increases with increase in surface area per unit mass of adsorbent at a given temp. & pressure.

$$\frac{x}{m} = \text{extent of adsorption}$$

Surface area $\propto$ Residual forces $\propto$ Extent of adsorp

For adsorption

$\Delta H = -ve$

$\Delta S = -ve$

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

$\because \Delta H > T\Delta S$ (in −ve sense)

$\Rightarrow \Delta G = -ve$

As adsorption proceeds, ΔH becomes less −ve and ultimately $\Delta H = T\Delta S$ & $\Delta G = 0$. At this state eqb. is attained.

During adsorption there is always a decreas in residual forces on the surfaces or surface energ is decreased which appears as heat. Therefore it is an exothermic process.

Types of adsorption:

1. Physical adsorption (Physisorption)
2. Chemical ..." (Chemisorption)

	Physisorption	Chemisorption
1.	The forces operating in these cases are weak van der Waal's forces.	1. The forces operating in these cases are similar to those of a chemical bond.
2.	The heats of adsorption are low, i.e about 20-40 KJ/mol. ΔH = -ve.	2. The heats of adsorption are high, i.e about 40-400 KJ/mol. ΔH = -ve.
3.	The process is reversible i.e desorption of the gas occurs by increasing the temp. or decreasing the pressure.	3. The process is irreversible
4.	It does not require any activation energy.	4. It requires activation energy.
5.	This types of adsorption usually takes place at low temp. and decreases with increase in temp.	5. This type of adsorption first increases with increase of temperature. The effect is called activated adsorption. But further increasing temp. beyond a limit it decreas
6.	The amount of the gas adsorbed is related to the ease of liquification of the gas. It depends on nature.	6. ~~There is no such~~ It depe on nature of gas ~~correlation~~ Gas which ca react with adsorbent shows chemisorption.
7.	It forms multimolecular layer on adsorbent surface under high pressure.	7. It forms unimolecular layer.
8.	It is not specific in nature.	8. It is highly specific
9.	It depends on surface area. It increases with an increase of surface area.	9. It also depends on surface ar It too increases with an increase of surface area.

10. High pressure is favoured. Pressure decrease causes desorption.	10. High pressure is favoured but on decreasing pressure desorption does not take place
Ex.	11 Ex.
12. Physisorption may transform into chemisorption at high temperature.	

* In some cases chemisorption is endothermic.

Ex. 1) Adsorption of H_2 gas on glass surface

$$H_{2(g)} \longrightarrow 2H(g) \qquad \Delta H = +ve$$

$$\Delta S > 0$$

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

$\Delta G < 0$ (feasible reac^n)

2) Highly hydrated solute when adsorbed on solid have $\Delta H = +ve$ and $\Delta S = +ve$ due to release of water molecules on adsorption.

Activation of adsorption:

1. By making surface rough.
2. By taking adsorbent in powder state.
3. By heating with super heated steam. Ex. Charcoal is activated by heating b/w 650 to 1330 K in vacuum or steam.

Example of adsorption & absorption :

1. H_2O vapour is absorbed by anhy $CaCl_2$ while it is adsorbed by silica gel.
2. H_2O is absorbed by sponge.
3. Ammonia is absorbed in H_2O while it is adsorbed by charcoal.
4. Acetic acid & I_2 are adsorbed by charcoal.
5. N_2 is adsorbed on Mica.
6. O_2 is adsorbed by Tungsten surface.
7. Decolourisation of sugar solⁿ by activated animal charcoal.
8. Bloating paper ~~it~~ first adsorbs ink & absorbs ink.

(Silica gel is sodium silicate + 10% HCl.)

9. Gases are adsorbed on solid surface.

Adsorption of gas on solid :

Following factors affect adsorption of gas

1. Nature of adsorbent.
2. Nature of adsorbate.
3. Surface area of adsorbent.
4. Activation of solid adsorbent.
5. Temperature
6. Pressure.

1. Nature of adsorbent :

Transition metals are good adsorbents for gases because of vacant & half-filled d-orbitals and high charge/size ratio. Activated charcoal is a good adsorbent for poisonous and polluting gases in gas masks. Metal oxides such as silica gel are good adsorbent fol moisture & aluminium oxides.

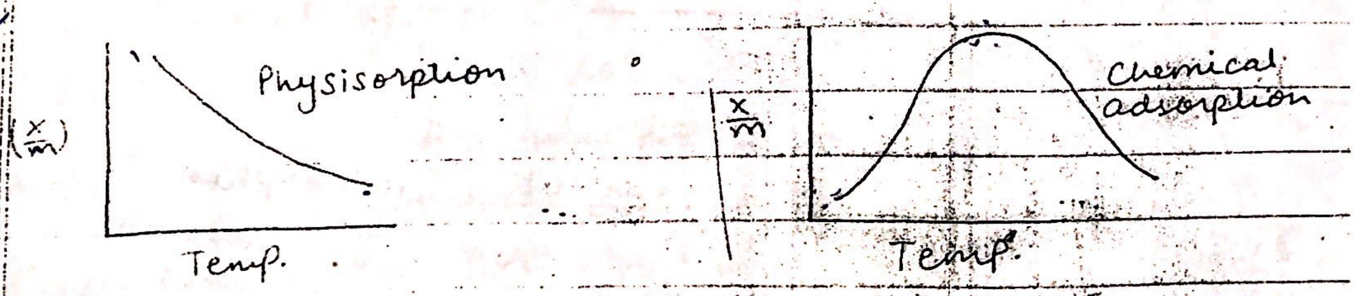
clay, etc. are other good adsorbents.

2. Nature of adsorbate:
Easily liquifiable gases (HCl, NH_3, CO_2) are adsorbed to a greater extent than others (ex. H_2, N_2, O_2).

3. Surface area of adsorbent:
Larger the surface area, more is adsorption. Surface area per gram of adsorbent is called specific surface area of adsorbent. That's why a porous or finely divided form of adsorbent adsorbs larger quantity of adsorbate.

4. Activation of solid adsorbent:
Activation of surface for adsorption can be made by rubbing or by passing in colloidal state or by passing super heated steam. Activated charcoal is commonly used for adsorption of easily liquifiable gases.

5. Temp.
An increase in temp. decreases physical adsorption whereas chemical adsorption first increases & then decreases.

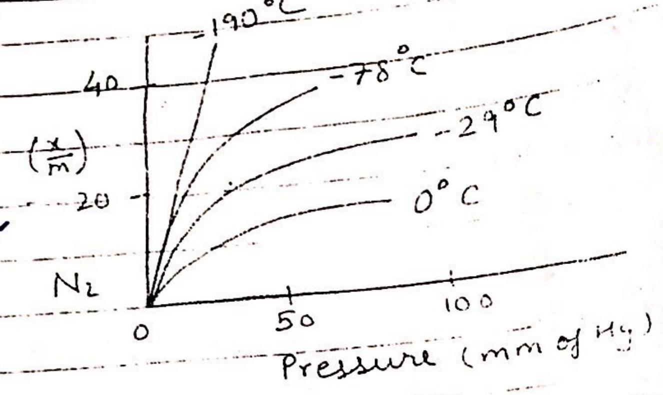


Const. Pressure

Adsorption isobars

Freundlich adsorption isotherm (at const. temp.)

6. ~~Fa~~ **Pressure:**



$\frac{x}{m} = Kp^{1/n}$, x = mass of adsorbate

m = mass of adsorbent

K, n = constants

(depend on nature of adsorbent and the gas at a particular temp.)

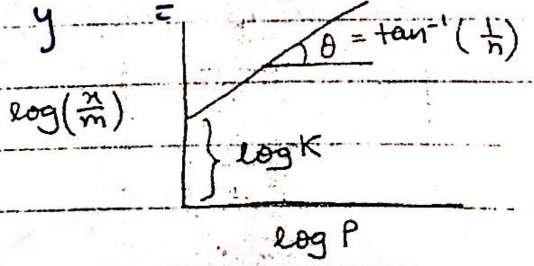
$0 < \frac{1}{n} < 1$ [possible range is 0.1 to 0.5]

× ———— × ———— × ———— × ———— ×

$\frac{x}{m} = Kp^{1/n}$

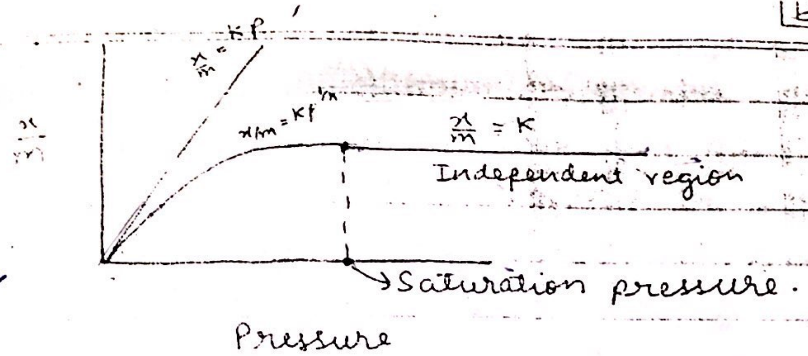
$$\log\left(\frac{x}{m}\right) = \underset{C}{\log K} + \underset{mx}{\frac{1}{n}\log P}$$

$$y = C + mx$$



Case I : $\frac{1}{n} = 0$, $\frac{x}{m} = K$ (adsorption independent of pressure)

Case II : $\frac{1}{n} = 1$, $\frac{x}{m} = Kp$ (adsorption varies with pressure)



Such isotherms are obtained where :

1. A unimolecular layer is formed on the surface of adsorbent (monolayer).
2. Adsorbed gas behaves ideally.
3. Increase in extent of adsorption with increas in pressure at const temp. is in agreement with Le-chatalier's principle which suggest that an increase in pressure will favour the change showing decrease in volume.

* In practice, graph is actually found to be reasonable straight line if result at low & high temp. pressure are neglected (the graph of log $(\frac{x}{m})$ vs log P).
Since value of $\frac{1}{n}$ is generally less than 1, therefor $\frac{x}{m}$ does not increase as rapidly as P.

Shortcomings of Freundlich isotherm :
The concept of " " is purely empirical. It does not consider the role of surface area of adsorbent. It cannot explain why $\frac{x}{m}$ is constant at high pressure. It is applicable only for physical adsorption because it consists of multi layers of adsorption.

* Extra
nly for IITS

Langmuir Adsorption isotherm:

It is based on kinetic theory of gases.

Assumptions of Langmuir's are:

1. The surface of solid consists of a fixed no of adsorption sites where only gaseous molecules can be adsorbed.
2. Each site can hold only gaseous molecules giving out heat of adsorption. Heat of adsorption for each site molecules adsorbed is constant at each point.
3. Adsorption being monolayer only unilayer adsorption of gaseous molecules can take place. ~~Mole~~
4. Molecules adsorbed at different sites **do not** interact with each other.
5. The adsorption shows dynamic **eqb. between** adsorbed sites (S) ~~and~~, adsorbed **molecules (AM)** and unadsorbed molecules (U.M).

$$UM + S \rightleftharpoons AM$$

Dynamic nature involves the forward reactions of adsorption as well as backward reactions of desorption taking place simultaneously with same rate of adsorption and **desorption** at eqb.

Rate of adsorption $= K_f [UM][S]$

Rate of desorption $= K_b [AM]$

at eqb.

$$K_f [UM][S] = K_b [AM]$$

$$K = \frac{K_f}{K_b} = \frac{[AM]}{[UM][S]}$$

Langmuir adsorption isotherm works well for chemisorption.

Derivation of Langmuir adsorption isotherm:
Consider a solid surface of definite area in contact with gaseous molecules. Let fraction θ of the surface is occupied by gaseous molecules to show adsorption at eqb.

rate of desorption $\propto \theta$

$= K_d\theta$

, K_d = desorption constant

rate of adsorption $\propto P(1-\theta)$

$= K_a P(1-\theta)$

, K_a = adsorption constant

At eqb. $K_d\theta = K_a P(1-\theta)$

$$\theta = \frac{K_a P}{K_a P + K_d} = \frac{\frac{K_a}{K_d}\cdot P}{\frac{K_a}{K_d}P + 1} = \frac{K_1 P}{1 + K_1 P} \quad \left[K_1 = \frac{K_a}{K_d}\right]$$

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

$$\frac{x}{m} = K_2\theta = K_2\left[\frac{K_1 P}{1+K_1 P}\right] = \frac{K_1 K_2 P}{1+K_1 P} = \frac{aP}{1+bP},$$

$$\boxed{\frac{x}{m} = \frac{aP}{1+bP}}$$

$a = K_1K_2$
$b = K_1 = \frac{a}{K_2}$
Langmuir parameters..

At very high pressure

$$\frac{x}{m} \simeq \frac{aP}{bP} \qquad (1+bP \simeq bP)$$

$$= \underline{a}$$

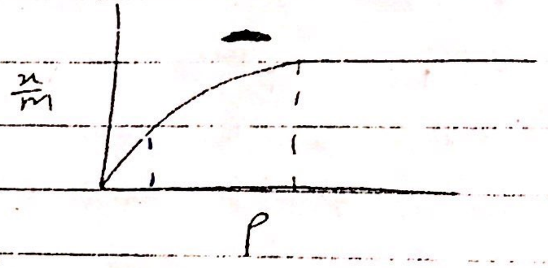
at very low pressure,

$$\frac{x}{m} = ap \quad [K.p <<< 1 \;,\; bp <<< 1]$$

$$\frac{m}{x} = \frac{1+bp}{ap} = \frac{b}{a} + \frac{1}{ap}$$

$$y = mx + c$$

- plot $\frac{m}{x}$ v/s $\frac{1}{p}$



See NCERT applications of adsorption, adsorption from sol.ⁿ pha

Q. catalyst ↑ the rate of rxn. T/F?
ans. → True.

1/3

Page
Date

Catalyst :

Catalyst is a substance which can change the speed of chemical reac^n^ without being used up in that reac^n^. This phenomenon is known as catalysis.

- If the catalyst increases the speed of reac^n^, it is known as positive catalyst.
- If the catalyst decreases the speed of reac^n^, it is known as ~~negative catalyst~~ or inhibitor.

Positive ~~ca~~talyst decreases activation energy, so rate of reac^n^ will increase. Negative catalyst increases activation energy, so rate of reac^n^ will decrease.

* Rate constant (K) depends on temp. and catalyst.

* In a reversible reac^n^, catalyst increases rate of forward reac^n^ & ~~do~~ also backward reac^n^. There is no effect on eqb. constant due to a catalyst. Catalyst lowers A.E for forward as well as backward reac^n^. As a result, reac^n^ follows an alternate path and rate of forward & rate of backward reac^n^s are accelerated to the same extent. Hence eqb. constant remains unaffected. ~~Some~~
Similarly, ΔH also remains unaffected in presence of catalyst.

- A catalyst can never initiate a chemical reac^n^.
- Small quantity of a catalyst is sufficient to influence the rate of reac^n^.
- A catalyst normally does not alter the nature of product in a reac^n^, however some

(14)

Imp **HABER'S PROCESS :**

$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

catalyst : Fe (s)
catalyst promoter : Mo
Nowadays,
$Fe_2O_3 + K_2O$ / $Al_2O_3 + Fe_2O_3$
used as catalyst.

CONTACT PROCESS :

$2SO_2 + O_2 \xrightarrow{Pt(s)} 2SO_3$

catalyst : Platinised Asbestos / V_2O_5 (s)

$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

→ **OSTWALD PROCESS (HNO_3)**

$4NH_3 + 5O_2 \xrightarrow{Pt(s)} 4NO + 6H_2O$

catalyst : Pt / Rh gauge

$2NO + O_2 \rightarrow 2NO_2$

$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$

→ **Deacon's process for Cl_2**

$2HCl + \frac{1}{2}O_2 \xrightarrow{CuCl_2(s)} Cl_{2(g)} + 4H_2O$

→ **Bosch process**

$CO^* + H_2O \xrightarrow{Fe_2O_3(cat)} CO_2 + H_2$

→ **Synthesis of petrol** (Fisher Tropsch process)

$CO + H_2 \xrightarrow[\text{on alumina}]{Ni, Co, Fe}$ mixture of hydro

→ **manufacture of CH_3OH**

$CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO / CuO} CH_3OH$

→ **Oxid^n of CO in automobile exhaust by $Pt_{(s)}$ catalyst** :

→ **Prep. of CH_3COOH**

$CH_3OH + CO \longrightarrow CH_3COOH$ catalyst $[Rh(CO)_2I_2]^-$

→ **Prep. of polythene.**

$n\,C_2H_4 \xrightarrow{\text{organo } Cr \,\&\, Ti}$ Polythene

→ Oxid^n of NH_3 to NO by 90% Pt – 10% Rh catalyst

*→ Polymerisation of propene to polypropene by $TiCl_4$ catalyst (Ziegler Natta)
↓ learn compositio from NCERT

→ Alkylation of benzene by $AlCl_3$ or H_3PO_4 catalyst

→ Vegetable $oil_{(l)} + H_{2(g)} \xrightarrow{Ni(s)}$ Vegetable ghee(s) exceptions are found :

$H-\overset{\overset{O}{||}}{C}-OH \xrightarrow{AlCl_3} H_2O + CO$

$H-\overset{\overset{O}{||}}{C}-OH \xrightarrow{Cu} H_2 + CO_2$

8 $CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O(g)$

$CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$

$CO + H_2 \xrightarrow{Cu} H-\overset{\overset{O}{||}}{C}-H(g)$

- A catalyst does not make the reac^n more exothermic. It simply reduces A.E & threshol energy level by changing the pathway of reac^n
- Catalyst activity is more or less specific. A cataly for one reac^n is not necessarily a catalyst for some other reac^n.

Types of catalysis :

1. Homogenous catalysis

Reac^n in which catalyst is present in same phase as reactant. It is of two types :

a) Gaseous phase catalysis

b) Solution phase catalysis

a) Gaseous phase catalysis :

i) $\boxed{2SO_2(g) + O_2(g) \xrightarrow[\text{cat.}]{NO(g)} 2SO_3(g)}$ ← Lead Chamber process

$2SO_3(g) \xrightarrow{H_2O} H_2SO_4$

ii) $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

contact process

ii) $2CO_{(g)} + O_2(g) \xrightarrow{NO(g)} 2CO_2(g)$

$O_3 + O \xrightarrow[\text{atom Cat}]{Cl} 2O_2$

b) Solution phase catalysis :

Reac^n in which reactants & catalyst are in solution phase or liquid phase or miscible in nature

$R-\overset{O}{\overset{\|}{C}}-O-R'_{(l)} + H_2O(l) \xrightarrow[\text{cat.}]{H^+(aq)} R-COOH + R'OH$

- $C_{12}H_{22}O_{11(aq)} + H_2O(l) \xrightarrow[\text{cat}]{H_2SO_4(l)} \underset{(\text{glucose})}{C_6H_{12}O_6(aq)} + \underset{(\text{fructose})}{C_6H_{12}O_6(aq)}$

2. Heterogenous catalysis :

Reac^n in which catalyst & reactants have phase greater than or equal to 2.

Examples of heterogenous & homogenous catalysts

i) Solid - Solid catalysis

Reactant : Solid , Cat : Solid

$2KClO_3(s) \xrightarrow[\text{Cat}]{MnO_2(s)} 2KCl + 3O_2$

473 - 653 K

$[\ 2KClO_3(s) \xrightarrow{653-873K} 2KCl + 3O_2)$

ii) Solid - liq. catalysis

Reactant : liq , Cat : Solid (Immiscible)

$2H_2O_2(l) \xrightarrow[\text{Cat.}]{Pt(s)} 2H_2O + O_2$

iii) Liq - Liq Catalysis

Reactant : Liq Cat : Liq (Immiscible)

$2H_2O_2(l) \xrightarrow[\text{Cat}]{Hg(l)} 2H_2O + O_2$

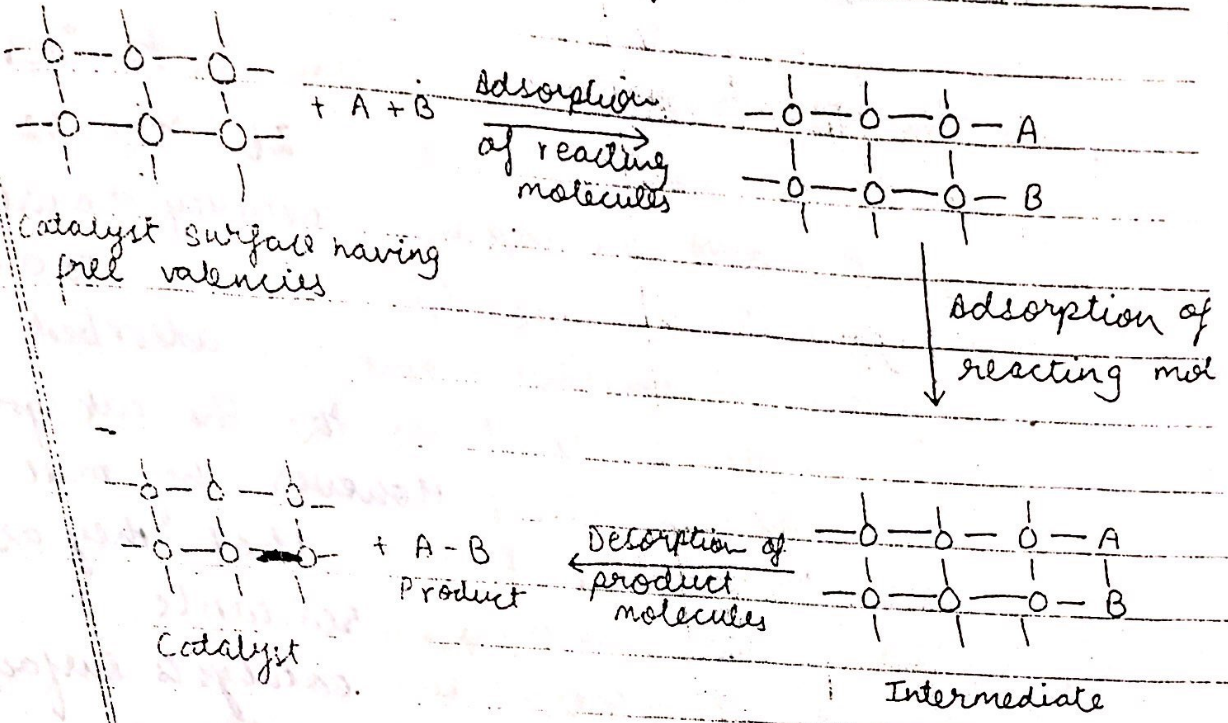
iv) Solid - gas catalysis

Reactant : Gas Cat : Solid

17

Page
Date

surface through formation of an intermediate.



iv) Desorption of reaction products from the catalys surface, & thereby, making the surface available again for more reac^n to occur.

v) Diffusion of reaction products away from the catalyst's surface. The surface of the catalyst unlike the inner part of the bulk, has free valencies whic provide the seat for chemical forces of attractio When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react with other resulting in the formation of new molecules. Thus, formed molecules may evaporate leaving the surface for the fresh reactant molecules.

Important features of solid catalysis :

1. Activity :

Activity of catalyst is its capacity to increase the speed of a chemical reac^n. It may be increased upto 10^{10} times. The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst to become active. However, they must get adsorbed so strongly that they are [illegible] immobilised and other reactants with no space on the catalyst surface for adsorption. ~~so strongly~~

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

In absence of platinum, H_2 & O_2 don't combine & can be stored as such for an indefinite period.

2. Selectivity :

The selectivity of a catalyst is its ability to direct a reac^n to yield a particular product. For ex, starting with H_2 & CO, and using diff. catalysts:

i) $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

ii) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$

iii) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

Thus action of catalysts is highly selective.

3. Shape - selective catalysis by Zeolites :

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolites are good shape-selective

ii) Induced fit model :
According to this model, the enzyme can change its shape when the substrate comes in contact with the active site so that there is a perfect fit rather than rigidly shaped lock & Key.

Kinetics of enzyme catalysis :
Enzyme catalysed reacⁿs take place in two steps as follows :

Step - I :
Formation of enzyme - substrate complex.

$$\underset{(Enzyme)}{E} + \underset{(substrate)}{S} \rightleftharpoons \underset{\text{Enzyme- Substrate complex}}{ES}$$

(fast & reversible)

Step - II :
Dissociation of enzyme - substrate complex to form the products.

$$ES \longrightarrow \underset{\text{Enzyme-product association}}{[EP]} \xrightarrow{\text{Slow step}} \underset{\substack{(Enzyme)\\(regenerated)}}{E} + \underset{Product}{P}$$

The rate of formation of product depends upon the conc. of E.P.

i) $C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$ (a
(Glucose) (Fructose)

ii) Conversion of glucose into ethyl alcohol :
The zymase enzyme converts glucose into ethyl alcohol & carbon dioxide.

$$\underset{Glucose}{C_6H_{12}O_6\,(aq)} \xrightarrow{Zymase} \underset{\text{Ethyl alcohol}}{2C_2H_5\text{-}OH\,(aq)} + 2CO_2\,(g)$$

iii) Conversion of starch into maltose :
The diastase enzyme converts starch into maltose

$2(C_6H_{10}O_5)_n\,(aq.) + nH_2O \xrightarrow{Diastase} nC_{12}H_{22}O_{11}\,(aq.)$

iv) Conversion of maltose into glucose:
The maltase enzyme converts maltose into glu

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6(aq)}$$

v) Decomposition of urea into ammonia and carbon dioxide:
The enzyme urease catalyses this decomposition.

$$NH_2CONH_2(aq) + H_2O(l) \xrightarrow{\text{Urease}} 2NH_3(g) + CO_2(g)$$

vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine the pancreatic trypsin converts proteins into amino acids by hydrolysis.

vii) Conversion of milk into curd.
It is an enzymatic reacⁿ brought about by lacto bacilli enzyme present in curd

Characteristics of enzyme catalysis:

1) Most highly efficient:
One molecule of an enzyme may transform one million molecules of the reactant per minute.

2) Highly specific nature:
Each enzyme is specific for a given reaction i.e one catalyst cannot catalyse more than one reacⁿ. For ex, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse hydrolysis of any other amide.

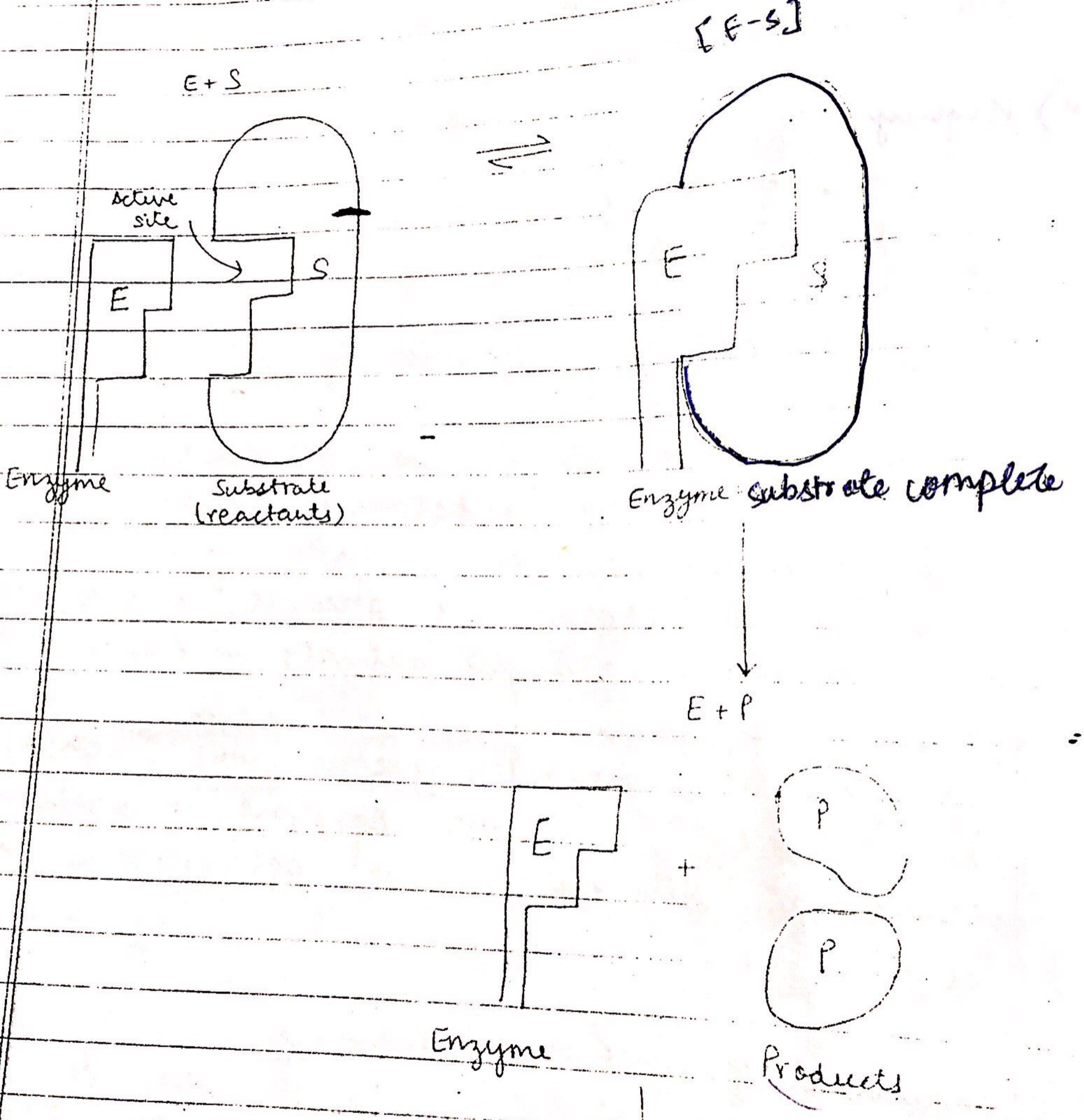
3) Highly active under optimum temperature:
The rate of an enzyme reaction becomes max. at a definite temperature, called the optimum temperature. ~~On either side~~ The optimum temperature range for enzymatic activity is 298 - 310 K. Human body temperature being 310 K is suited for enzymatic activity.

4) **Highly** active under optimum pH:
The rate of an enzyme-catalysed reaction is max. at a particular pH, which is b/w 5-7

5) Increasing activity in presence of activators & co-enzymes:
The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein is present along with an enzyme, the catalytic activity is enhanced considerably.
Activators are generally metal ions such as Na^+, Mn^{2+}, Co^{2+}, Cu^{2+}, etc. Amylase in presence of sodium chloride, Na^+, are catalytically very active.

6) Influence of inhibitors & poisons:
Like ordinary catalysts, enzymes are also inhibited or poisoned. The poisons interact with the active functional groups on the enzyme surface and often reduce or destroy the catalytic activity of the enzymes. Ex. Drugs are related to their action as enzyme inhibitors in

the body.


[E-S]
E + S
active site
E
S
Enzyme
Substrate (reactants)
E
S
Enzyme substrate complete
E + P
E
+
P
P
Enzyme
Products

23

Page
Date

[redacted] or inhibitors :

The phenomenon in which ~~pressure~~ presence of foreign substance retards the rate of $reac^n$.

Ex. 1) Acetanilide or glycine or H_3PO_4 act as -ve cat. for decomposition of H_2O_2.

2) Aldehyde & alcohol act as -ve cat. for oxidation of Na_2SO_3.

3) 1% alcohol acts ~~or~~ as -ve cat. for oxidation of $CHCl_3$

4) Lead tetra acetate or $Ni(CO)_4$ act as -ve cat for combustion of petrol.

5) Oxidation of benzaldehyde to benzoic acid is retarded by di-phenyl amine.

Negative catalyst function to remove active intermediate from the $reac^n$ or terminate the chain $reac^n$.

Catalytic poisoning or inhibitor for catalyst:

1. Phenomenon in which presence of a foreign substance in a small amount decreases the activity of catalyst.

2. Ex. i) CO acts as a poison for Fe in Haber process for NH_3.

ii) ~~Pt~~ CO acts as a poison for Pt(s) asbestos in contact process.

iii) $BaSO_4$ acts as a poison for Pd in a Rosenmund reac^n^.

iv) Catalytic poisoning although is specific in nature, but interesting fact about them is that, substances poisonous for human body also act as a poison for catalyst.

Temporary poisoning	Permanent poisoning
1. Poisoners are held at active centre by weak force.	1. Poisoners are held at active centres by free valencies.
2. Catalyst surface is generated by scratching the surface.	2. Catalyst surface is generated only by chemical treatment.
~~3. Poisoners are preferentit~~	

Poisoners are preferrentially adsorbed on surface of catalyst to make it inert.

Catalytic promotion:

The phenomen in which the presence of a foreign substance in small amounts increases the activity of a catalyst.

Ex. i) MO acts as a promoter in Haber's process of NH_3.

ii) Cr_2O_3 acts as a promoter for Fe_2O_3 in Bosch process ~~th~~ of H_2

iii) As_2O_3, ThO_2 acts as a promoter for Ni & CO cat. in synthesis of petrol

iv) Cr_2O_3 acts as a promoter for ZnO catalyst in preparation of CH_3OH.

v) Cu or Te act as a promoter for Ni catalyst in hydrogenation of vegetable oil.

vi) HCl or H_2O act as a promoter for $AlCl_3$ cat. in decomposition of paraffin.

Action of promoters is probably due to formation of loose compound b/w catalyst & promoters which help in increasing adsorption of reactants.

Auto catalysis :

The phenomenon in which either of the product formed during reac^n & acts as a cat. for the reac^n.

Ex. i) Decomposition of HNO_3 by Cu is auto-catalised by NO_2^- ion.

*
$$\left[\begin{array}{l} 3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO \text{ (Redox} \\ 2NO + H_2O + O \longrightarrow 2H^+ + \boxed{2NO_2^-} \text{ Auto-caty.} \end{array}\right.$$

ii) Hydrolysis of ester becomes fast after some time due to formation of H^+ ion or acetic acid.

iii) Colour of $KMnO_4$ disappears slowly on treating it with oxalic acid but becomes faster after some time due to formation of Mn^{+2} ion which acts as an auto-catalyst for the reac^n.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4$$
$$\downarrow$$
$$K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

S.No.	Property	True solutions	Colloidal Sol^{n}s	Suspension
1.	Nature	Homogeneous	~~Homogeneous~~ Heterogeneous	Heterogeneous
2.	Particle size (diameter)	Less than 10^{-9} m or 1 nm (1nm)	Between 10^{-9} m to 10^{-6} m	More than 10^{-6} m
3.	Filtrability	Pass through ordinary filter paper as well as animal membrane	Pass through ordinary filter paper but not through animal membrane.	Do not pass through filter paper and animal membrane
4.	Settling	Do not settle.	Do not settle	Settle on standing
5.	Visibility	Particles are invisible	Scattering of light by the particles is observed under ultra-microscope.	Particles are visible to naked eye or under a microscope
6.	Diffusion	Diffuse quickly	Diffuse slowly	Do not diffuse.
7.	Appearance	Clear & transparent	Translucent	Opaque

Classification of colloids:

Colloids are classified on the basis of the following criteria :

a) Physical state of dispersed phase and dispersion medium.

b) Nature of interaction between dispersed phase and dispersion medium.

c) Type of particles of the dispersed phase.

Page
Date

1. Classification based on physical state of dispersed phase & dispersion medium:

Depending upon whether the dispersed phase and the medium are solids, liquids or gases eight types of colloidal systems are possible. A gas mixed with another gas forms a homogenou mixture and hence is not a colloidal system. The examples of the various of colloids along with their typical names are listed in table:

	Dispersed phase	Dispersion medium	Type of colloid	Example
1.	Solid	Solid	Solid Sols	Alloys, ruby glass, gems, marbles, etc.
2.	Solid	Liquid	Sols	Gold sol, protein, starch, Agar, gelatin in water, etc
3.	Solid	Gas	Aero sols of solid	So Smoke, storm.
4.	Liq.	Solid	Gels	Cheese, gems, gellies, curd, etc
5	Liq.	Liq.	Emulsions	Butter, milk, blood, shampo
6.	Liq.	Gas	Aerosols of liq.	Fog, clouds, mist, etc.
7.	Gas	Solid	Solid foams	Pumice stone, styrene foam, porous pot, mattresses, etc
8.	Gas	Liq.	Foams	Froths, air bubble, whipped cream, etc.

S	Dispersion medium	Name of the sol
1.	Water	Aquasol or hydrosol
2.	Benzene	Benzosol
3.	Gases	Aerosol

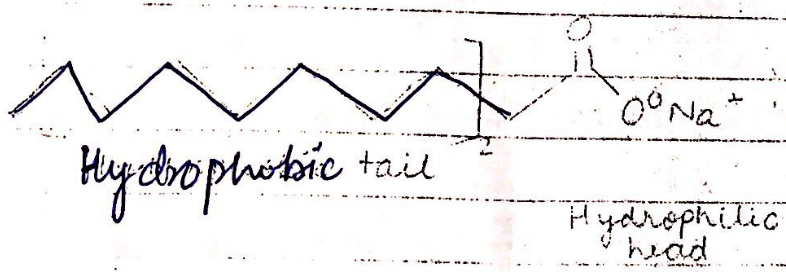
2. Based on the nature of interaction between dispersed phase & dispersion medium :

i) Lyophilic colloids : The word 'lyophilic' means solvent loving. Colloidal sols directly formed by substance like gum, gelatine, starch, rubber etc. on mixing with a suitable liquid (the dispersion medium) are called lyophilic sols. If the dispersion medium is separated from the dispersed phase (by evaporation), the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called reversible sols.

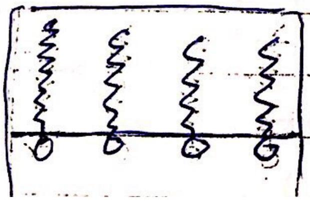
ii) Lyophobic colloids : The word 'lyophobic' means solvent hating substances. When substances are simply mixed with the dispersion medium they do not form the colloidal sol. Their ~~&~~ colloidal sols (can be prepared by any spe. method. Their sol) are ~~so~~ ~~ready~~ readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence are not stable. Further, once precipitated they do not give back the colloidal sol by addition of the dispersion medium. Hence these sols need stabilizing agents for their preservation.

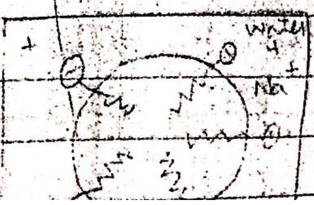
Mechanism of micelle formⁿ:

Let us take the example of soap solution. Soap is sodium salt of higher fatty acid and may be represented as RCOONa, ex. sodium stearate $CH_3(CH_2)_{16}COO^-Na$ or sodium palmitate, viz. $CH_3(CH_2)_{14}COO^-Na^+$. When dissolved in water, $RCOO^-$ separates from Na^+. The $RCOO^-$ ions ~~has~~ have two part non-polar long hydrocarbon chain R, called the tail, which is hydrophobic (water repelling) and the polar group COO^-, called the head, which is hydrophilic, i.e water loving. The $RCOO^-$ groups in water & the hydrocarbons chain R staying away from it & remain at the surface. However, at higher conc. these ions do not remain ~~at~~ on the surface but are pulled into the bulk of the solⁿ. As a result, at higher conc. the $RCOO^-$ ions form an aggregate of spherical shape with their hydrocarbon chains. An aggregate thus formed is known as 'ionic micelle'. Each of these may contain upto 100 ions.



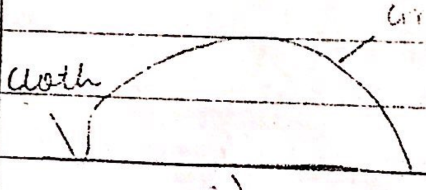
Cleansing action of soaps - an application of ionic micelles formation:



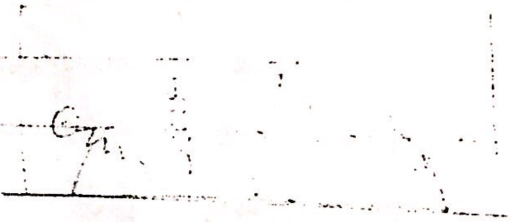


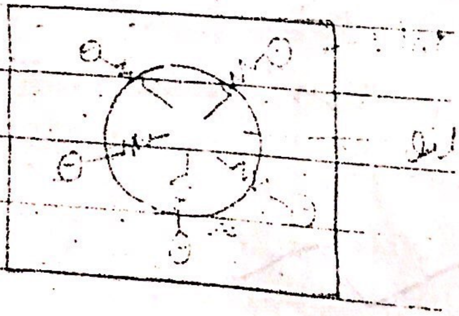
The cleansing action of soaps - an application of ionic micelles formation :

Suppose some grease or oil is sticking on the surface of a cloth. When it comes in contact with soap solⁿ, the stearate ions arrange themselves around it in such a way that hydrophobic parts of the stearate ions are in the oil (or grease) and the hydrophilic parts project outside outside the grease droplets. As hydrophilic part is polar these polar groups can ~~interect~~ interact with the water molecules present around the oil droplet. As a result, the oil droplet is pulled ~~away~~ away from the surface of the cloth.



a)





Preparation of colloidal sols:

A) Preparation of lyophobic sols

i) Condensation method:

In this method, particles of atomic or molecu sizes are induced to combine to form aggregates having colloidal dimensions. For this purpose chemical as well as physical ~~estu~~ methods can be applied.

a) Chemical method:

Colloidal solⁿs can be prepared by chemical reactions leading to formation of molecules b double decomposition, oxidation, reduction o hydrolysis.

$$As_2O_3 + 3H_2S \xrightarrow{\text{double decomp.}} As_2S_3\,(sol) + 3H_2$$

$$SO_2 + 2H_2S \xrightarrow{\text{oxidation}} 3S\,(sol) + 2H_2O$$

$$2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{reduction}} 2Au\,(sol) + 3HCO + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{hydrolysis}} Fe(OH)_3\,(sol) + 3HCl$$

$$2AuCl_3 + 3SnCl_2 \xrightarrow{\text{red.}} 2Au + 3SnCl_4$$

$$4AuCl_3 + 3N_2H_4 \xrightarrow{\text{red.}} 4Au + 3N_2 + 12HCl$$

b) Physical methods:

- Exchange of solvent: When a true solⁿ is mixed with an excess of the other solvent i which the solute is insoluble but solvent i miscible, a colloid is obtained. For example, when a solution of sulphur in alcohol is poured in excess of water, a colloidal sol of sulphur is obtained.

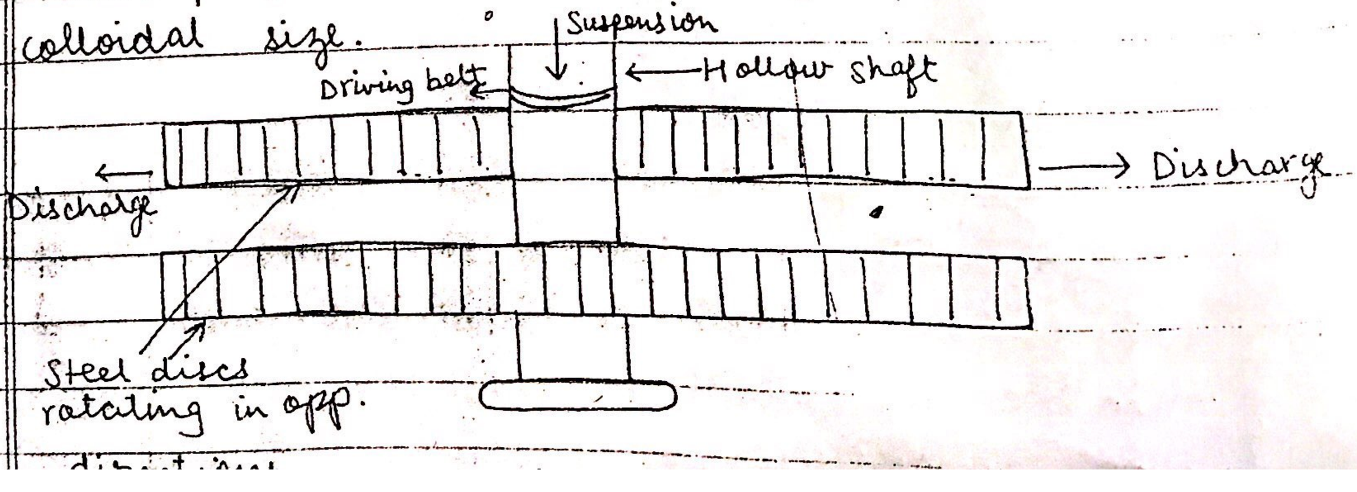
- Excessive cooling: The colloidal sol of ice in an organic solvent such as $CHCl_3$ or ether can be obtained by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution separately combine to form particles of colloidal size.

ii) Dispersion methods:

In these methods large particles of the substance are broken into particles of colloidal dimensions in the presence of dispersion medium. They are stabilized by adding some suitable stabilizer. Some of the methods employed for carrying out dispersion are given below.

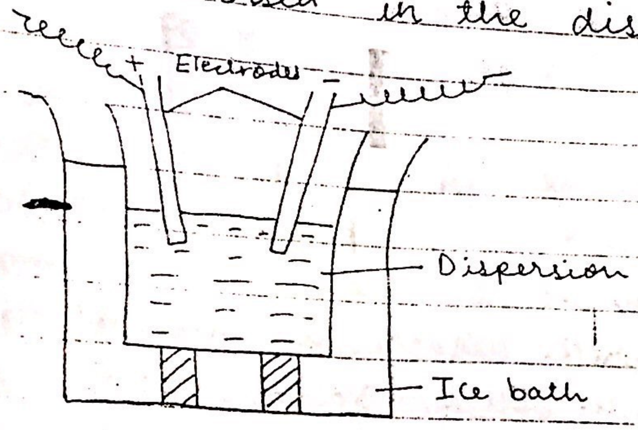
a) Mechanical dispersion:

The coarse suspension of the substance is brought into a colloidal state in the dispersion medium by grinding it in a colloid mill, ball mill or ultrasonic disintegrator. ~~the~~ The colloid mill consists of two metal discs close together rotating at high speed (7000 rev. per minute) in opp. directions. The suspension particles are formed to the colloidal size.



b) Electrical disintegration or Bredig's arc methods:

This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum etc. can be prepared by this method. In this method electric arc is struck between electrodes of the metal immersed in the dispersion medium.



The intense heat produced vaporises the metal, which then condenses to form particles of colloidal size.

c) Peptization :

Peptization is a process of converting a fresh precipitat into colloidal particles by shaking it with the dispersion medium in the presence of a small amount of a suitable electrolyte. The electrolyte added is called peptizing agent.

Ex. i) A reddish brown coloured colloidal solution is obtained by adding small quantity of ferric chloride solution to the freshly precipitated ferric hydroxide.

ii) A ppt. of silver iodide can be peptized by shaking with a dil. sol^n of $AgNO_3$ or KI.

Cause of peptization :

As the electrolyte is added to a freshly precipitated substance, the particles of the ppt. preferentially adsorb one particular type of ions of the electrolyte (ions common with the ppt.) As a result, they get dispersed due to electrostatic repulsions. This gives particles of colloidal size.

B) Preparation of lyophilic sols :

Lyophilic sols are quite stable and can be easily prepared by shaking the lyophilic material with dispersion medium. Some examples are colloidal sols of gelatin, gum, starch, egg.

Purification of colloidal solutions :

The process of reducing the impurities of the electrolytes to the minimum required level is known as purification of the colloidal solution. The following methods are used for purification :

1) Dialysis :

The process of separating the particles of colloids from those of crystalloids by diffusion of the mixture through a parchment or an animal membrane is known as dialysis.

Particles of true solⁿ can pass through parchment paper or cellophane membrane, sol particles can not pass through these membranes. A bag made up of such membrane is filled with the colloidal solution and is then suspended in fresh water. The electrolyte particles pass out leaving behind the colloidal sol.

Movement of ions across the membrane

expedited by applying electric potential through two electrodes. This method is faster than simple dialysis & is known as electrodialysis.

2) Ultra - filtration :

In this method carrying out colloidal sols are purified by filtration through special type of graded filters called ultra-filter. These filter pape allow only the electrolytes to pass through. These filter papers are made of particular pore size by ~~impegr~~ impregnating ordinary filter paper with colloidal particles. In order to accelerate the filtration through such filter papers, increased pressure ~~or~~ on section is employ

3) Ultra - centrifugation :

In this method, the colloids sol is taken in a tub which is placed in an ultra-centrifuge. On rotation of the tube at high speeds, the colloidal particles settle down at the bottom of the tube and the impurities remain in the solution called the centrifugate. The settled colloidal particles are mixed with an appropria dispersing medium to regenerate the sol.

Properties of colloidal solutions :

1. Physical properties :

a) Heterogenous character :

Colloidal sols form heterogenous mixture consisting of particles of dispersed phase and the dispersion medium. The phenomena of Tyndall effect, electrophores & electroosmosis confirm heterogeneity.

b) Stability :
Colloids are quite stable.

c) Filtrability :
Ordinary filter paper cannot be used for removing the dispersed phase because size of pores of filter paper is bigger than the colloidal particles. Animal membrane or parchment paper does not allow the colloidal particles to pass through it.

d) Visibility & colour :
The particles in colloidal solution are not visible to naked eye or under ordinary microscope. However, they scatter light falling on them. The colour of the colloid depends upon the wavelength of the light scattered by the colloidal particles which in true depends upon the size & nature of the particles.

2. Colligative properties - Osmotic pressure :
There are four colligative properties = osmotic pressure, elevation in b.p, depression in f.p & rel. lowering of vapour pressure. Colloidal particles have very high avg. molecular masses, and hence the number of moles present in solution will be extremely small. Some colloids have measurable osmotic pressures which have been determined with a reasonable degree of accuracy.

3. Mechanical properties - Brownian movement :
When viewed under an ultramicroscope colloidal particles are seen continuously moving in a zig-zag way.

Brownian movement does not depend upon the nature of the colloid but depends upon the siz of the colloidal particles & viscosity of the sol. Smaller the size & lesser the viscosity, faster is the movement of the particles.

The reason for Brownian movement is based on the fact that the molecules of dispersion med due to their kinetic motion strike against the colloidal particles (dispersed phase) from all sides with diff. forces. The resultant force cau them to move. However, colloidal particles bein comparatively heavier, move with a slower spee

Imp. of Brownian movement:

- Brownian movement opposes the force of gravity & does not allow the colloidal particles to settle down.
- It has also helped in the determination of N_A.

4. Optical properties - Tyndall effect:

If a strong converging beam of light is passed through a colloidal sol" placed in a dark room the path of light gets illuminated with a bluish light when viewed at right angles to the directio of the passage of light. The path becomes visible d to scattering of light by the colloidal particles.

It may be noted that Tyndall effect is observed only when the following two conditions are satisfied:

- The diameter of the dispersed particles is not much smaller as compared to the wavelengths.

of the light.

- There is a large difference in the refractive indices of the dispersed phase and the dispersion medium.

5. Electrical properties:

a) Stability of colloidal sols - Electrical charge on colloidal particles.

The stability of a colloid is due to the fact that the colloidal particles are charged. The particle therefore repel each other and do not coalesce. All the dispersed particles in a colloidal solⁿ carry the same charge while the dispersion med. has an equal & opposite charge.

	Negatively charged	Positively charged
1.	Metallic particles (ex. Cu, Ag, Au sols).	1. Metallic hydroxides like $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, $Ca(OH)_2$.
2.	Metal sulphides like As_2S_3, CdS, etc.	2. Hydrated metal oxides, ex. $Al_2O_3.xH_2O$, $Fe_2O_3.xH_2O$, $Cr_2O_3.xH_2O$, etc.
3.	Starch, gum, gelatin, clay, charcoal, silicic acid sols.	3. Oxides like TiO_2, etc.
4.	Acidic dyes like congo red, eosin sols	4. Haemoglobin
5.	—	5. Basic dyes like methylene blue, prussian blue, etc.

Origin of electrical charge on colloidal properties:

1) Frictional electrification

2) Electron capture by particles from air & during electro-disperlion in Bredig's arc method.

3) Preferential adsorption of ions from solutions.

An ionic colloid adsorbs ions common to its own lattice during the prep. of the colloid. For ex. if colloid sol of AgI is prepared by adding KI sol^n to $AgNO_3$ sol^n till KI is in slight excess, iodide ions (I^-) will be adsorbed on the surface of AgI particles, thereby giving them a -ve charge

$$AgI + \underset{\text{(from KI)}}{I^-} \longrightarrow \underset{\text{Negative sol.}}{AgI \vdots I^-}$$

On the other hand, if the colloid sol of AgI is prepared by $AgNO_3$ & KI with $AgNO_3$ in excess Ag^+ ions will be adsorbed

$$AgI + \underset{\text{(from } AgNO_3\text{)}}{Ag^+} \longrightarrow \underset{\text{+ve sol}}{AgI | Ag^+}$$

When one types of ions of the electrolyte are adsorbed on the colloidal particles, it forms a 'fixed layer'. It attracts the counter ions from the med. forming a second layer which is mobile & is called 'diffused layer'.

$\boxed{\begin{matrix} AgI \\ AgI \end{matrix}}$ $I^- | K^+$
$I^- | K^+$
Fixedlayer

or

$\boxed{\begin{matrix} AgI \\ AgI \end{matrix}}$ $Ag^+ | NO_3^-$
$Ag^+ | NO_3^-$
mobile layer.

The potential diff. b/w the two layers is known as electrokinetic or zeta potential.

The combination of the two layers of opp. charges around the colloidal particle is called Helmholtz electrical double layer.

b) Electrophoresis or cataphoresis:

The movement of colloidal particles under the influence of an electric field is called ~~as~~ electrophoresis.

c) Electro-osmosis:

It may be defined as a phenomenon in which the molecules of the dispersion medium are allowed to move under the influence of an electric field whereas colloidal particles are not allowed to move due to the presence of spm (semi-permeable memberane).

d) Coagulation or Flocculation or precipitation:

It is a process of aggregating together the colloidal particles so as to change them into large sized particles which ultimately settle as a ppt.

It is brought about by the add^n of electrolytes. When an electrolyte is added to a colloid, the particles of the sol take up the ions which are oppositely charged & thus get neutralized. The neutral species then start accumulating to form particles of larger size which settle down.

When a small amount of the electrolyte is added, i.e, when the conc. of the electrolyte added is low, the process is called flocculation. It can be reversed on shaking. However at higher conc., coagulation takes place and the process cannot be reversed simply by shaking.

- The min. amount of an electrolyte (millimoles) that must be added to one litre of a colloid solution so as to bring about complete coagulation is called the coagulation or flocculation or precipitation value of the electrolyte. Thus, smaller is the coagulation value of an electrolyte, greater is its coagulation or precipitating power.

It has been observed that generally, the greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as Hardy-Schulze rule. In the coagulation of a negative sol the flocculating power is in the order:

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

& for a +ve sol

$Fe(CN)_6^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$

Coagulation can also be caused by:

- Electrophoresis: In electrophoresis, the particles of dispersed phase move towards oppositely charged electrodes & get neutralized. These neutral particles unite, grow in size & settle down.
- By mutual precipitation: In it oppositely charged sols neutralise each other causing the coagulation of both the sols.
- By prolonged dialysis: The stability of a colloidal sol is due to a small amount of electrolyte. On prolong dialysis, electrolyte is removed. As a result, the sol

becomes unstable and gets coagulated.

- By heating or cooling : when a sol is boiled the adsorbed layer is disturbed because the number of collisions on them by the molecules of the dispersion med. increases. Consequently the charge on particle decrease.
  Ex. Heating of butter ; cooling milk (fats start floating on the surface).

Gold number :

Gold number of a protective colloid is the min. mass of it in mg which must be added to 10 mL of a standard red gold sol (containing 0.0053 to 0.0058 per cent gold) so that no coagulation of the gold sol (i.e. the change of colour from red to blue) takes place when 1 mL of 10% sodium chloride solution is rapidly added to it.

Out of albumin, gelatin, starch, gelatin has the min. gold number and hence has the highest protective power.

* loosing water slowly is known as synerisis.