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NEET/JEE 2019

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UNIT - 2 : Electrochemisty | Chemical Kinetics | Surface Chemistry

ELECTROCHEMISTRY

ELECTROCHEMICAL CELL

(Converts chemical energy into electrical energy in a redox reaction or vice-versa)

	Galvanic cell	Electrolytic cell
Anode	Oxidation, negative (–) terminal	Oxidation, positive (+) terminal
Cathode	Reduction, positive (+) terminal	Reduction, negative (–) terminal

Electrode Potential

- It is defined as the tendency of an electrode to gain or lose electrons when it is in contact with the solution of its own ions.

Nernst Equation

$$M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$$
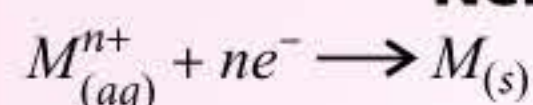
$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[M_{(s)}]}{[M^{n+}_{(aq)}]}$$

For pure solid or liquid or gas at 1 atm pressure, the molar concentration is taken as unity; $[M] = 1$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}_{(aq)}]}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}_{(aq)}]}$$

- The electrode potential difference between the two half-cells is known as electromotive force (EMF) of the cell or cell potential or cell voltage.

- EMF can be calculated from the values of electrode potentials of the two half-cells constituting the cell using following methods :
  - $E^{\circ}_{cell} = E^{\circ}_{ox}$ (anode) $+ E^{\circ}_{red}$ (cathode)
  - When only reduction potential is taken into account,
    $E^{\circ}_{cell} = E^{\circ}_{red}$ (cathode) $- E^{\circ}_{red}$ (anode) $= E^{\circ}_{right} - E^{\circ}_{left}$
  - When only oxidation potential is taken into account,
    $E^{\circ}_{cell} = E^{\circ}_{ox}$ (anode) $- E^{\circ}_{ox}$ (cathode)

Applications

- To calculate electrode potential of a cell :

$$aA + bB \xrightarrow{ne^-} xX + yY$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

- To calculate equilibrium constant :
  At equilibrium, $E_{cell} = 0$

$$E^{\circ}_{cell} = \frac{0.0591}{n} \log K_c \quad \text{at 298 K}$$

- Relation between electrochemical cell and Gibbs energy

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}; \Delta G^{\circ} = -2.303 \, RT \log K_c$$

CONDUCTANCE

The reciprocal of the electric resistance is called the conductance. It is usually represented by G. Thus, $G = 1/R$.

Property	Specific conductance	Equivalent conductance	Molar conductance
Definition	Reciprocal of specific resistance or conductance of solution of 1 cm length and 1 cm² area of cross-section.	Conductance produced by all the ions of 1 g equivalent electrolyte in a given solution.	Conduction produced by all the ions of 1 mol electrolyte in a given solution.
Representation	κ (kappa)	Λ_{eq} (lambda)	Λ_m (lambda)
Formula	$\kappa = \dfrac{1}{\rho} = \dfrac{l}{Ra} = G\dfrac{l}{a}$	$\Lambda_{eq} = \kappa \times V = \kappa \times \dfrac{1000}{\text{Normality}}$	$\Lambda_m = \kappa \times V = \kappa \times \dfrac{1000}{\text{Molarity}}$
Units	ohm^{-1} cm^{-1}	ohm^{-1} cm^2 eq^{-1}	ohm^{-1} cm^2 mol^{-1}
SI units	S m^{-1}	S m^2 eq^{-1}	S m^2 mol^{-1}

Variation of G, κ, Λ_m and Λ_{eq} with dilution :

- On dilution, as no. of ions increases, conductance (G) increases.
- On dilution as no. of ions per cm^3 decreases, specific conductance (κ) decreases.
- On dilution, though specific conductance decreases but volume (V) increases much more hence, equivalent conductance (Λ_{eq}) or molar conductance (Λ_m) increases.
- When concentration approaches zero i.e., at infinite dilution, the molar conductivity is known as limiting molar conductivity (Λ_m°).

Variation of molar conductance with concentration (C) :

- **For strong electrolytes,** Λ_m increases slowly with dilution and can be represented by the equation :
$\Lambda_m = \Lambda_m^\circ - AC^{1/2}$ (Debye—Huckel Onsager equation)
Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ_m° and slope equal to '$-A$'.
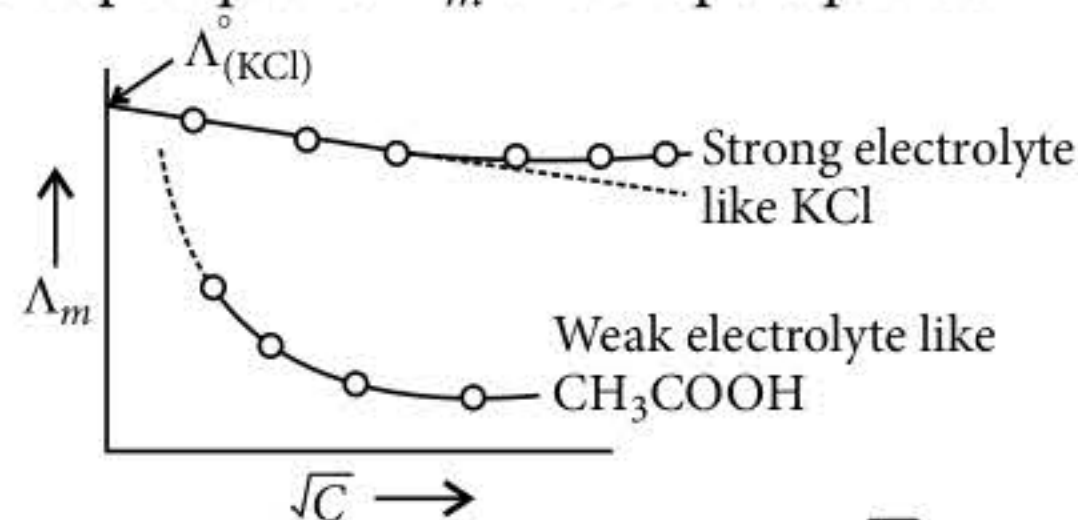
Thus, Λ_m^c decreases linearly with $\sqrt{C}$, when $C = 0$, $\Lambda_m^c = \Lambda_m^\circ$ and Λ_m° can be determined experimentally.

- **For weak electrolytes,** Λ_m^c increases as C decreases but does not reach a constant value even at infinite dilution. Hence, there Λ_m° cannot be determined experimentally.

KOHLRAUSCH'S LAW

The limiting molar conductivity of an electrolyte is the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte.
$$\Lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ$$

λ_+° and λ_-° are called ionic conductivities of cation and anion at infinite dilution respectively.
$$A_xB_y \longrightarrow xA^{y+} + yB^{x-}\ ;\ \Lambda_m^\circ = x\lambda_{A^{y+}}^\circ + y\lambda_{B^{x-}}^\circ$$
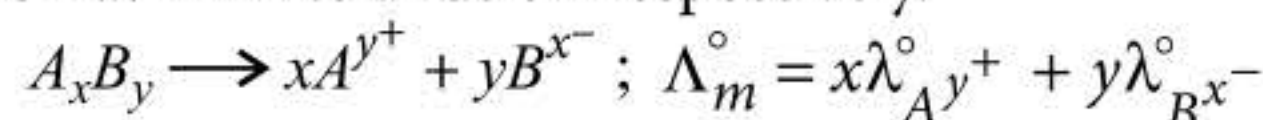
Applications

- Calculation of molar conductivity of weak electrolytes at infinite dilution :
$\Lambda_{m\,(CH_3COOH)}^\circ = \lambda_{CH_3COO^-}^\circ + \lambda_{H^+}^\circ$
- The above equation can be obtained as $\Lambda_{m\,(CH_3COOH)}^\circ$
$= \Lambda_{m\,(CH_3COONa)}^\circ + \Lambda_{m\,(HCl)}^\circ - \Lambda_{m\,(NaCl)}^\circ$
$= \lambda_{CH_3COO^-}^\circ + \lambda_{Na^+}^\circ + \lambda_{H^+}^\circ + \lambda_{Cl^-}^\circ - \lambda_{Na^+}^\circ - \lambda_{Cl^-}^\circ$
- Calculation of degree of dissociation :

Degree of dissociation $(\alpha) = \dfrac{\Lambda_m^c}{\Lambda_m^\circ}$
- Calculation of dissociation constant of a weak electrolyte :

Dissociation constant $(K_c) = \dfrac{C\alpha^2}{1-\alpha}$
- Calculation of solubility of a sparingly soluble salt solutions are considered saturated at infinite dilution so, $\Lambda_m = \Lambda_m^\circ$ and molarity = solubility.

Thus, $\Lambda_m^\circ = \dfrac{\kappa \times 1000}{\text{molarity}}$

or   Solubility (mol^{-1}) $= \dfrac{\kappa \times 1000}{\Lambda_m^\circ}$

ELECTROLYSIS

It is the process of decomposition of an electrolyte by passing electricity through its aqueous solution or molten state.

- **Faraday's first law of electrolysis :** The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte.
$w \propto Q$ or $w = ZQ = Z \times I \times t$
where, Z is electrochemical equivalent of the substance deposited.
$$Z = \frac{\text{Eq. wt. of substance}}{96500}.$$

- **Faraday's second law of electrolysis :** The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.
$$\frac{w_1}{w_2} = \frac{E_1}{E_2} \text{ where } E \text{ is the equivalent weight.}$$

SOME COMMERCIAL CELLS

- **Primary cells :** Cells once exhausted cannot be used again e.g., dry cell and mercury cell.

- **Secondary cells :** Rechargeable cells which can be used again and again e.g., nickel-cadmium storage cell and lead storage battery.

- **Fuel cells :** Cells which can convert the energy of combustion of fuels such as H_2, CO, CH_4 etc., into electrical energy e.g., $H_2 - O_2$ fuel cell.

CHEMICAL KINETICS

RATE OF CHEMICAL REACTION

- The rate of reaction is the change in the concentration of any one of the reactants or products per unit time.
$$\text{Rate} = \frac{\text{Decrease in conc. of reactant}}{\text{Time taken}}$$
$$= \frac{\text{Increase in conc. of product}}{\text{Time taken}}$$
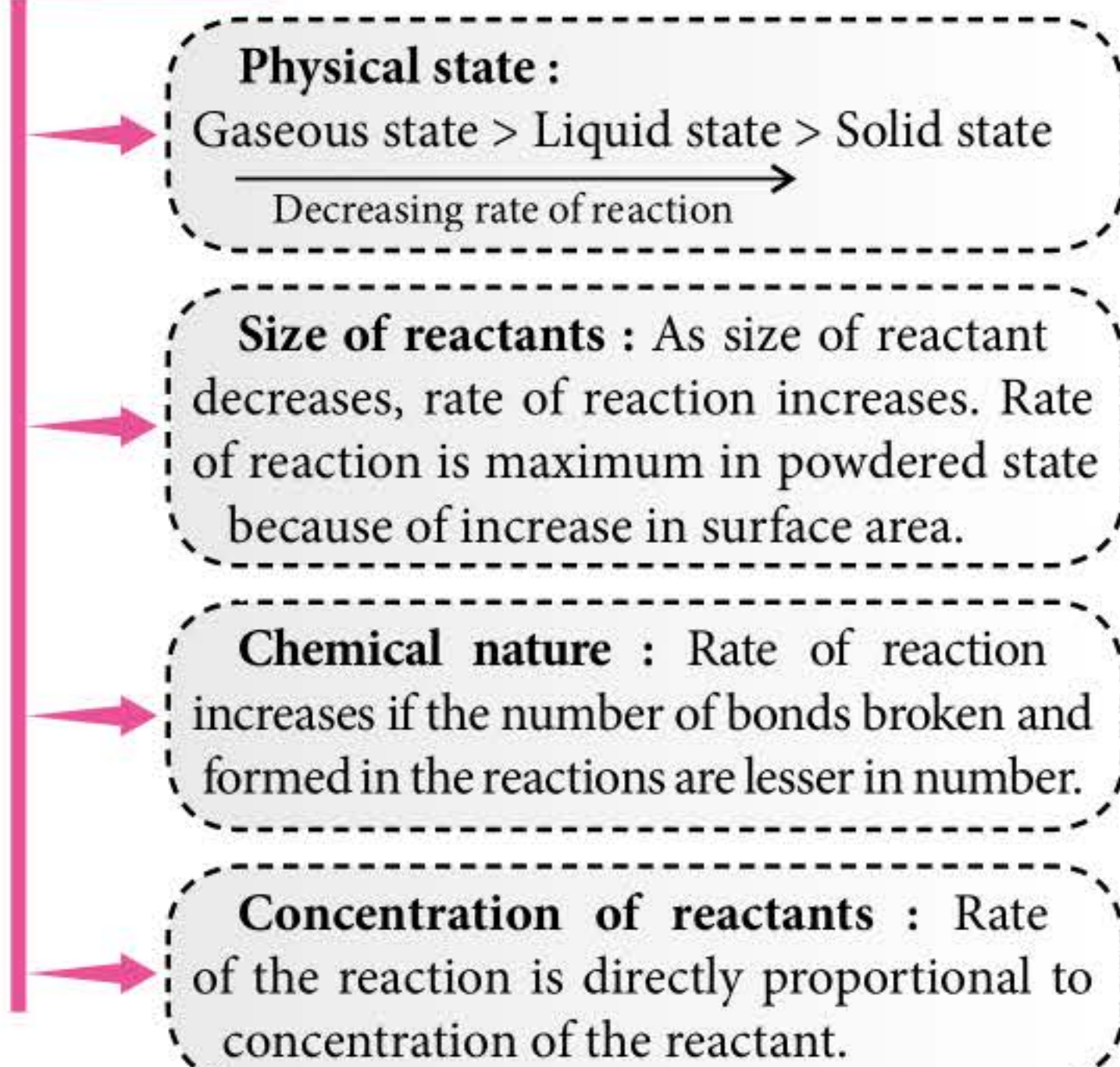$A + B \longrightarrow C + D$

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$$
Negative sign shows decrease in concentration with time and positive sign shows increase in concentration with time.

- **Units :**
$$\text{Rate} = \frac{\text{Concentration}}{\text{Time}} = \frac{\text{mol/litre}}{\text{sec}}$$
$$= \text{mol litre}^{-1}\text{sec}^{-1}$$

Nature

> **Physical state :**
> Gaseous state > Liquid state > Solid state
> $\xrightarrow{\text{Decreasing rate of reaction}}$

> **Size of reactants :** As size of reactant decreases, rate of reaction increases. Rate of reaction is maximum in powdered state because of increase in surface area.

> **Chemical nature :** Rate of reaction increases if the number of bonds broken and formed in the reactions are lesser in number.

> **Concentration of reactants :** Rate of the reaction is directly proportional to concentration of the reactant.

Factors Affecting Rate of Reaction

Exposure to radiation : The rate of chemical reaction is considerably increased by the use of radiations of certain frequency.

Catalyst : A positive catalyst increases the reaction rate by changing the path of reaction and lowering the activation energy.

Surface area : Larger the surface area of the reactants, faster is the rate of reaction.

Temperature : Rate of reaction increases considerably with an increase in temperature.

RATE LAW AND RATE CONSTANT (LAW OF MASS ACTION)

- The rate of reaction is proportional to the product of effective concentrations of the reacting species, each raised to a power which is equal to the corresponding stoichiometric number of the molecules appearing in the chemical reaction.

$$aA + bB \longrightarrow cC + dD$$
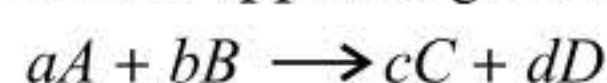
$$r \propto [A]^a [B]^b \quad \text{or} \quad r = k[A]^a [B]^b$$

k is the constant of proportionality.

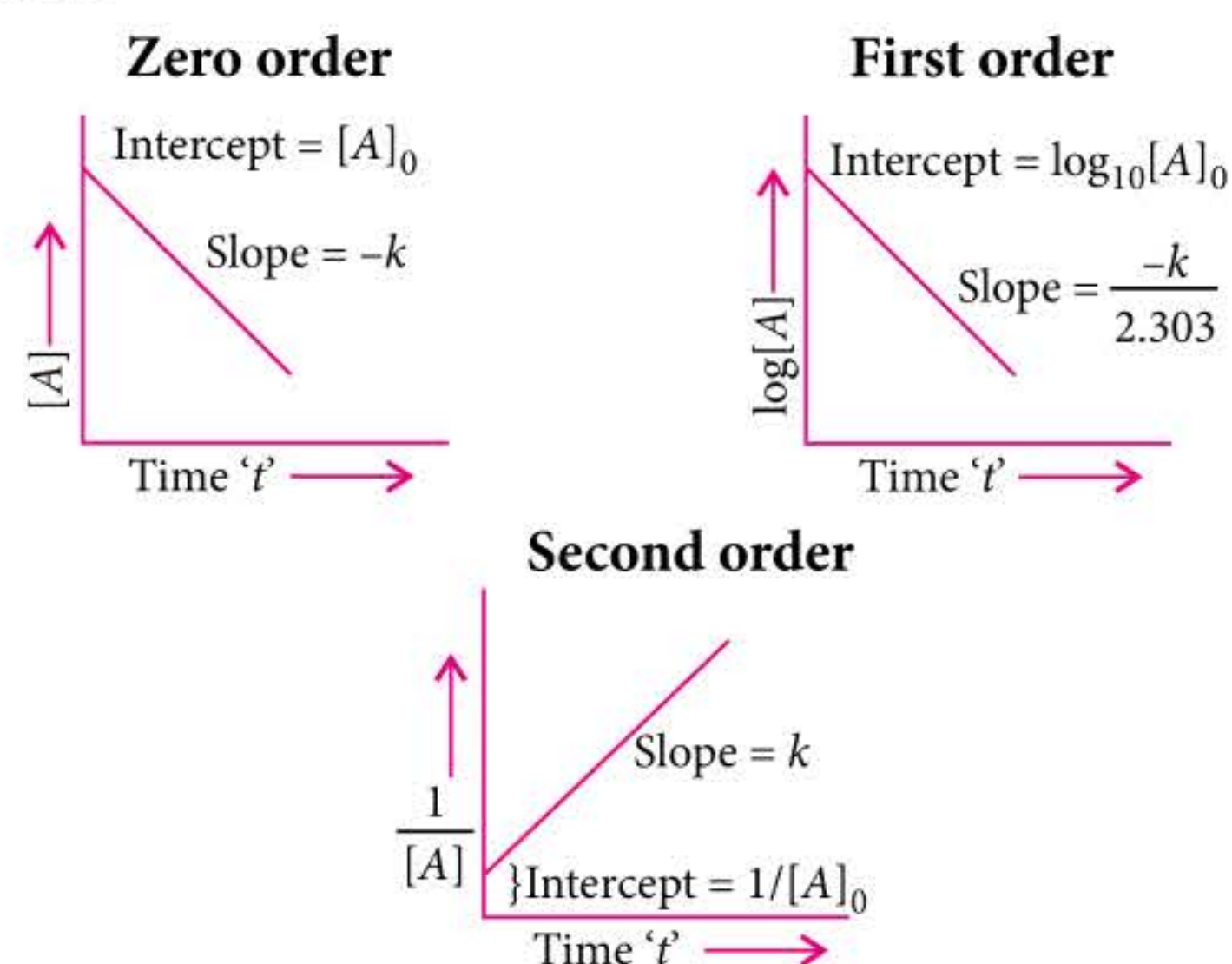Rate of reaction at unit concentration of reactants is called rate constant.

ORDER AND MOLECULARITY OF THE REACTION

- The sum of powers of the concentration of the reactants in the rate law expression is called the order of reaction.
  For the rate law equation, Rate $= k[A]^x [B]^y$
  $x + y$ gives the overall order of a reaction.
  Order of a reaction can be 0, 1, 2, 3 and even a fraction.
- The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

FOR REACTIONS OF DIFFERENT ORDERS

Order	Rate law	Integrated rate law	Half-life	Unit of rate constant	Graph
0	Rate $= k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	mol L^{-1} s^{-1}	$[A]$ vs t; slope $= -k$
1	Rate $= k[A]^1$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 0.693/k$	s^{-1}	$\ln[A]$ vs t; slope $= -k$
2	Rate $= k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k[A]_0$	L mol^{-1} s^{-1}	$1/[A]$ vs t; slope $= k$
n	Rate $= k[A]^n$	$(n-1)kt = \dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A_0]^{n-1}}$	$t_{1/2} = \dfrac{2^{n-1}-1}{k(n-1)[A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n}$ s^{-1}	$\dfrac{1}{[A]^{n-1}}$ vs t; slope $= k$

Some typical linear plots for reactions of different orders :

Zero order

Intercept $= [A]_0$
Slope $= -k$
[A]
Time 't' →

First order
Intercept $= \log_{10}[A]_0$
Slope $= \dfrac{-k}{2.303}$
log[A]
Time 't' →

Second order
Slope $= k$
$\dfrac{1}{[A]}$
} Intercept $= 1/[A]_0$
Time 't' →

TEMPERATURE DEPENDENCE OF THE RATE OF A REACTION :

For a chemical reaction with rise in temperature by 10 °C, the rate constant is nearly doubled.

Arrhenius equation

$k = Ae^{-E_a/RT}$ where A is pre-exponential factor (Arrhenius factor or frequency factor), E_a is activation energy and $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy equal to or greater than E_a.

$$\ln k = -\frac{E_a}{RT} + \ln A \quad \text{or} \quad \log k = -\frac{E_a}{2.303RT} + \log A$$

The plot of log k vs $1/T$ gives a straight line with slope $= -\dfrac{E_a}{2.303\,R}$ and intercept $= \log A$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where, k_1 and k_2 are the values of rate constant at temperatures T_1 and T_2 respectively.

COLLISION THEORY

- Reactions occur when molecules collide with appropriate orientation and sufficient energy, not

all molecular collisions result successfully in the formation of product.

- **For any successful collision :**
  - ➤ Particles must collide with sufficient energy $> E_a$.
  - ➤ They need to have correct alignment (collision geometry) to keep E_a as low as possible.

- ➤ To account for effective collision, another factor P, called orientation factor or steric factor or probability factor is introduced.
  $$k = PZ_{AB}\, e^{-E_a/RT}$$
  where, Z_{AB} represents the collision frequency of reactants A and B.

SURFACE CHEMISTRY

ADSORPTION

- The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid.
- Spontaneous, exothermic and leads to lowering of entropy.
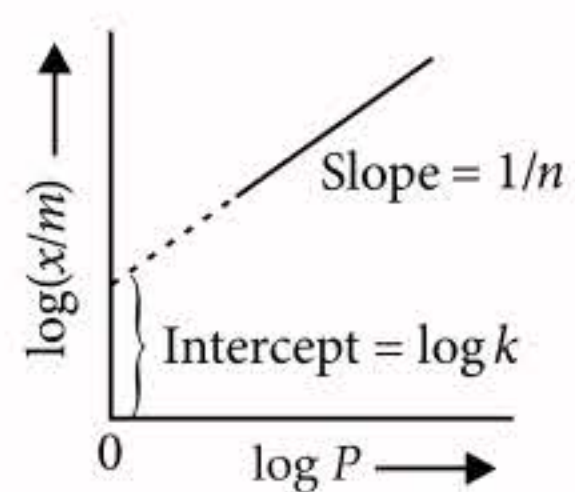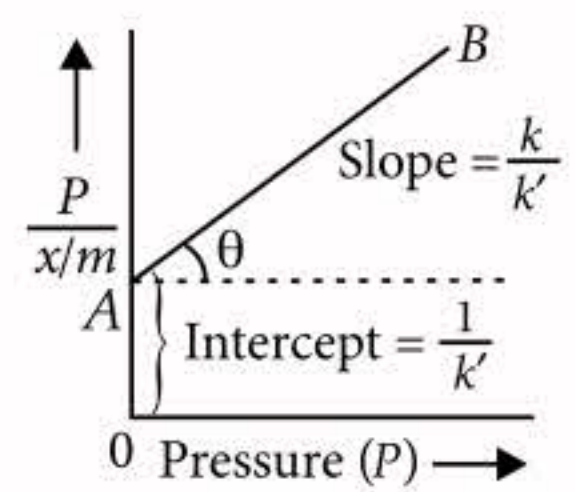
Types of Adsorption

Physisorption
- Molecules are held by weak van der Waals' forces.
- Low heat of adsorption and non specific.
- No compound is formed.
- Decreases with increase in temperature.
- Forms multimolecular layer and is reversible.

Chemisorption
- Molecules are held by strong chemical bonds.
- High heat of adsorption and specific.
- Surface compounds are formed.
- Increases with increase in temperature.
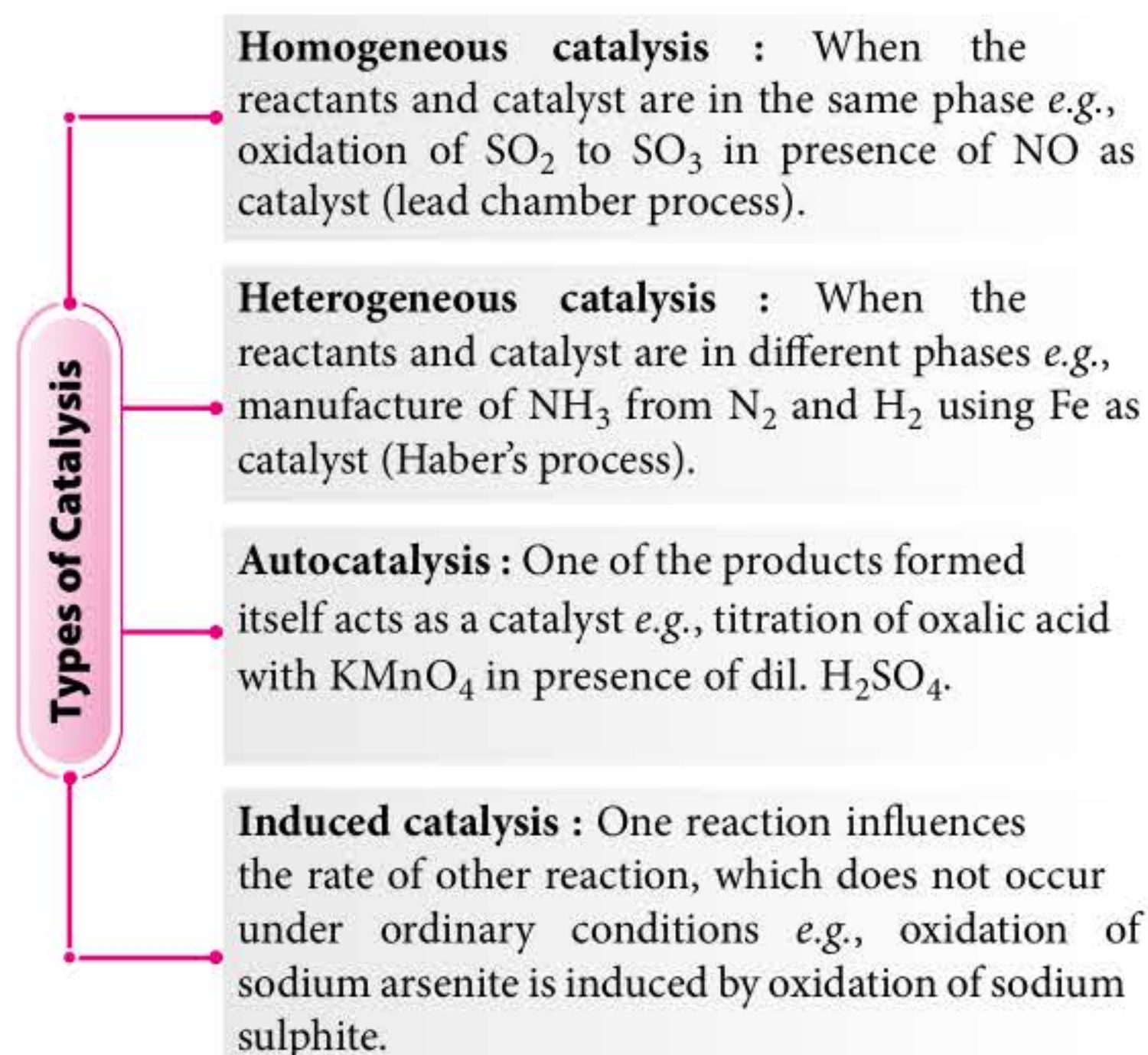- Forms unimolecular layer and is irreversible.

Adsorption Isotherms

Adsorption Isotherms

Freundlich adsorption isotherm	Langmuir adsorption isotherm
Relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.	On the basis of kinetic theory, Langmuir derived an expression for adsorption isotherm.

$\dfrac{x}{m} = k.P^{1/n}\,(n>1)$	$\dfrac{P}{(x/m)} = \dfrac{1}{k'} + \left(\dfrac{k}{k'}\right)P$
$\log \dfrac{x}{m} = \log k + \dfrac{1}{n}\log P$	$\dfrac{x}{m} = \dfrac{k'P}{1+kP}$
The factor $1/n$ can have values between 0 and 1.	When pressure is very high then $1 + kP \approx kP$ $\Rightarrow \dfrac{x}{m} = \dfrac{k'P}{kP} =$ constant
When $1/n = 0$, $x/m =$ constant which shows that adsorption is independent of pressure.	When pressure is very high then $1 + kP \approx 1$ $\Rightarrow x/m = k'P$
When $1/n = 1$, $x/m = kP$, the adsorption varies directly with pressure.	When pressure is moderate then $x/m = kP^{1/n}$, $1/n$ lies between 0 and 1.

CATALYSIS

- The phenomenon of enhancing the rate of a chemical reaction by using a catalyst.
- **Activity :** Capacity to increase the speed of the chemical reaction.
- **Selectivity :** Ability of a catalyst to direct the reaction to yield a particular product.

Types of Catalysis

Homogeneous catalysis : When the reactants and catalyst are in the same phase *e.g.*, oxidation of SO_2 to SO_3 in presence of NO as catalyst (lead chamber process).

Heterogeneous catalysis : When the reactants and catalyst are in different phases *e.g.*, manufacture of NH_3 from N_2 and H_2 using Fe as catalyst (Haber's process).

Autocatalysis : One of the products formed itself acts as a catalyst *e.g.*, titration of oxalic acid with $KMnO_4$ in presence of dil. H_2SO_4.

Induced catalysis : One reaction influences the rate of other reaction, which does not occur under ordinary conditions *e.g.*, oxidation of sodium arsenite is induced by oxidation of sodium sulphite.

Enzymes

- Bio-chemical catalysts.
- Highly efficient and specific in nature.
- Highly active under optimum temperature and pH.
- Activity increases in the presence of activators and co-enzymes.
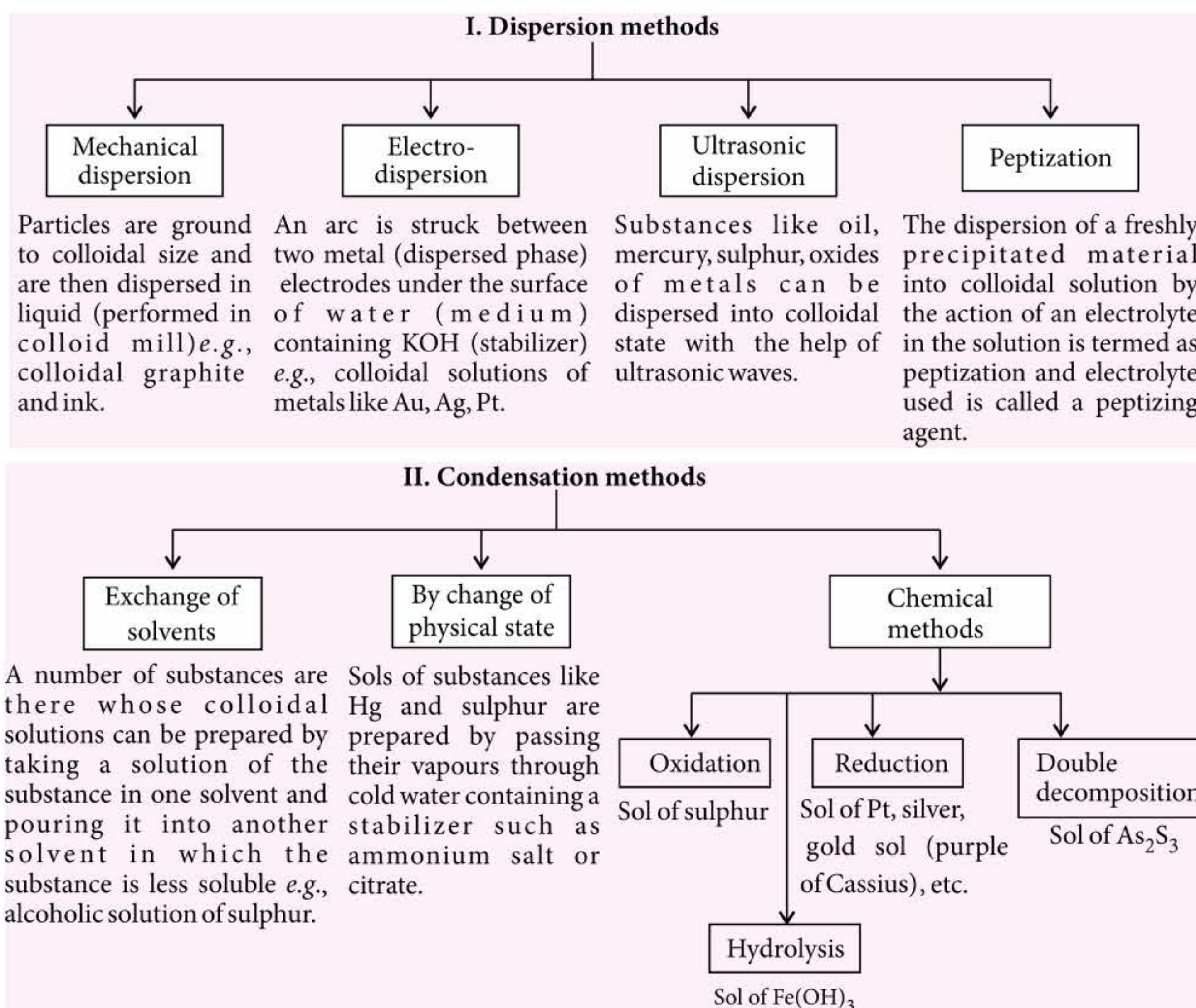- Activity inhibited by inhibitors and poisons.

COLLOIDS

Suspension, colloid and true solution :

| Suspension	Colloid	True solution
Size : $> 10^{-5}$ cm	10^{-7} to 10^{-5} cm	$< 10^{-7}$ cm
Visible with naked eyes	Visible with ultramicroscope	Not visible by any optical means
Does not diffuse	Diffuses very slowly	Diffuses rapidly
Settles under gravity	Only under centrifugation.	Does not settle
Heterogeneous	Heterogeneous	Homogeneous
Opaque	Generally clear	Clear

Preparation of Colloidal Solutions

I. Dispersion methods

Mechanical dispersion	Electro-dispersion	Ultrasonic dispersion	Peptization
Particles are ground to colloidal size and are then dispersed in liquid (performed in colloid mill)*e.g.*, colloidal graphite and ink.	An arc is struck between two metal (dispersed phase) electrodes under the surface of water (medium) containing KOH (stabilizer) *e.g.*, colloidal solutions of metals like Au, Ag, Pt.	Substances like oil, mercury, sulphur, oxides of metals can be dispersed into colloidal state with the help of ultrasonic waves.	The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in the solution is termed as peptization and electrolyte used is called a peptizing agent.

II. Condensation methods

Exchange of solvents	By change of physical state	Chemical methods
A number of substances are there whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is less soluble *e.g.*, alcoholic solution of sulphur.	Sols of substances like Hg and sulphur are prepared by passing their vapours through cold water containing a stabilizer such as ammonium salt or citrate.	

Chemical methods:

Oxidation — Sol of sulphur

Reduction — Sol of Pt, silver, gold sol (purple of Cassius), etc.

Double decomposition — Sol of As_2S_3

Hydrolysis — Sol of $Fe(OH)_3$

Purification of Colloidal Solutions

- **Dialysis :** It is the process of separating the particles of colloidal dimensions by means of diffusion through a suitable membrane.
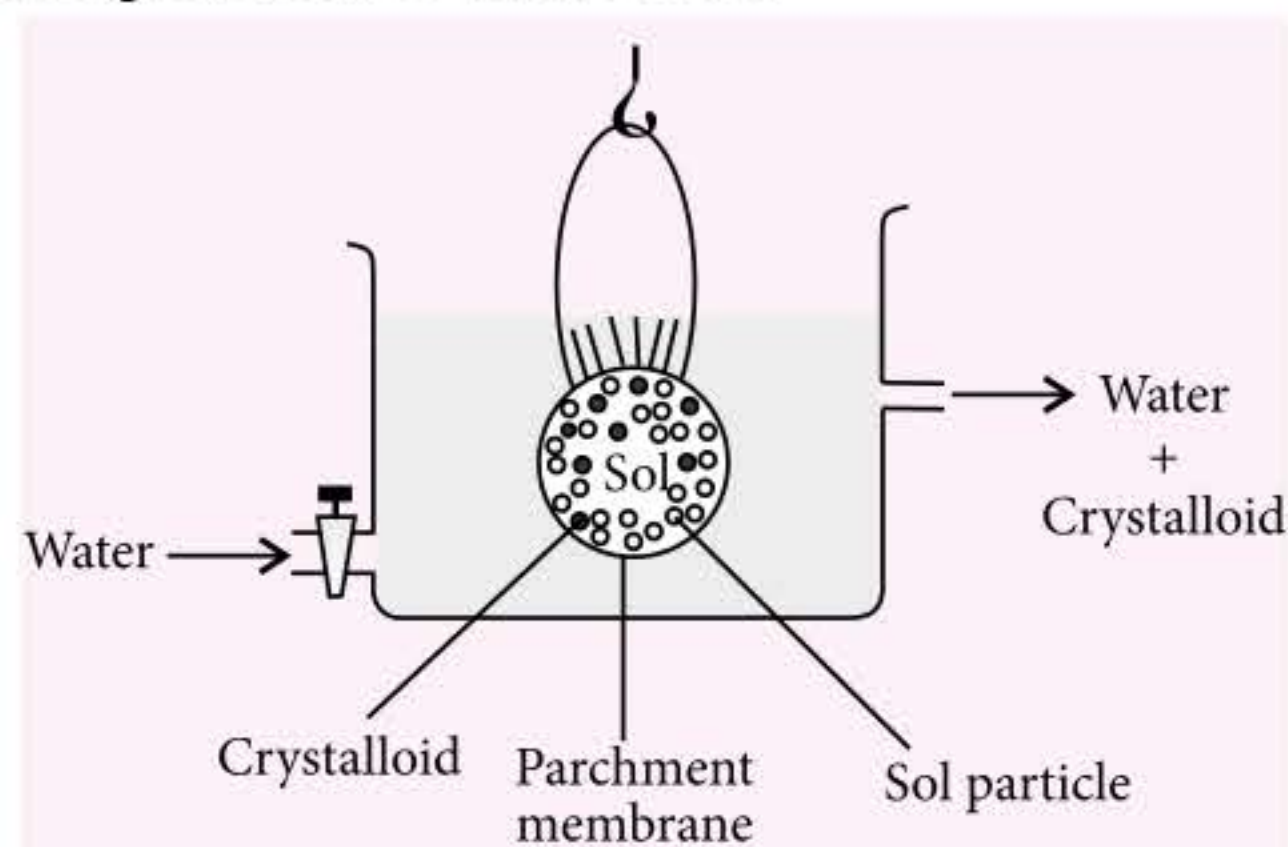
- **Electrodialysis :** In this process, electric field is applied during dialysis.

- **Ultrafiltration :** Separation of colloidal particles from crystalloids by filtration using ultrafilter papers.
- **Ultra-centrifugation :** In this process, colloidal particles settle down at the bottom of tube whereas crystalloids remain in the solution.

Important Properties

- **Tyndall effect :** Scattering of light by the colloidal particles.
- **Brownian movement :** Continuous zig-zag movement of colloidal particles.
- **Coagulation :** Settling of colloidal particles.
- **Zeta potential :** Potential difference between the fixed layer and the diffused layer of opposite charges, also called electrokinetic potential.
- Colloidal particles possesses electrical charge, positive or negative, which are responsible for their stability.

SPEED 🏃 PRACTICE

1. If $E^\circ_{Fe^{2+}/Fe} = x_1\ V$, $E^\circ_{Fe^{3+}/Fe^{2+}} = x_2\ V$, what is the $E^\circ_{Fe^{3+}/Fe}$?

   (a) $\dfrac{2x_1 + x_2}{4}$ (b) $\dfrac{2x_1 + x_2}{3}$

   (c) $\dfrac{2x_1 + x_2}{2}$ (d) $2x_1 + x_2$

2. The rate constant, activation energy and Arrhenius parameter of a chemical reaction at 25 °C are $3.0 \times 10^{-4}\ s^{-1}$, 104.4 kJ mol^{-1} and $6.0 \times 10^{14}\ s^{-1}$ respectively. The value of the rate constant as $T \to \infty$ is

   (a) $2.0 \times 10^{18}\ s^{-1}$ (b) $6.0 \times 10^{14}\ s^{-1}$
   (c) infinity (d) $3.6 \times 10^{30}\ s^{-1}$

3. The rate of a first order reaction is 1.8×10^{-3} mol L^{-1} min^{-1} when the initial concentration is 0.3 mol L^{-1}. The rate constant is

   (a) $1 \times 10^{-2}\ s^{-1}$ (b) $1 \times 10^{-4}\ s^{-1}$
   (c) $6 \times 10^{-2}\ s^{-1}$ (d) $4 \times 10^{-4}\ s^{-1}$

4. What is the value of $1/n$, in Freundlich adsorption isotherm?

   (a) Between 2 and 4 in all cases
   (b) Between 0 and 1 in all cases
   (c) 1 in case of chemisorption
   (d) 1 in case of physical adsorption

5. Following two half cells form a complete cell which has ΔG° (in kJ) value

   $2H^+ + 1/2\ O_2 + 2e^- \to H_2O$; $E^\circ = +1.23$ V
   $Fe^{2+} + 2e^- \to Fe_{(s)}$; $E^\circ = -0.44$ V

   (a) –122 (b) –222 (c) –322 (d) –422

6. Zinc is used to protect iron from rusting. This is because

   (a) E°_{red} of Zn is greater than that of Fe
   (b) E°_{ox} of Zn is greater than that of Fe
   (c) E°_{red} of Zn is nearly equal to that of Fe
   (d) Zn is cheap.

7. Which of the following is not correct?

   (a) Rate of zero order reaction depends upon initial concentration of reactant.
   (b) Rate of zero order reaction does not depend upon initial concentration of reactant.
   (c) $t_{1/2}$ of first order reaction is independent of initial concentration of reactant.
   (d) $t_{1/2}$ of zero order reaction is dependent of initial concentration of reactant.

8. When the concentration of an adsorbate is higher on the surface of adsorbent than in the adjoining bulk, the phenomenon is called

   (a) chemisorption (b) physisorption
   (c) positive adsorption (d) negative adsorption.