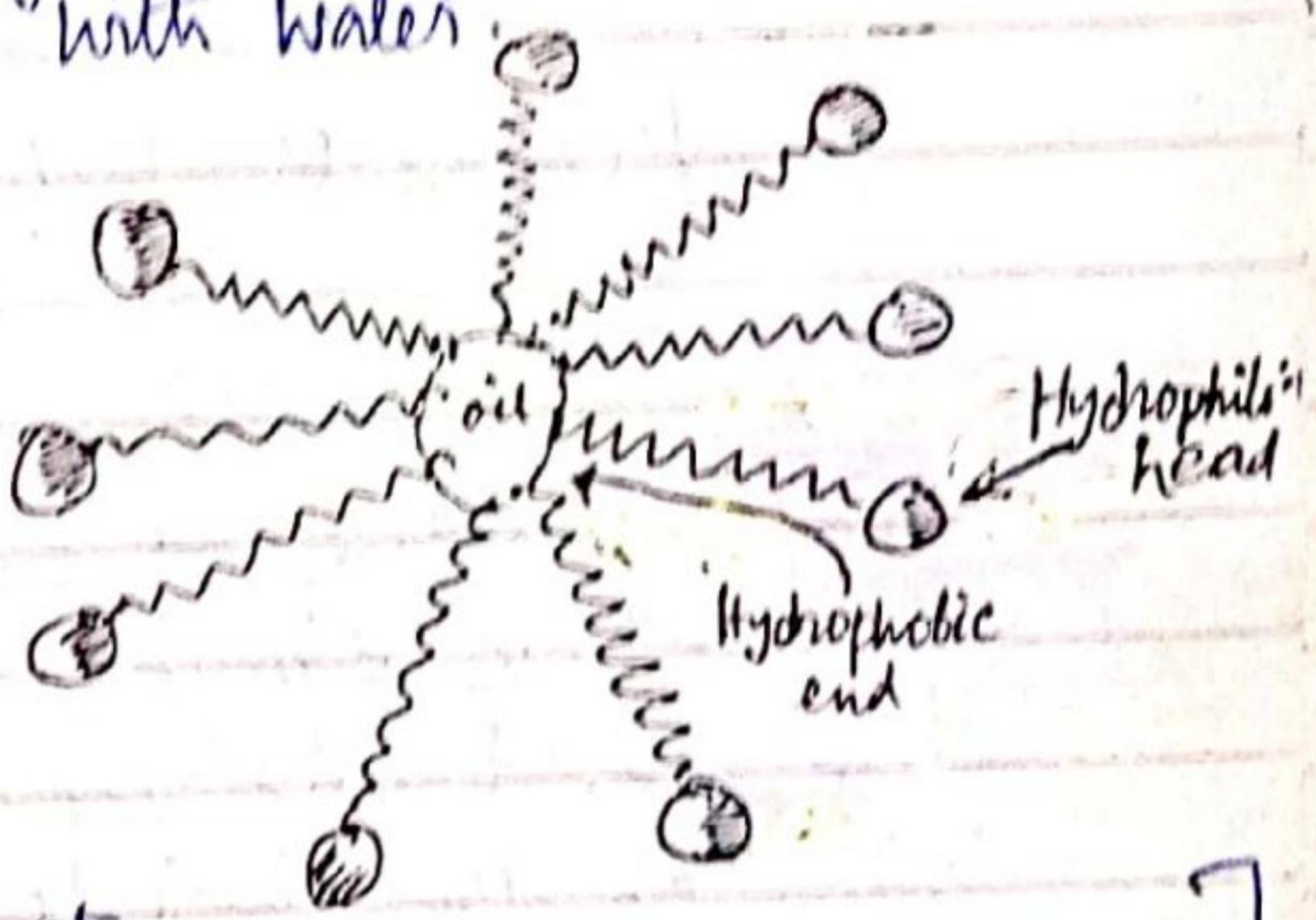
sol (purple)

of CuSO<sub>4</sub>

- Nonionic surfactants: Many long chain alcohols exhibit some surfactant properties. Prominent among these are the fatty alcohols, cetyl alcohol, steryl alcohol.

Larger the hydrophobic fragment of surfactant, easier will be the micellization. Smaller the critical micelle concentration.

Surfactants, when dissolved in H<sub>2</sub>O, micelle results due to the hydrophobic interaction which allows the aggregation of nonpolar (hydrophobic) tails of the surfactant. In this way the polar head groups only remain in contact with water.



Micelle when soap concn exceeds CMC, Micelle may contain 100 or more molecules.

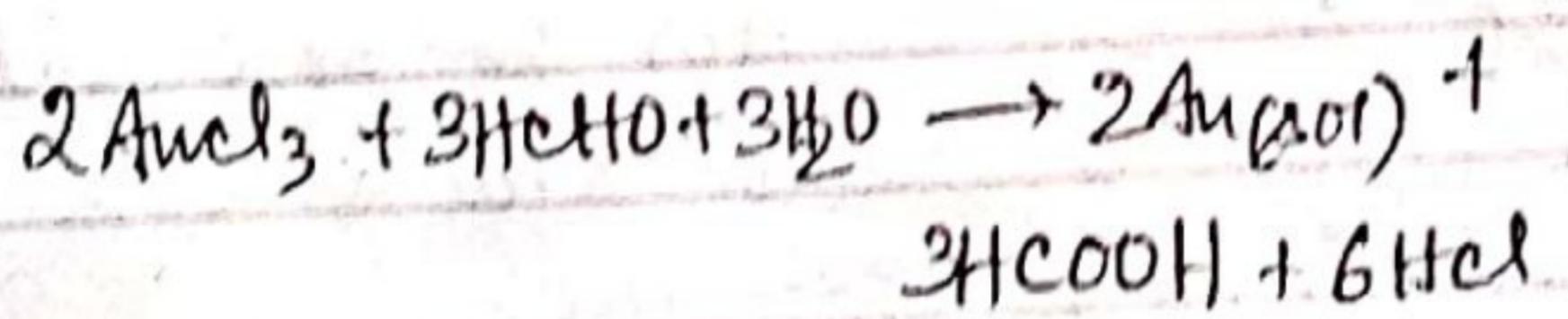
$$CMC \propto \frac{1}{\text{length of alkyl group}} \text{ or } \frac{1}{\text{size of R-group}}$$

(i) Double decomposition :  $As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$  (sol)

(ii) Oxidation :  $2H_2S + SO_2 \rightarrow 2H_2O + 3S$  (sol)

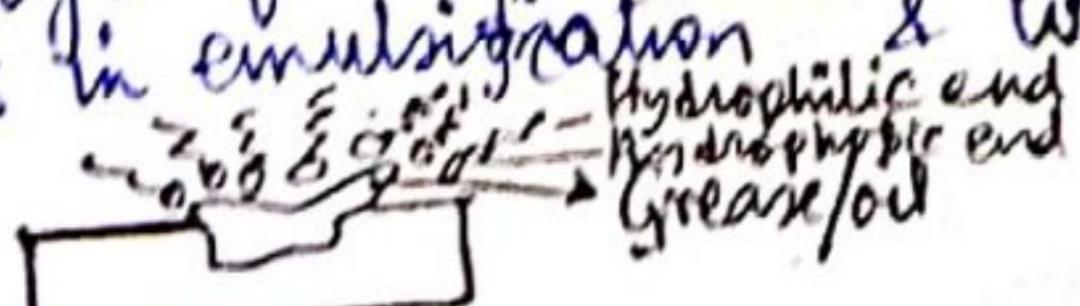
(iii) Reduction :  $AgNO_3 + \text{Tannic acid} \rightarrow Ag$  (sol)

$AuCl_3 + \text{Tannic acid} \rightarrow Au$  (sol)



(iv) Hydrolysis :  $Fe(OH)_3(sol) + 3HCl$

**Cleaning action of soap**: The cleaning action of soap is due to the fact that soap molecules form micelle around the oil droplet (dirt or grease) in such a way that hydrophobic part is in the oil droplet & hydrophilic part projects out of the grease droplet like the bristles. The surfactant gets adsorbed at the interface b/w the dispersed droplets & dispersion medium in the form of a monomolecular layer & lowers the interfacial tension between oil & water so as to facilitate the mixing of 2 liquids. Since the polar groups can interact with water, the oil droplet surrounded by surfactant is now pulled in water and removed from the dirty surface. Thus soap helps in emulsification & washing away of oils & fats.



Emulsions are the colloidal solutions in which both the dispersed phase & the dispersion medium are liquid.

IT I.T.E.S

#### a. Classification based on the nature of dispersion medium:-

<u>Dispersion Medium</u>	<u>Colloid</u>
Air	Aerosol
Benzene	Benzosol
Water	Hydrosol or Aquasol
Alcohol	Alcosol

#### b. Classification based on the nature of charge:-

+ ve sol : Dispersed phase particles carry +ve charge.

- ve sol : Dispersed phase particles carry -ve charge.

**Emulsions** The dispersion of finely divided liquid droplets in an immiscible liquid dispersion medium is defined as Emulsion. Generally, in emulsion one liquid is water and the other is oil. Emulsions are broadly classified into 2 types.

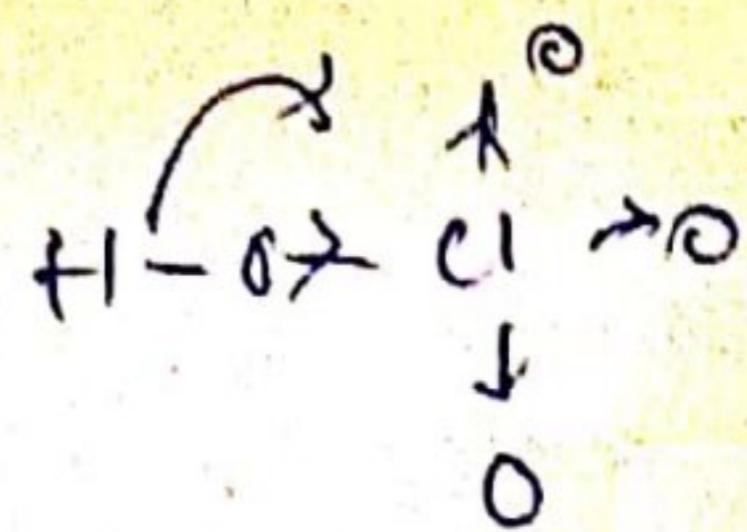
<u>Emulsion</u>	<u>DP</u>	<u>DM</u>	<u>Example</u>
Oil in water (O/w)	Oil	Water	Milk, Vanishing cream etc.
Water in Oil (w/o)	Water	Oil	Greases, Codliver oil, Cold cream, butter etc.

**Emulsifying agents or Emulsifier** Some substances are added to stabilise the emulsions are called emulsifiers/emulsifying agents. Emulsions are unstable as obtained by vigorously mixing of immiscible liquids. Addition of a small quantity of a third substance known as Emulsifier is essential which coat the dispersed droplet of an emulsion and check them from coming together i.e. impart stability.

<u>Emulsion</u>	<u>Emulsifier</u>	<u>Emulsion</u>	<u>Emulsifier</u>
Kerosene in water	Soap	Milk	Caesin
Olive oil in water	Egg albumin	Icecream	Gelatin
Water in Benzene	Solid $HgI_2$		

#### Characteristics of Emulsions

<u>Property</u>	<u>Oil in Water (O/w) Type</u>	<u>Water in Oil (w/o) Type</u>
Appearance	Watery, opaque and translucent	oily, opaque and translucent
Emulsifier	Water soluble substance	oil soluble substance
Dilution	water added is soluble but not oil	oil added is soluble but not water



26/8/19

spreading	Spreads easily on water surface	spreads easily on oil surface.
Viscosity	Little more than water.	More than water.
Dye test	A water soluble dye gives uniform coloured background when added.	An oil soluble dye gives uniform coloured background when added.

### Applications of Emulsions:

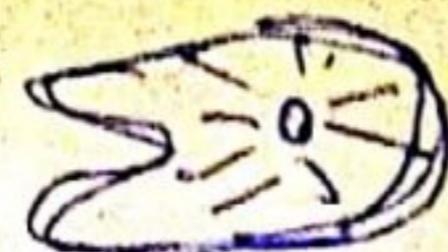
- In washing process of clothes and crockery.
- In the digestion of fats in intestine. A little amount of fat in the intestines forms a soap with alkaline solution of intestine. This soap emulsifies the rest of the fat.
- As lotions, creams & ointments in pharmaceuticals & cosmetics.
- In the metallurgy, concentration of ores is carried out through emulsification process.
- In the conversion of cream into butter by churning. This is breaking of emulsion (or de-emulsification) of fats in water.
- In natural oil wells, oils and water form emulsions. Hence de-emulsification is necessary. De-emulsification means "the breaking of an emulsion into aqueous & nonaqueous phases". An emulsion can be demulsified by physical methods like - freezing, boiling or centrifugation.  
Ex: Centrifugation leads to separation of milk cream while the remaining milk contains very little amount of fat called, "Skinned milk".

Gels : Colloidal system in which a liquid is dispersed in a solid.

Ex: Gum arabic, gelatin, processed cheese, silicic acid, ferric hydroxide etc.

Syneresis or Weeping When the gels are allowed to stand for long time they give out small quantity of trapped liquid which accumulates on its surface. This action of gels is known as syneresis or weeping. Gels may be classified into 2 types :-

- Elastic gels : Gelatin, agar agar, starch
- Non-elastic gels : Silica gel.



## Elastic Gels

- ① Possess elasticity
- ② They readily change their shape on applying force and return to original shape when the applied force is removed.
- ③ They change to solid mass on dehydration which can be changed to original form by addition of water followed by warming.
- ④ They absorb water when placed in it with simultaneous swelling to get body. This phenomenon is called imbibition.

## Nonelastic gels

- ① Doesn't possess elasticity
- ② They are rigid
- ③ They change to solid mass on dehydration which can't be changed back to original form by addition of water & warming.
- ④ They don't imbibe.

## Preparation of Colloidal Solutions by physical methods:

Change of Solvent: When ethanolic solution of sulphur is added to an excess of water, sulphur sol is obtained.

Dispersion Method: Here lumps of the substance is broken down to colloidal size in the presence of dispersion medium and suitable stabilizer.

a) Braedig's arc method (Electrical disintegration): An arc is struck between 2 metal electrodes of silver, gold or platinum held at the surface of cold water containing traces of alkali when sol of metal is obtained.

b) By Peptization: The process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte called as peptizing agent.

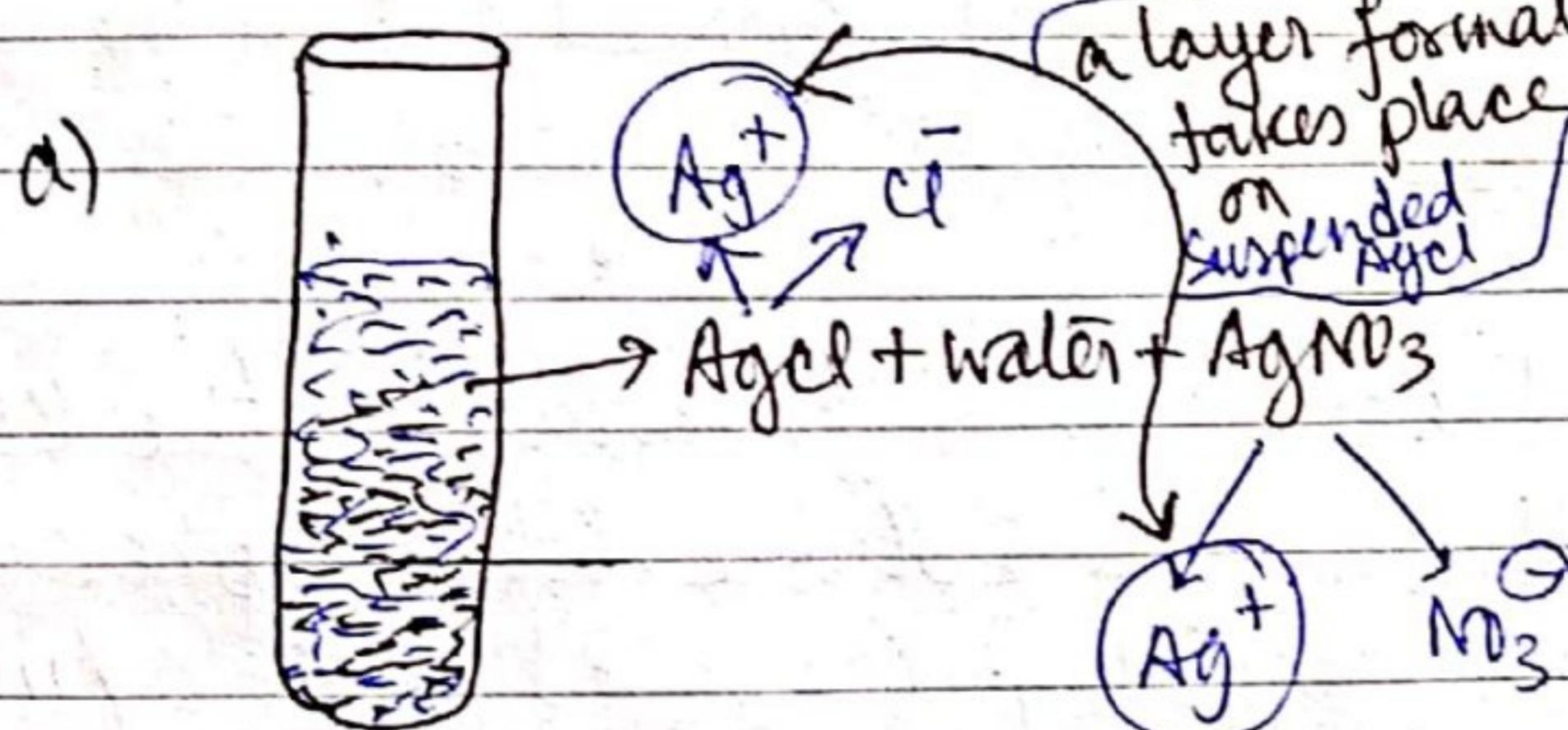
• What is peptisation? The phenomenon of conversion of freshly precipitated into lyophobic colloidal solution with the help of salt or peptising agent is called peptisation.

Precipitate	Peptizing agent	Sol
$\text{Fe(OH)}_3$	$\text{FeCl}_3$	$\text{Fe(OH)}_3/\text{Fe}^{3+}$ (+ve sol)
b) $\text{AgCl}$	HCl	$\text{AgCl}/\text{Cl}^-$ (-ve sol)
a) $\text{AgCl}$	$\text{AgCl}$	$\text{AgCl}/\text{Ag}^+$ (+ve sol)
Cds	$\text{H}_2\text{S}$	$\text{Cds}/\text{S}^{2-}$ (-ve sol)

Role of peptising agent:

- ① ppt
- ② water
- ③ electrolytes

If we want to prepare Silverchloride Colloidal solution then taking a testtube and add  $\text{AgCl}$  sol into it -

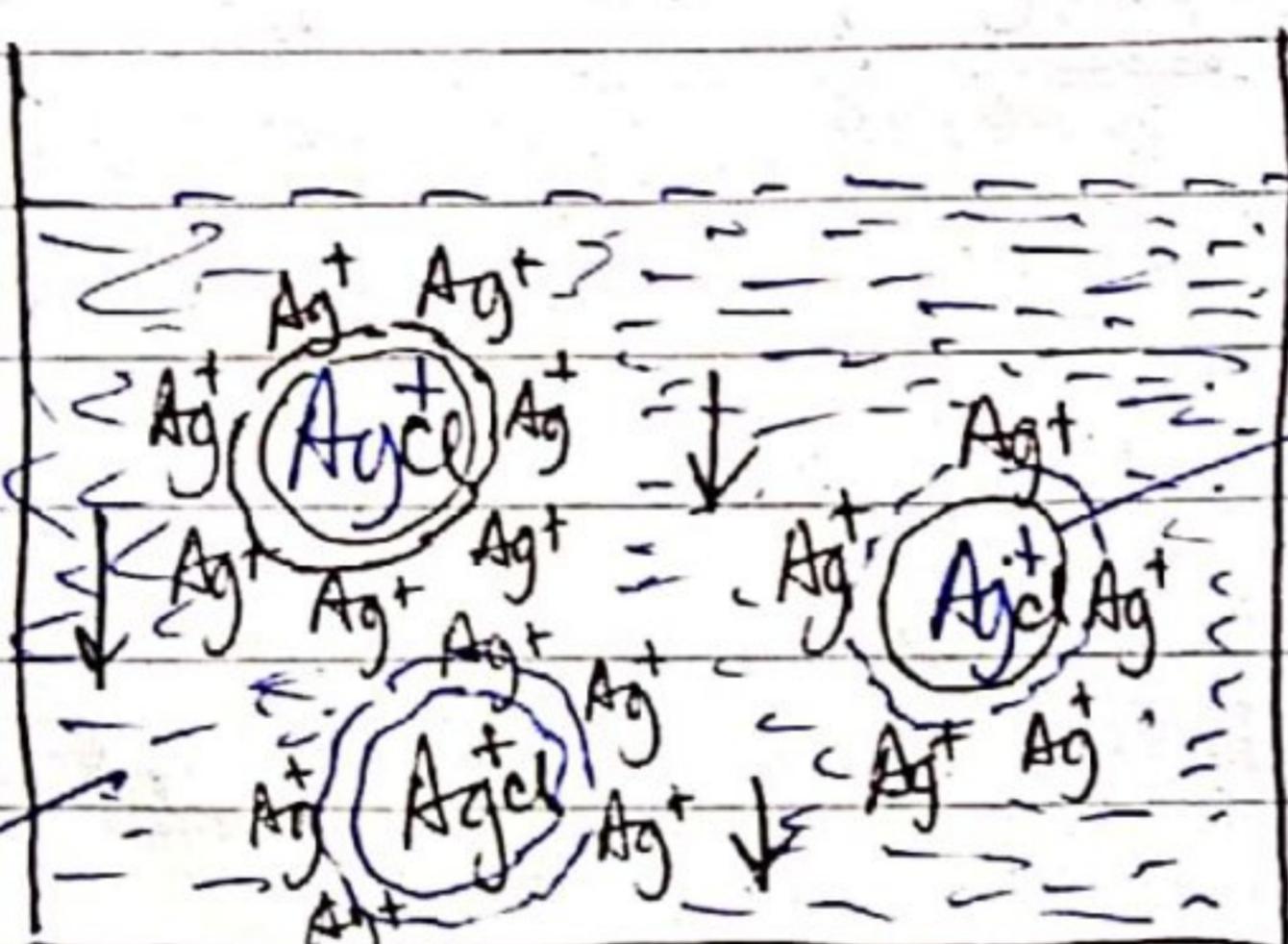


after closing the mouth of the testtube & shaking it  
vigorously we'll prepare silver chloride colloidal soln.

a) due to same (+ve) charge - (+ve) same charge

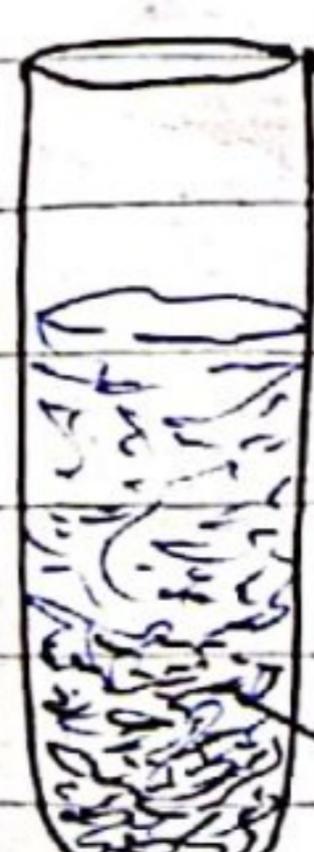
repulsion makes the destabilisation of the colloidal solution.

b) run away from each other and striking to each other.



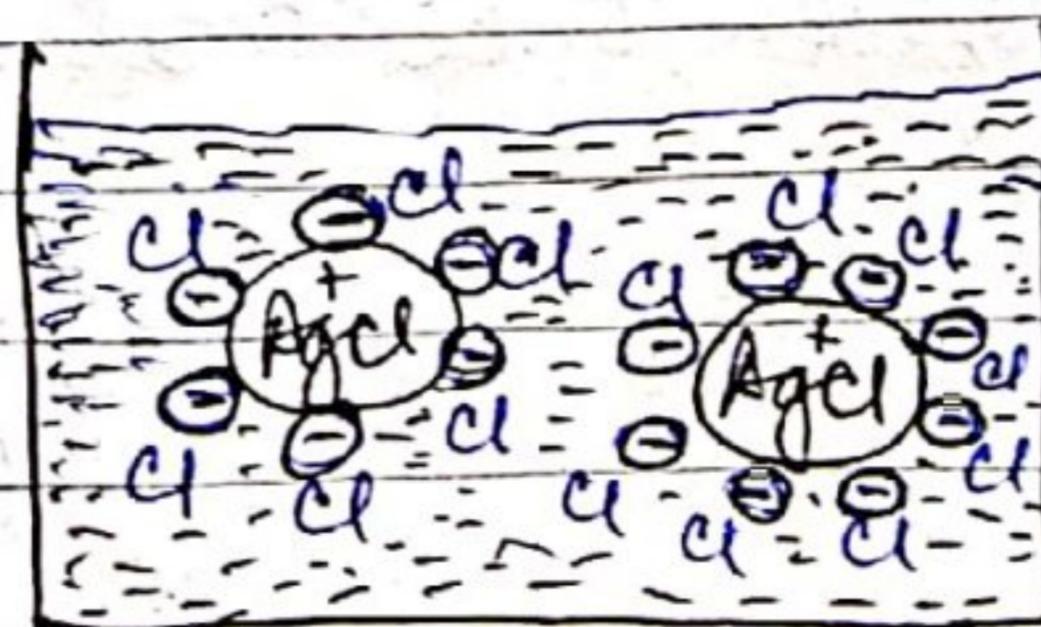
dispersed phase or medium

+ve  $\text{AgCl}$  sol



b)

Now if we'll add HCl then  
 $\text{AgCl} + \text{HCl} \rightarrow \text{AgCl} + \text{HCl}$



Then  $\text{Cl}^-$  (-ve) ions are adsorbed

on  $\text{AgCl}$  suspended particles or  $\text{AgCl}$  sol then -ve layer of  $\text{Cl}^-$  ion is formed on the particles and run away from each other and also strike on one another and then suspended particles combine to colloidal solution.

2/9/19

What is "COLLOIDION"?  $\rightarrow$  Cellulose nitrate peptized by a mixture of ethanol and water.

Purification of Colloids Generally colloidal solution associate with excessive amount of electrolyte & some other soluble substances, which act as impurities. Removal of such impurities is done as follows:-

(i) Dialysis  $\rightarrow$  The process of removal of dissolved substance (impurity) ~~is done~~ from a colloidal solution by means of diffusion through a suitable membrane is called dialysis.

$\rightarrow$  Electrodialysis if dialysis is carried out in the presence of electric field it is called electrodialysis.

$\rightarrow$  Ultrafiltration The process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters (ultra filter) is known as ultrafiltration.

Properties of Colloids

(Colligative properties) colloidal particles being bigger aggregates the number of particles in a colloidal solution is comparatively small as compared to a true solution.

At a given concentration:  $(O.P / \Delta P / \Delta T_b / \Delta T_f)_{\text{true solution}} > (O.P / \Delta P / \Delta T_b / \Delta T_f)_{\text{colloidal solution}}$

Optical properties: All colloidal solutions are capable of scattering light.

What is Tyndall effect?

Ans. When a beam of converging rays falls on the colloidal solution, scattering of light by sol particles in all the directions, gives rise to a bright glowing cone when looked at it sideways. This is known as Tyndall effect.

scattering of light depends upon the :-

- (i) Wavelength of light used : Scattering  $\propto \frac{1}{\lambda^4}$ , that's why scattering of blue light is maximum.
- (ii) Size of particles : larger sized dispersed phase particles show more scattering. That's why lyophobic sols show more scattering.
- (iii) Difference in refractive indices of dispersed phase and dispersion medium : i.e.  $\Delta n_p \sim \mu_M$

Larger is  $\Delta n$  more is scattering.

Some examples of Tyndall effect:

- (i) Blue colour of sky and sea water.
- (ii) Visibility of tails of comets
- (iii) Twinkling of stars.
- (iv) Visibility of projector path and circus light.
- (v) Visibility of sharp ray of sunlight through a slit in dark room.

Kinetic properties The continuous zig-zag movement executed by colloidal particles in a liquid dispersion medium is called Brownian movement.

All colloidal particles in colloidal solution exhibits Brownian motion. This is due to - the bombardment of the particles of the dispersion medium on the particles of the dispersed phase.

Brownian motion is independent of the nature of the colloid but depends on the size of the particles & viscosity of the solution. Smaller the size & lesser the viscosity  $\rightarrow$  faster is the motion of colloidal particles. Brownian movement  $\uparrow$  with  $\uparrow$  in temperature. It offers an explanation for the stability of the colloidal solutions.

Colour The colour of colloidal solution depends on the  $\lambda$  of the light scattered by the dispersed particles, which further depends on the size & nature of the particles.

1105  
example - Finest gold sol is red in colour, as the size of particles,  
it appears purple, then blue and finally golden.

Electrical Properties Colloidal particles always carry an electrical charge. The nature of this charge is the same on all the particles in a given colloidal solution and may be either +ve or -ve. The origin of the charge may be due to -

- (i) Electron capture by sol particles during electrodialysis of metals.
- (ii) Preferential adsorption of ions from solution.
- (iii) Self dissociation : When colloidal particles such as - Soaps or detergents are dissolved in water ionised molecules associate to form micelle. The outer surface will be thus charged depending on the charge of the ions from which it's formed. This sodium stearate solution will have negative charge on its sol particles.

+vely charged sols	Negatively charged sols
Hydrated metallic oxides e.g. $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ & $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$	Metals e.g., Cu, Ag, gold sols
Basic dye stuffs, e.g.: Methylene blue sol	metallic sulphides, e.g.: $\text{As}_2\text{O}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{CdS}$ sols
Haemoglobin (blood)	Acid dye stuffs, e.g. eosin, congo red sols.
Oxides e.g. $\text{TiO}_2$ sol	sols of starch, gum, gelatin, clay, charcoal, etc.

Each sol particle is surrounded by either +ve or -ve ions in the form of fixed layer or compact layer. The second layer is diffused or mobile layer consisting of ions with charge being equal and opposite to the fixed layer. This is known as Helmholtz electrical double layer. The potential

\* The ion which is responsible for the coagulation of colloidal solution is known as effective ion. The effectiveness of an ion or electrolyte in causing coagulation is dependent on the charge sign & charge magnitude. This fact is enunciated by Hardy & Schulze rule.

Difference developed between the two layers is known as zeta potential or electric kinetic potential.

**Electrophoresis** The movement of sol particles under an applied electric potential.

**Electroosmosis** The movement of the dispersion medium under the influence of applied electric potential.

**Stability of Sols** The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from coalescing or aggregating when they come closer to one another.

**Coagulation or precipitation of colloidal solution:**

The process of settling of colloidal particles is called coagulation or precipitation.

The solubility of the lyophobic sols is due to the presence of charge on colloidal particles. If the charge is removed, the particles will come nearer to each other to form aggregates (or coagulation) and settle down under the force of gravity. A colloidal solution can be coagulated by the addition of electrolyte.

**Hardy and Schulze Rules** (i) The ion with charge opposite to the charge of the colloidal particles is effective in coagulating the colloid. Greater the charge of the ion, greater is the coagulating ability of the ion.

(ii) The colloids are coagulated by -ve ions/anions of the salt added.

**Coagulating ability** :  $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

(iii) Negative colloids are coagulated by positive ions/cations of

the salt added. [Coagulating ability] :  $\text{Al}^{3+} > \text{Ba}^{2+} > \text{K}^+$

Flocculation value (or coagulation value/ precipitation value)

It's the minimum amount of electrolyte in millimoles that must be added to 1 litre of the colloidal sol to bring about complete coagulation/ precipitation.

$$\text{Coagulating power} \propto \frac{1}{\text{Flocculation value}}$$

The relative coagulating powers of 2 electrolytes for the same colloidal sols, we've the following relation:

$$\frac{\text{Coagulating power of electrolyte 1}}{\text{Coagulating power of electrolyte 2}} = \frac{\text{Coagulation value of } \text{A}_2}{\text{Coagulation value of } \text{electrolyte}_1}$$

Coagulation can also be caused by electrophoresis, mutual precipitation (mixing colloidal sols of opposite charge), prolonged dialysis or by heating/ cooling the sol.

### Protection of Colloids

- ① Lyophobic sols are less stable than lyophilic colloids.
- ② A lyophobic sol can be protected from coagulation by adding a lyophilic colloid.
- ③ The lyophilic sol added is called protective colloid.

④ Zsigmondy introduced the term "gold no." to measure the protective power of different colloids.

What is "gold no" ?

Weight in milligram of a protective colloid which checks the coagulation of 10 ml of a given gold sol on adding 1 ml of a 10% solution of NaCl. is called gold no.

$$\text{Protective power} \propto \frac{1}{\text{Gold Number}}$$

## Gold number of some protective colloids.

Protective colloids → Gold no. →

Gelatin	0.005 - 0.01
Haemoglobin	0.03 - 0.07
Caesin	0.01 - 0.02
Albumin	0.1 - 0.2
Gum Arabic	0.15 - 0.25
Potato Starch	25

## Applications of Colloids →

- ① Purification of drinking water.
- ② Electrical precipitation of smoke : Cottrell's precipitator.  
Smoke carry (-ve) charge & is removed by the principle of electrophoresis in Cottrell's precipitator.
- ③ Artificial rains : Clouds are aerosols (dispersed in air). Aggregates of particles of water cause the rainfall which can be artificially achieved by throwing electrified sand or  $\text{AgI}$  on clouds and cause the artificial rain.
- ④ Sewage disposal, Electroplating of rubber, Leather tanning, photographic plate and films.

Q1. 0.025 g of a starch sol is required to prevent coagulation of 10 ml gold sol when 1 ml of 10% NaCl solution is present. What's gold number of starch sol?

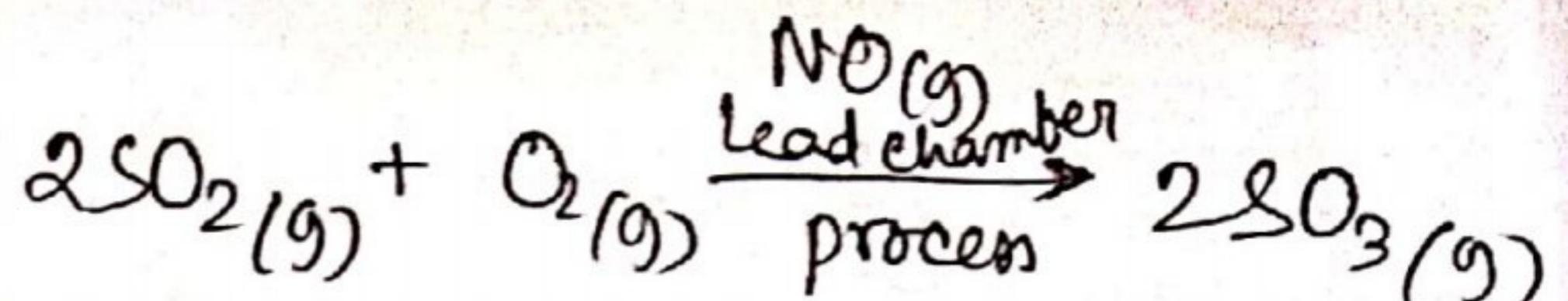
From the definition of "gold no" - it is the amount of protective sol (here, starch) in milligrams that prevents coagulation of 10 ml of gold sol on the addition of 1 ml of 10% NaCl solution.

For such case the amount of starch required is 0.025 g  
 $= 25 \text{ mg}$

∴ The gold no. of starch is 25.

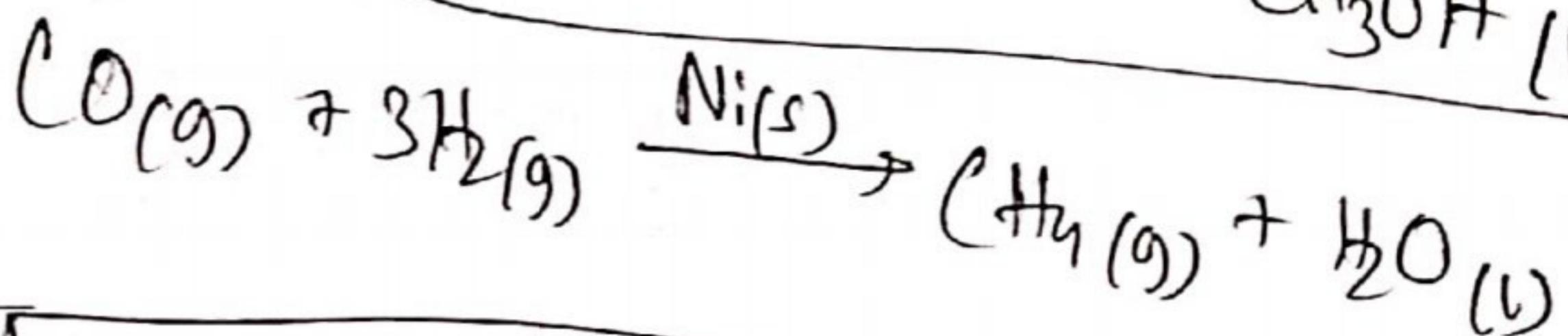
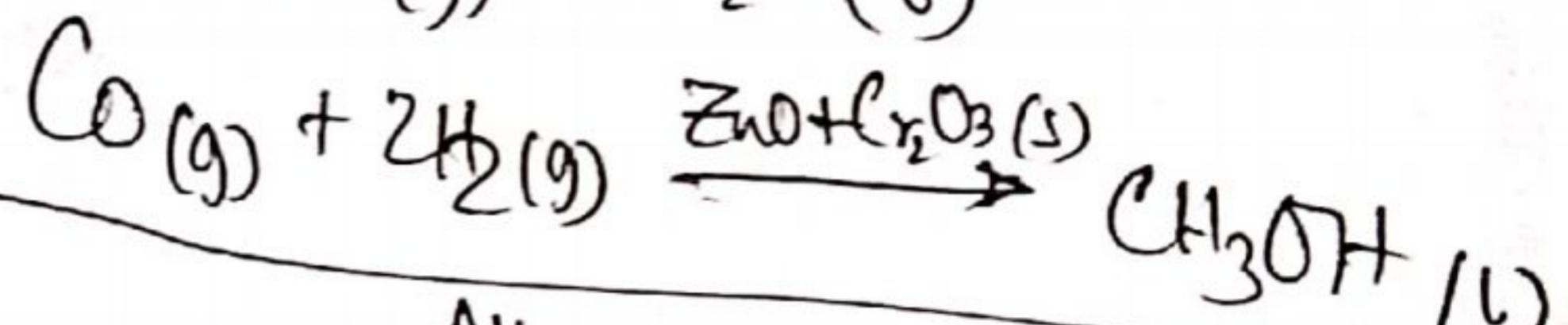
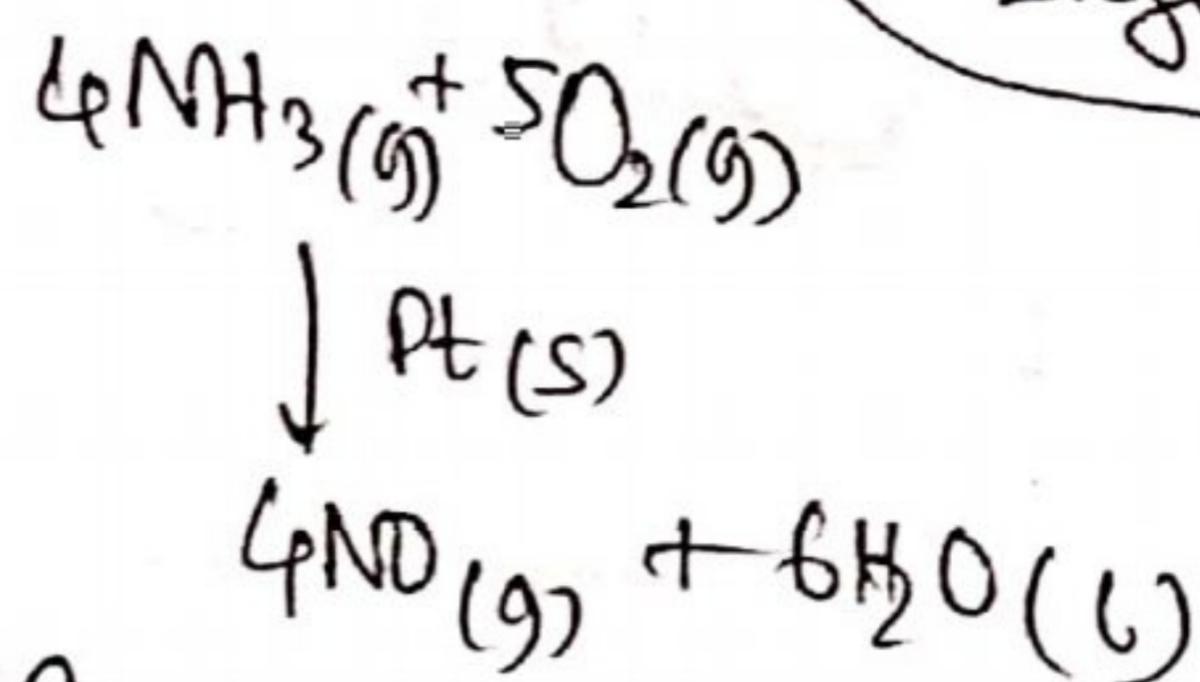
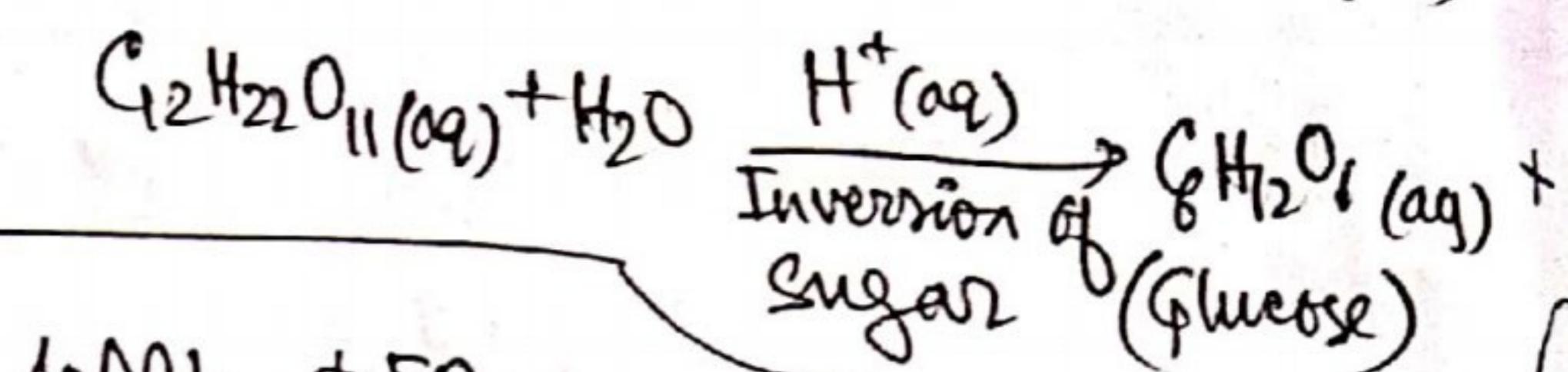
### Homogeneous Catalysis

Reactants and the catalyst are in the same phase.



### Heterogeneous catalysis

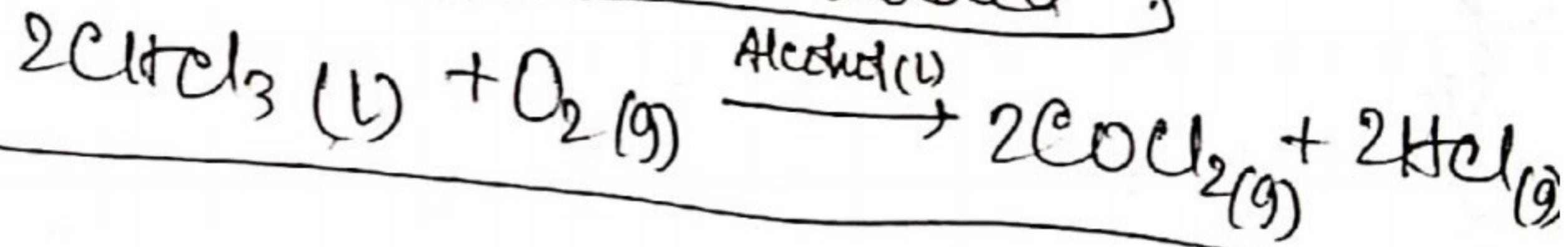
Reactants & the catalyst are in different phases:



### Negative Catalysis

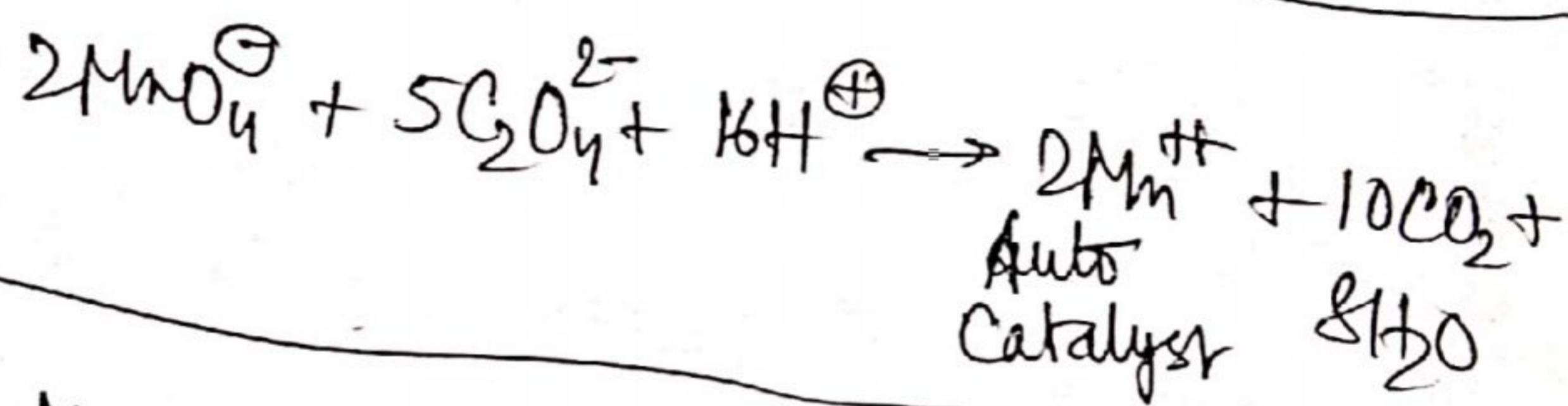
Catalyst  $\downarrow$  the rate of rxn.

Oxidation of chloroform by air is retarded if some alcohol is added.



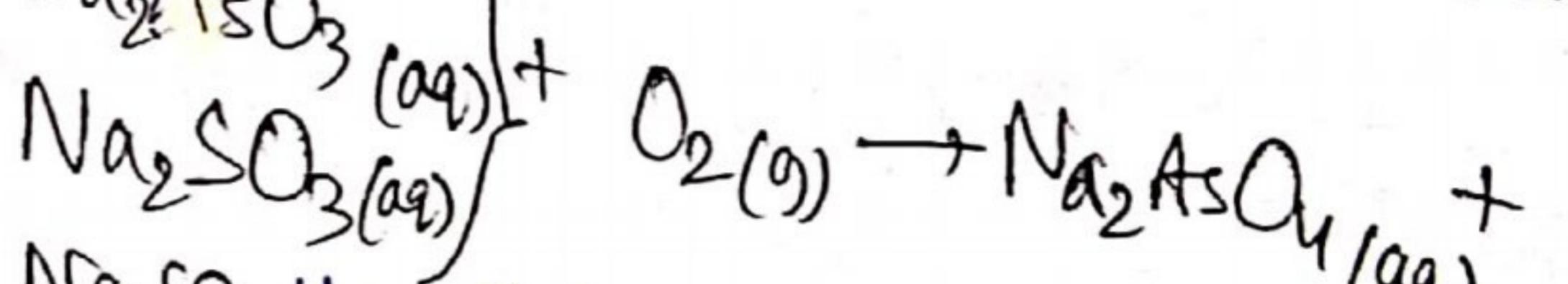
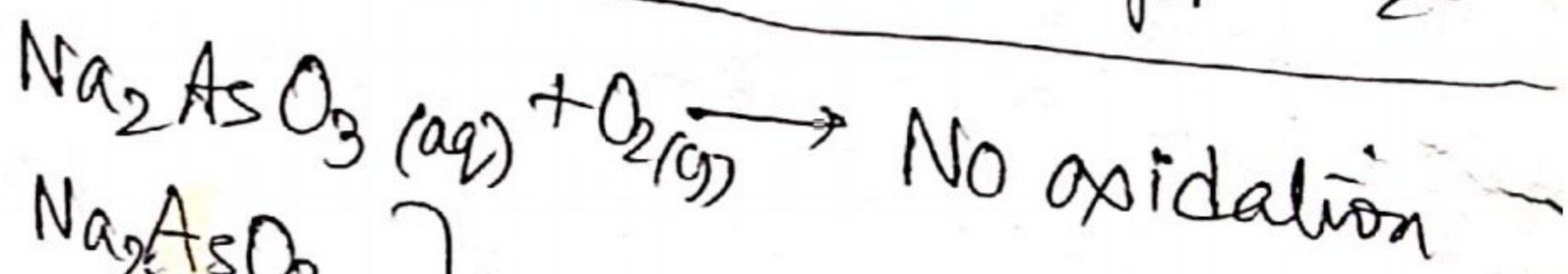
### Autocatalysis

One of the product acts as catalyst

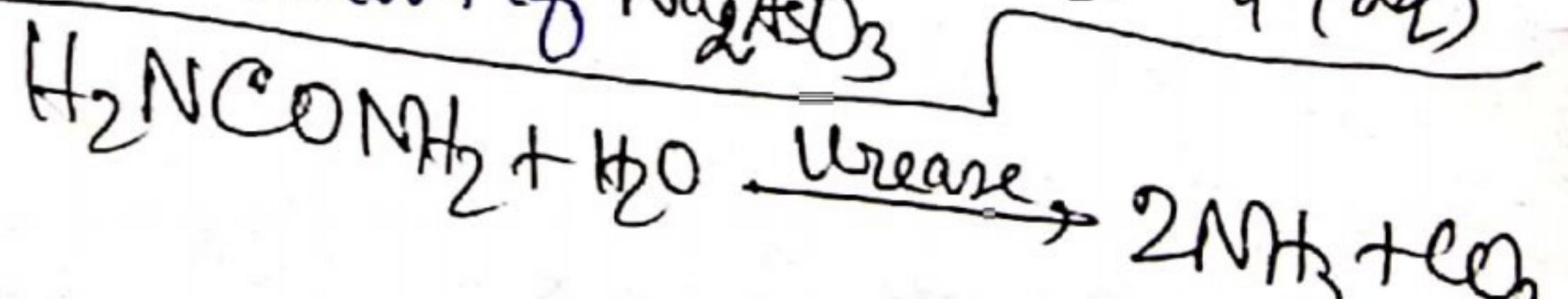


### Induced Catalysis

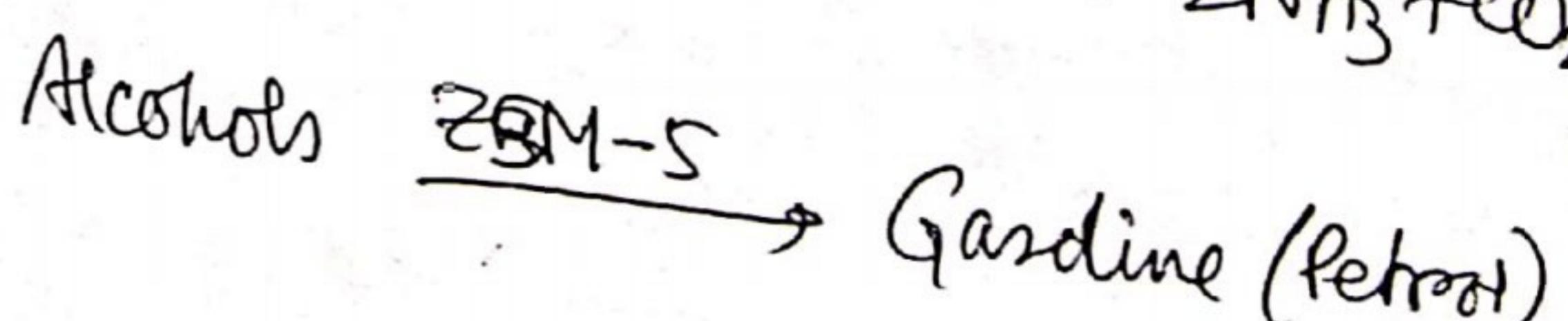
One rxn influences the rate of other rxn, which doesn't occur under ordinary conditions



$\text{Na}_2\text{SO}_3$  thus, induces the oxidation of  $\text{Na}_2\text{AsO}_3$



### Enzyme Catalysis



### Shape Selective Catalysis

