NEET | JEE ESSENTIALS

Class XII

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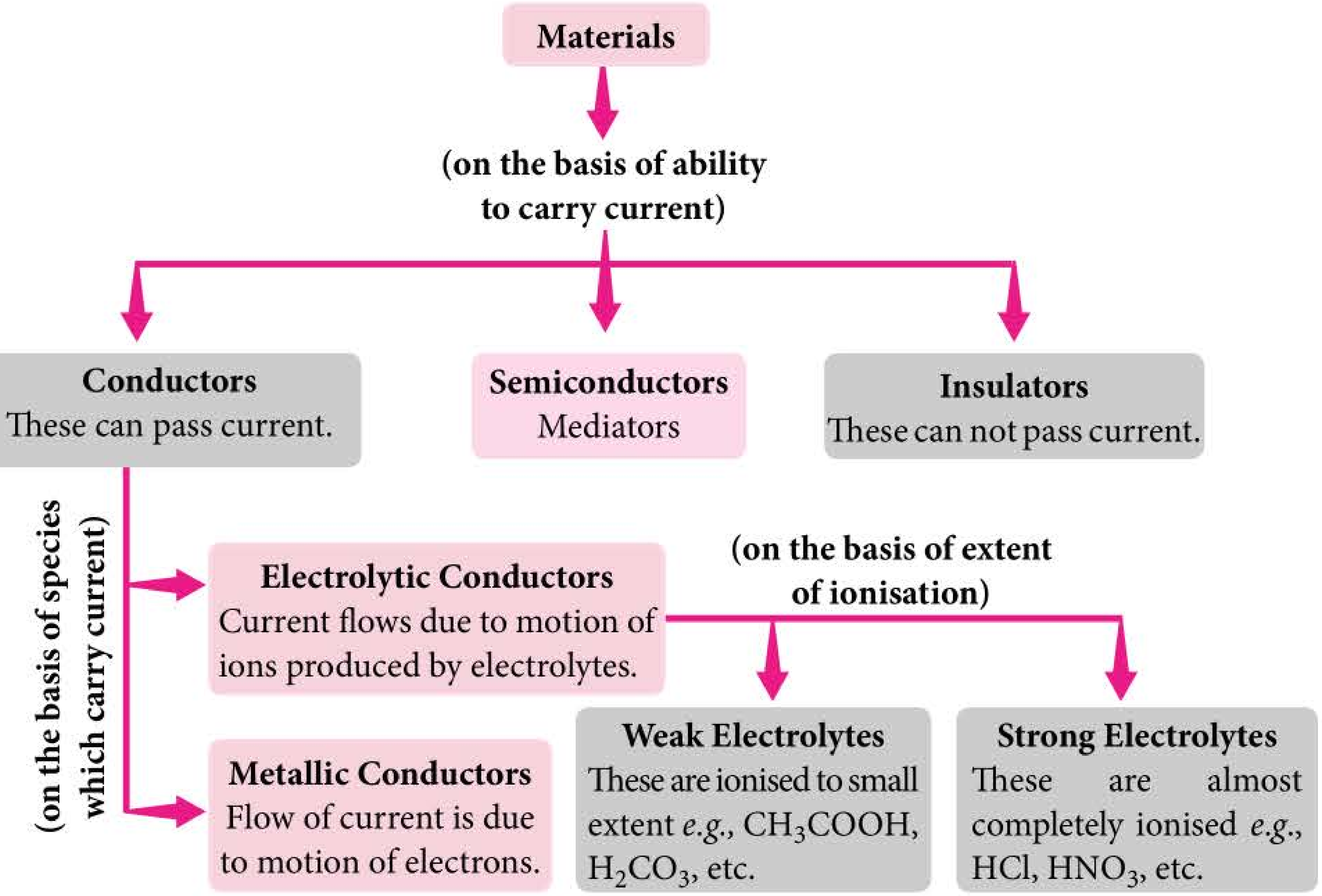
Unit 2

Electrochemistry | Chemical Kinetics | Surface Chemistry

ELECTROCHEMISTRY

GENERAL INTRODUCTION

- Electrochemistry is the branch of physical chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions.



Equivalent Conductivity (Λ_{eq})

$\Lambda_{eq} = \kappa \times V\text{ (in mL)} = \kappa \times \frac{1000}{C} = \kappa \times \frac{1000}{N}$

Unit = S cm^2 eq^{-1} or Ω^{-1} cm^2 eq^{-1}

Specific Conductance or Conductivity (κ)

$\kappa = G \times \frac{l}{a} = \frac{1}{R} \times \frac{l}{a}$

$\frac{l}{a}$ = cell constant

Unit = S m^{-1} = Ω^{-1} m^{-1}

Conductance / Conductivity

Molar Conductivity (Λ_m)

$\Lambda_m = \kappa \times V\text{ (in mL)} = \kappa \times \frac{1000}{M}$

Unit = S cm^2 mol^{-1} or Ω^{-1} cm^2 mol^{-1}

Conductance (G) : $G = \frac{1}{R}$

Unit = Ω^{-1} or mho

VARIATION OF CONDUCTIVITY AND MOLAR CONDUCTIVITY WITH CONCENTRATION

- With increase in dilution, conductivity of the electrolytic solution decreases.
- In case of strong electrolytes, molar conductivity increases slowly with dilution and approaches a certain limiting value when concentration approaches zero (infinite dilution) and is given by *Debye Huckel Onsager equation.*

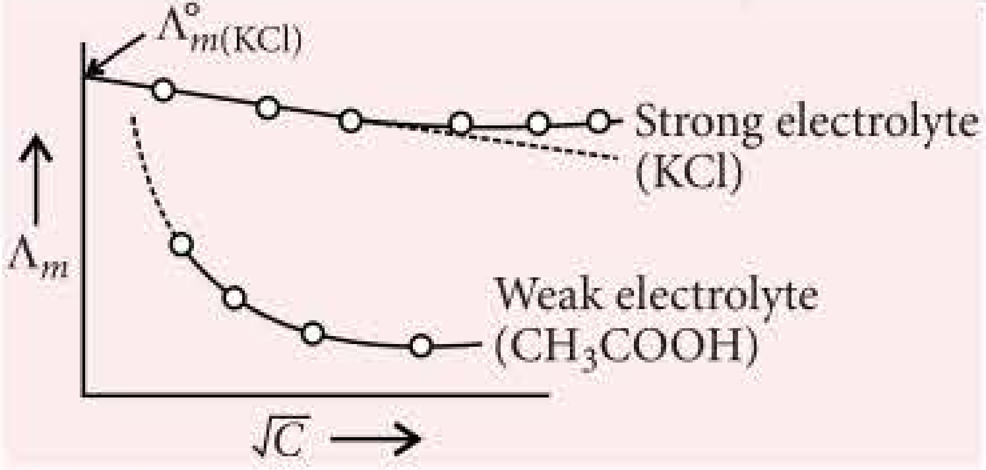
  $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$

  Here, Λ_m° = Limiting molar conductivity at infinite dilution

  Λ_m = Molar conductivity

  A = Constant which depends upon nature of solvent and temperature

  C = Concentration
- In case of weak electrolytes, the molar conductivity is low as compared to that of strong electrolytes.



KOHLRAUSCH'S LAW

- At infinite dilution, $\Lambda_m^\circ = \lambda^\circ(\text{cation}) + \lambda^\circ(\text{anion})$

  for A_xB_y ; $\Lambda_m^\circ = x\lambda_+^\circ + y\lambda_-^\circ$

ELECTROLYSIS

- The passage of charge through an electrolyte brings chemical changes involving reduction as well as oxidation of ions, the phenomenon is known as electrolysis.

Electrolysis

Electrolytic Cell

The device in which the process of electrolysis is carried out, is called electrolytic cell.

- Oxidation at anode.
- Reduction at cathode.
- Cathodic reaction will be with higher E°_{red} value.
- Anodic reaction will be with higher E°_{ox} value.

Faraday's Law of Electrolysis

- First law of electrolysis :

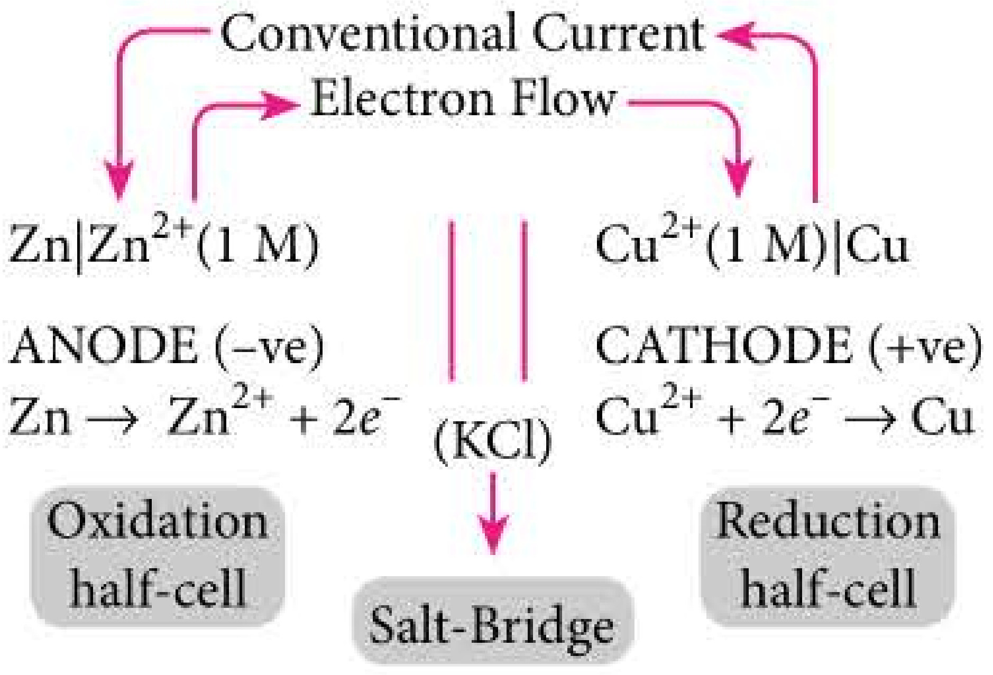
  $m \propto Q \propto (I \times t) = ZIt$

  (m = mass liberated at electrode,
  Q = quantity of electricity
  Z = electrochemical equivalent)
- Second law of electrolysis :

  $\frac{\text{Mass of } x}{\text{Mass of } y} = \frac{\text{Chemical equivalent mass of } x}{\text{Chemical equivalent mass of } y} = \frac{Z_x}{Z_y}$
- 1 Faraday (1F) = 96,500 coulombs

ELECTROCHEMICAL CELL

- The device in which chemical energy is converted into electrical energy is called galvanic cell or electrochemical cell or voltaic cell.



ELECTRODE POTENTIAL

- The electrode potential is the tendency of an electrode to lose or gain electrons when it is in contact with the solution of it own ions.
- **EMF or Cell Potential :** The difference in electrode potentials of the two electrodes of the cell is known as EMF or Cell potential.

$$E^\circ_{cell} = E^\circ_{ox(anode)} + E^\circ_{red(cathode)}$$
$$= E^\circ_{red(cathode)} - E^\circ_{red(anode)} \qquad [\because\ E^\circ_{ox} = -E^\circ_{red}]$$
$$= E^\circ_{red\ (right)} - E^\circ_{red\ (left)}$$

Electrode Potential

Oxidation Potential (E°_{ox})

When electrode is negative charged (anode), oxidation occurs.

$M \rightarrow M^{n+} + ne^-$

Potential of oxidation half reaction $= E^\circ_{ox}$

Reduction Potential (E°_{red})

When electrode is positively charged (cathode), reduction occurs.

$M^{n+} + ne^- \rightarrow M$

Potential of reduction half reaction $= E^\circ_{red}$

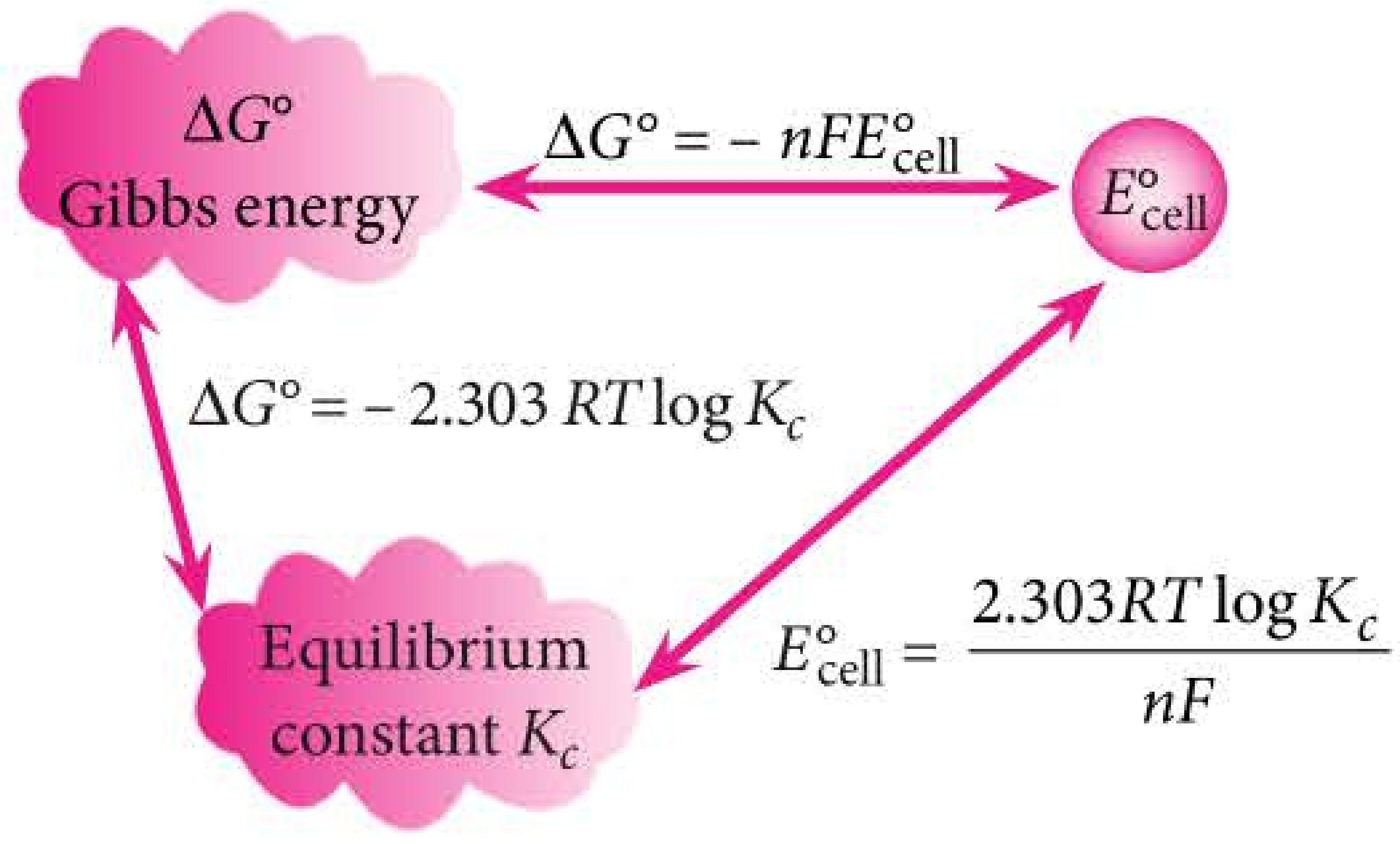
Standard Electrode Potential

The potential difference developed between metal electrodes and the solution of its ions of 1 M at 25°C.

NERNST'S EQUATION

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

RELATIONSHIP BETWEEN ELECTRODE POTENTIAL, GIBBS ENERGY AND EQUILIBRIUM CONSTANT



INFOSHOTS

Li-S batteries : Firing for compactness !

Conventional Li-S batteries have a non-compact cathode structure containing low areal loading of active materials. Now, a strategy of burning Li foils in a CS_2 vapour is presented, which leads to the formation of highly compact Li_2S nano-particles as a lithiated sulphur cathode, offering promising battery performance.

BATTERIES

- The term battery is used when two or more galvanic cells are connected in series.

Batteries

Primary Batteries

Not rechargeable, *e.g.*, voltaic cell, mercury cell, Leclanche cell.

Secondary Batteries

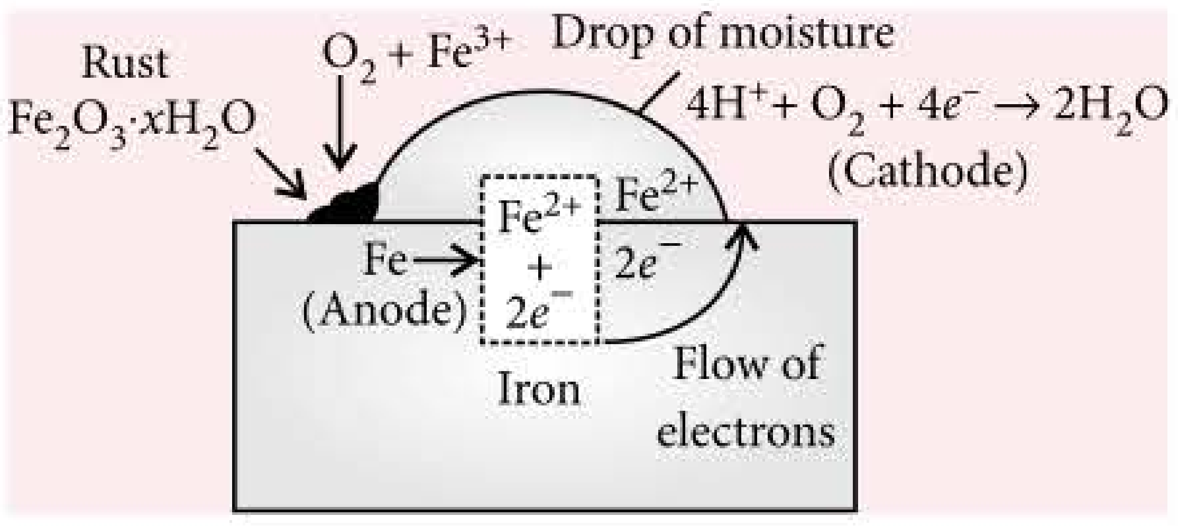
Rechargeable *e.g.*, lead-storage batteries, nickel-cadmium storage batteries.

Cell	Cathode/Anode	Electrolyte	Cell reactions
Dry cell	Graphite/Zinc	$MnO_2 + C$ (Around cathode) $NH_4Cl + ZnCl_2$ (Around anode)	**Anode :** $Zn \rightarrow Zn^{2+} + 2e^-$ **Cathode :** $MnO_{2(s)} + NH^+_{4(aq)} + e^- \rightarrow MnO(OH) + NH_3] \times 2$ $Zn + 2MnO_{2(s)} + 2NH^+_{4(aq)} \rightarrow Zn^{2+} + 2MnO(OH) + 2NH_3$
Mercury cell	Hg(II) oxide/ Zinc	Paste of KOH and ZnO	**Anode :** $Zn(Hg) + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O + 2e^-$ (Amalgam) **Cathode :** $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)}$ $Zn(Hg) + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$
Lead storage cell	Lead packed with PbO_2/Lead	38% H_2SO_4 solution	**Anode :** $Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$ **Cathode :** $PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$ $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$
Nickel - Cadmium storage cell	NiO_2/Cd	KOH solution	**Anode :** $Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_2 + 2e^-$ **Cathode :** $2NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \rightarrow Ni(OH)_2 + 2OH^-_{(aq)}$ $Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_2 + Ni(OH)_2$

CORROSION

- Corrosion is a process of deterioration of a metal as a result of its reaction with air or water (environment) surrounding it.
- Corrosion of iron is known as rusting. Rust is hydrated form of ferric oxide, $Fe_2O_3 . xH_2O$.

MECHANISM OF RUSTING



CHEMICAL KINETICS

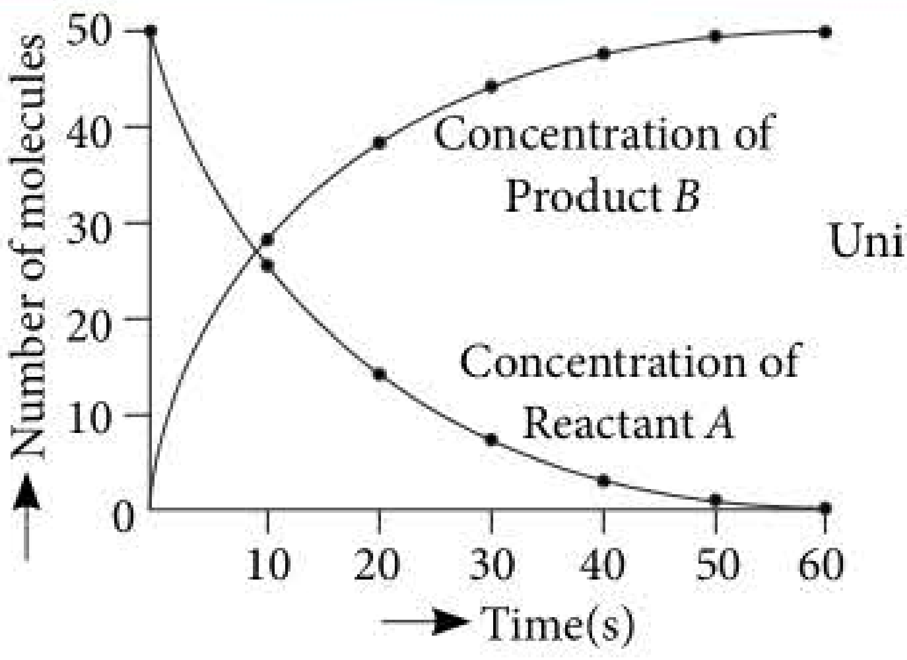
RATE OF A CHEMICAL REACTION

- Change in the concentrations of reactants or products per unit time is known as rate of reaction.

  Progress of a reaction : Reactant, $A \longrightarrow$ Product, B

  For a reaction : $aA + bB \longrightarrow cC + dD$
- Rate of reaction is defined as :

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$



Unit of rate = mol L^{-1} s^{-1}

Factors Affecting the Rate of the Reaction

Catalyst

- A substance that increases the reaction rate without undergoing a chemical change itself. Catalyst lowers the activation energy for a chemical reaction.
- Activation energy = Threshold energy – Average kinetic energy of reacting molecules.

Concentration of Reactants

- The rate of reaction increases with increase in concentration of reactants as the number of collisions increases.

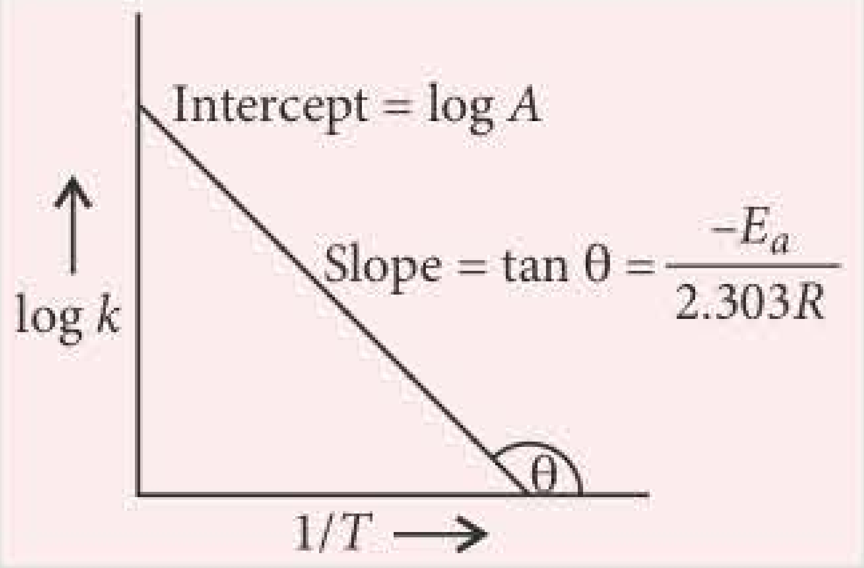
Nature of Reactants

- The reactants with weak bonds react quickly whereas reactants with strong bonds react slowly.
- Molecular reactions are slow while ionic reactions are fast.

Temperature

- As T increases, average $K.E.$ increases.
- As average $K.E.$ increases, the particles move faster so, collision energy and collision frequency increase and hence, rate increases.
- **Arrhenius equation :** $k = Ae^{-E_a/RT}$;

$$\log k = \log A - \frac{E_a}{2.303\,RT}$$



Surface Area of Reactants

- Greater the surface area of reactants, faster is the reaction.

RATE LAW

For a reaction
$aA + bB \rightarrow cC + dD$

Law of mass action
Rate $\propto [A]^a[B]^b$

Rate law
Rate $= k[A]^m[B]^n$
m = order of reaction w.r.t. A, n = order of reaction w.r.t. B

MOLECULARITY AND ORDER OF A REACTION

Molecularity

- Number of reacting species which collide to result in reaction.
- Only positive integral values *e.g.*, 1, 2, 3 and never have negative value.
- Theoretical concept and value is derived from mechanism of reaction.

Order of the reaction

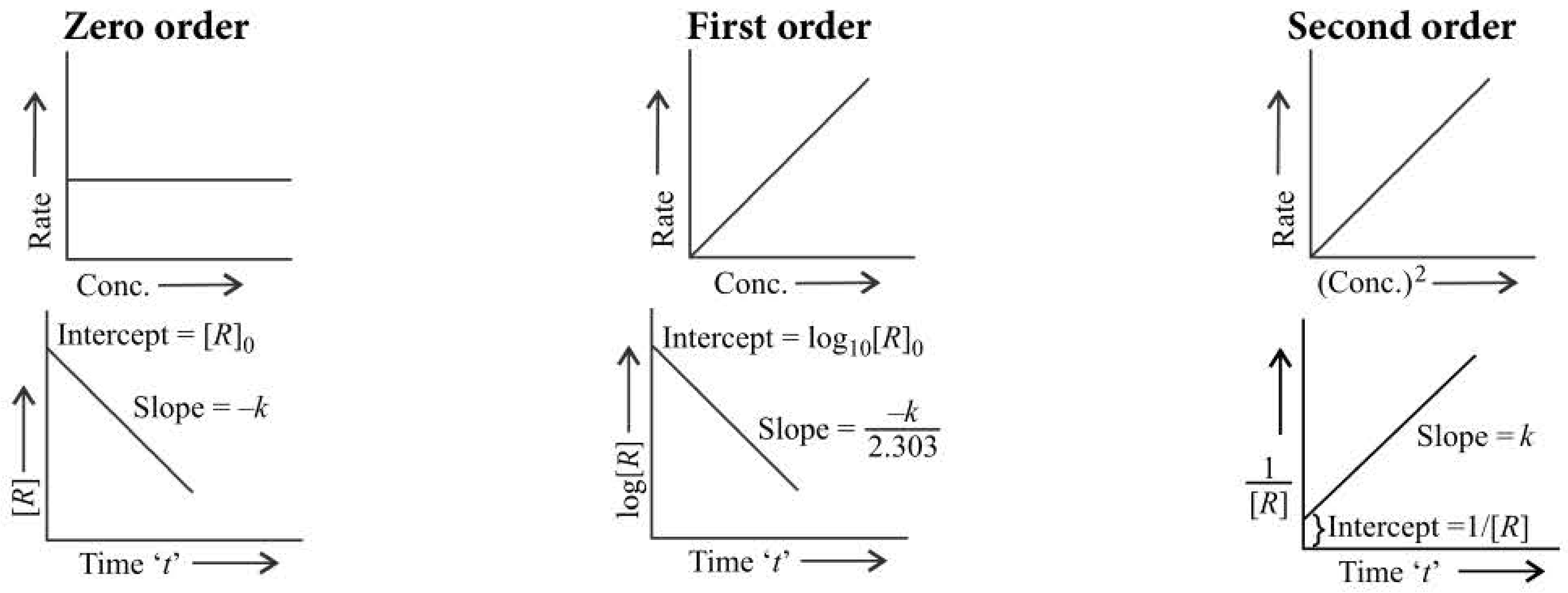
- Sum of powers to which concentration terms are raised in the rate law expression.
- Zero, fractional or even negative.
- Experimental fact and derived from rate law.

RATE LAW EXPRESSION FOR DIFFERENT ORDER REACTIONS

For the reaction : $A \longrightarrow$ Product

Reaction order n	Rate variation with conc.	Differential rate law	Integrated rate law	Units of rate constant	$t_{1/2}$
1	Rate doubles when $[A]$ doubles	Rate = $k[A]^1$	$\ln[A]_t / [A]_0 = -kt$	s^{-1}	$\frac{0.693}{k}$
2	Rate quadruples as $[A]$ doubles	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$L\ mol^{-1}\ s^{-1}$	$\frac{1}{k[A_0]}$
0	Rate does not change with $[A]$	Rate = $k[A]^0$	$[A]_t - [A]_0 = -kt$	$mol\ L^{-1}\ s^{-1}$	$\frac{A_0}{2k}$

Graphical Representation



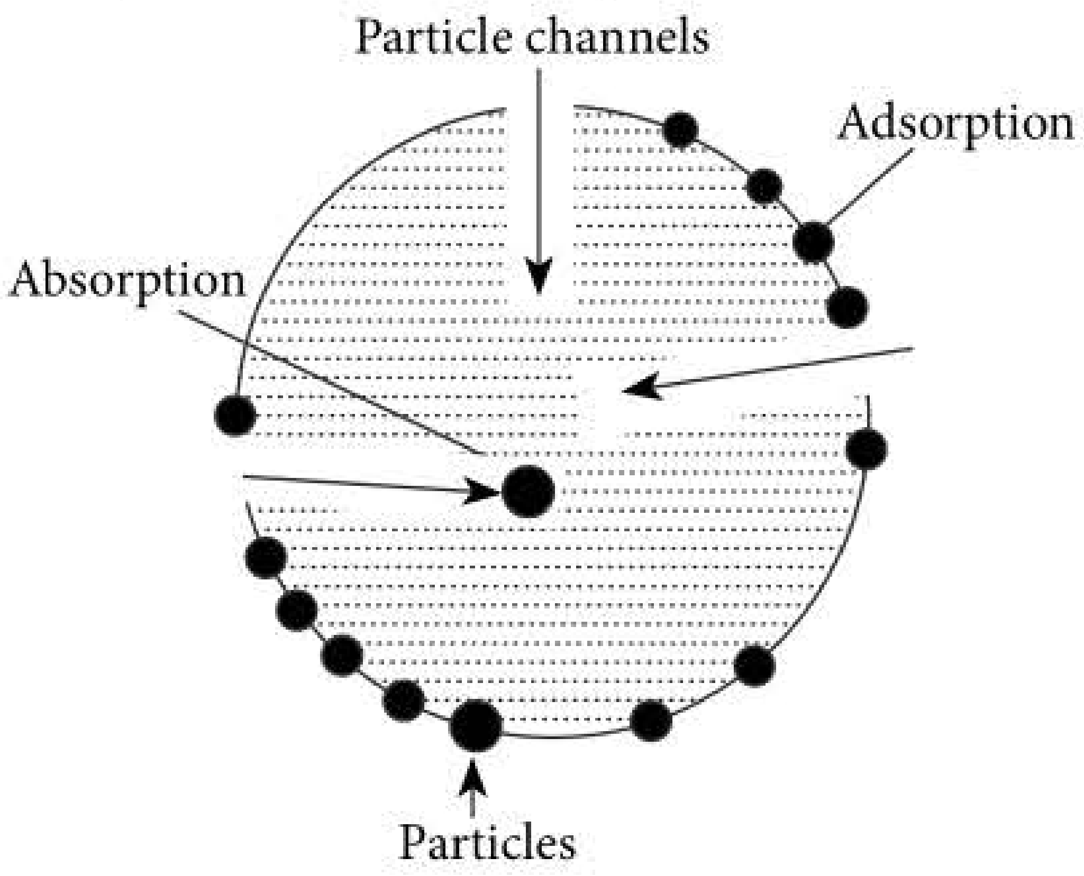
SURFACE CHEMISTRY

- Surface chemistry is a branch of chemistry that deals with phenomena, which occur at the surface.

ADSORPTION

- Existence of higher concentration of any particular component (known as adsorbate) at the surface of the liquid or solid phase (known as adsorbent).

Adsorption *vs* Absorption

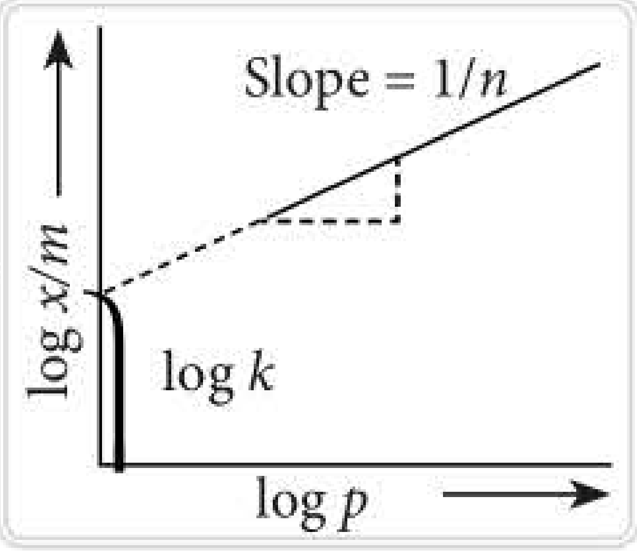


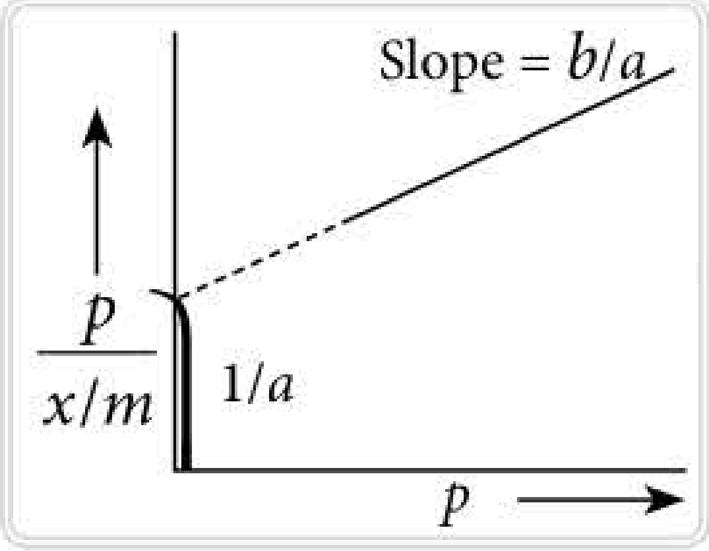
Types of Adsorption

Physical adsorption	Chemical adsorption
Caused by intermolecular van der Waals forces.	Caused by chemical bond formation.
It is not specific.	It is highly specific.
It is reversible.	It is irreversible.
Heat of adsorption is low (20-40 kJ/mol).	Heat of adsorption is high (80-240 kJ/mol).
Low temperature is favourable.	Increases with high temperature.
It forms multimolecular layers.	It forms monomolecular layers.

Freundlich Isotherm — **Adsorption Isotherms** — **Langmuir Isotherm**

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





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

Applications of Adsorption

- To decolourise the solution
- In gas mask
- Dehumidification
- Heterogenous catalysis
- Softening of hard water
- De-ionisation of water

COLLOIDS

True solutions	Colloidal solutions	Suspensions
The solute particles having size less than 1 nm.	The particles size lies in the range of 1 nm to 1000 nm.	The size of the particles is greater than 1000 nm.
The solute particles are invisible by naked eyes as well as under the powerful microscope.	The solute particles are invisible by naked eyes but their scattering effect can be viewed with the help of a microscope.	The solute particles are visible by naked eyes and can be seen with the help of a microscope.

Types of Colloidal Solutions

Dispersed Phase	Dispersion Medium	Common Name	Examples
Solid	Solid	Solid sol	Coloured gems and glasses, some alloys, rock salt.
Solid	Liquid	Sol	Arsenious sulphide sol, gold sol, starch, paints, muddy water.
Solid	Gas	Aerosol	Smoke, dust storm.
Liquid	Solid	Gels	Jellies, cheese, iron hydroxide, shoe polish.
Liquid	Liquid	Emulsion	Milk, cod-liver oil.
Liquid	Gas	Liquid aerosol	Mist, fog, cloud, insecticide sprays.
Gas	Solid	Solid foam	Pumice stone, occluded gases, rubber.
Gas	Liquid	Foam	Soap lather, whipped cream, lemonade froth.

CONCEPT
MAP

Class XI **Class XII**

CONCEPT
MAP

MOLECULAR ORBITAL THEORY (MOT)

MO Theory was originally called Hund-mulliken theory. The molecular orbital theory was first published in 1929 paper of Lennard-Jones. This paper notebly predicted a triplet ground state for dioxygen molecule. The molecular orbital theory was introduced by Mulliken in 1932. By 1933, the molecular orbital theory has been accepted as a valid and useful theory.

OXIDATION REACTIONS

Oxidation reactions are very useful in organic synthesis as well as for distinguishing different organic compounds. In daily life also oxidation reactions are involved in various processes such as metabolism, photosynthesis, corrosion, rancidity, etc.

Chemical Bonding Models

Molecular Orbital Theory

Atomic orbitals combined to form molecular orbitals as atoms are moved towards each other.

Valence Bond Theory

Bonding electrons occupy orbitals of hybridised (*s*, *p*, *d*) character.

Shared Electron Pair

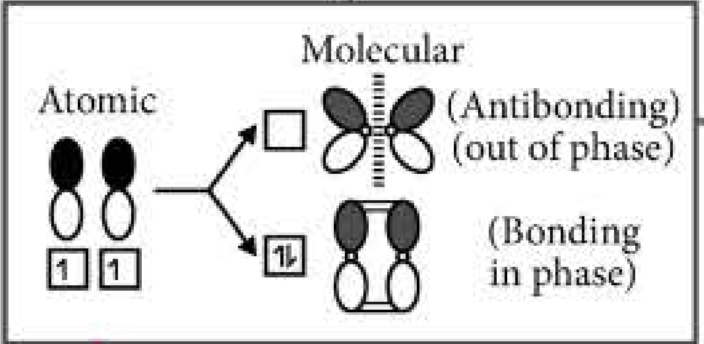
Bonding electrons occupy atomic orbitals.

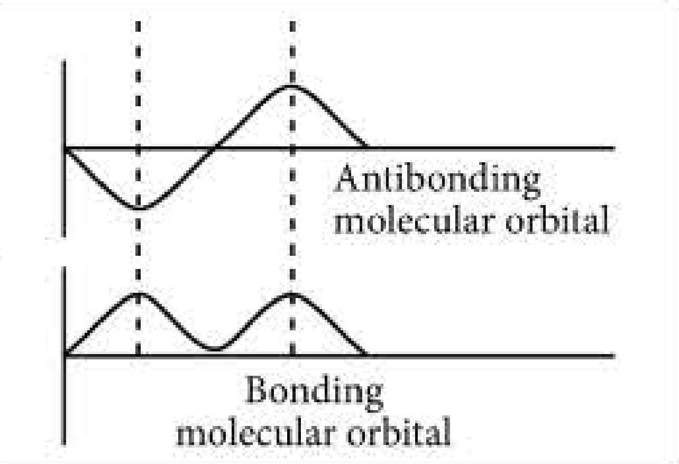
Order of Energy of Molecular Orbitals

From H_2 to N_2 Molecules
$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \pi(2p_x) = \pi(2p_y) < \sigma(2p_z) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$

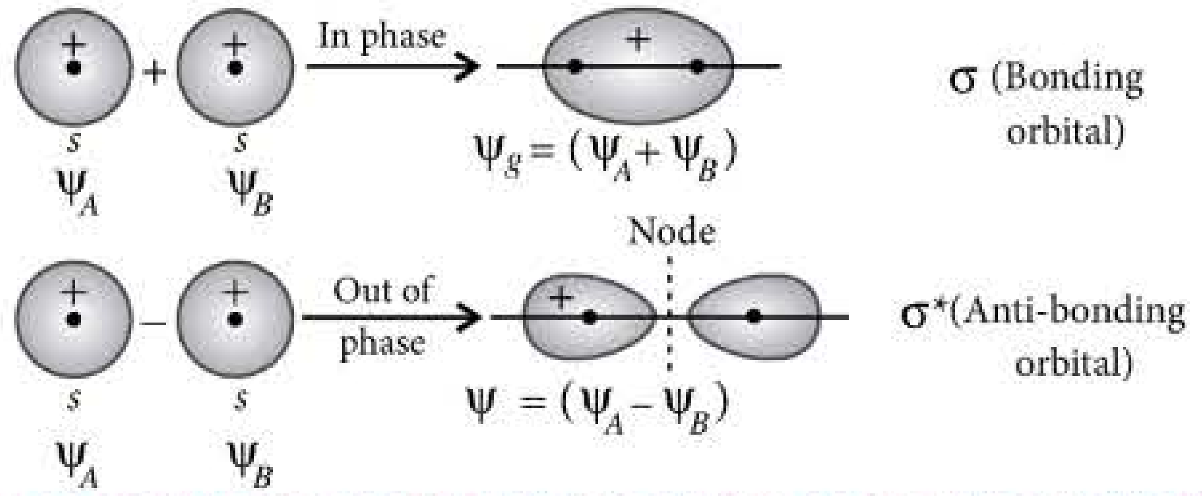
For O_2, F_2 and Ne_2 Molecules
$\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < \pi(2p_x) = \pi(2p_y) < \pi^*(2p_x) = \pi^*(2p_y) < \sigma^*(2p_z)$

Formation of Molecular Orbitals

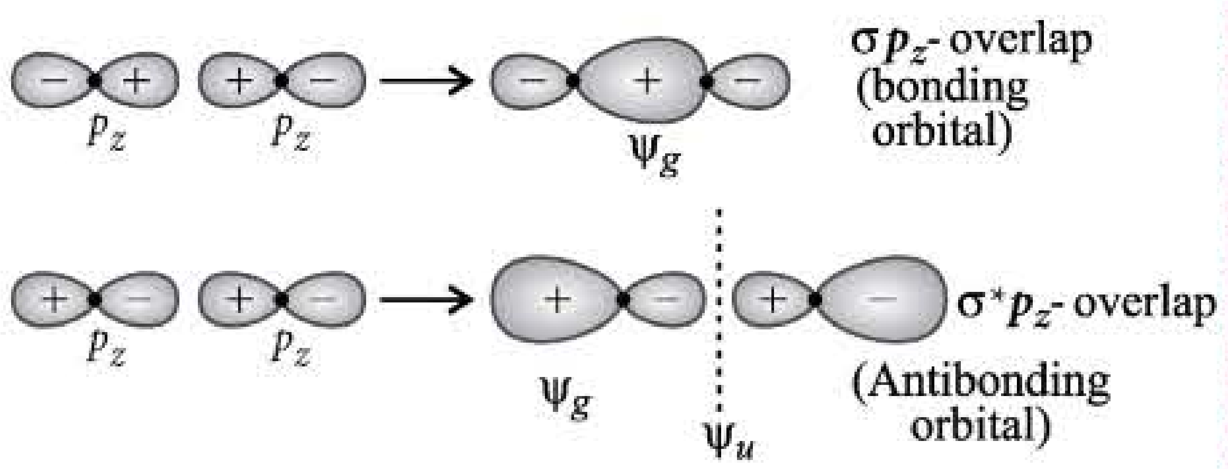




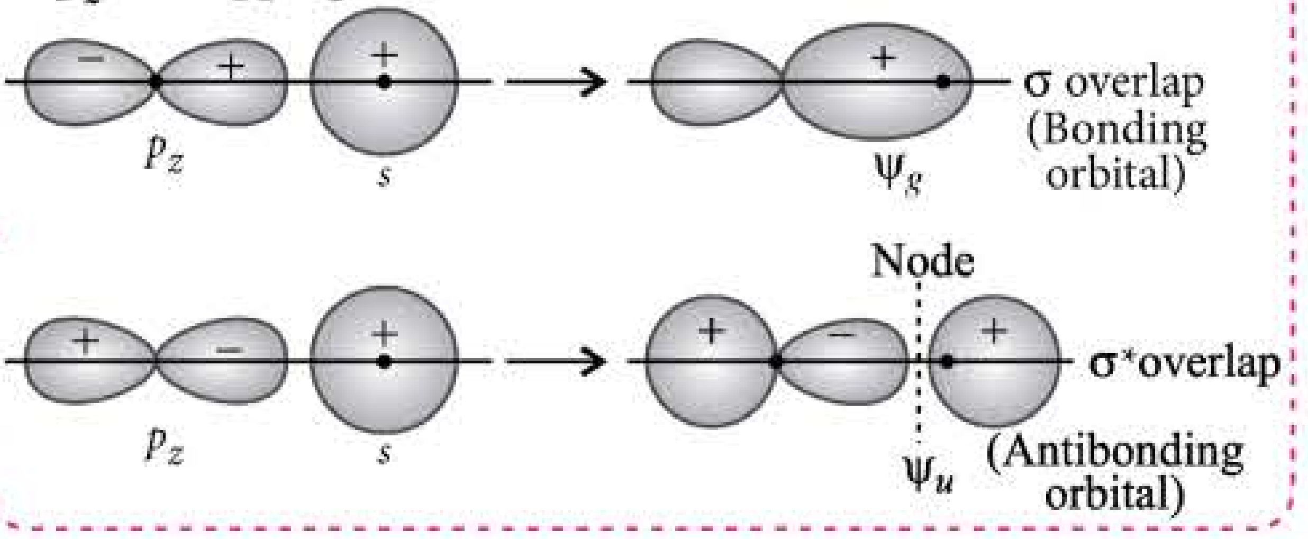
***s*-*s* overlapping :**



***p*-*p* lateral overlapping :**



***s*-p_z overlapping :**



Merits of MOT

- Best for predicting stability of molecules.
- Best for predicting magnetic behaviour of molecules.

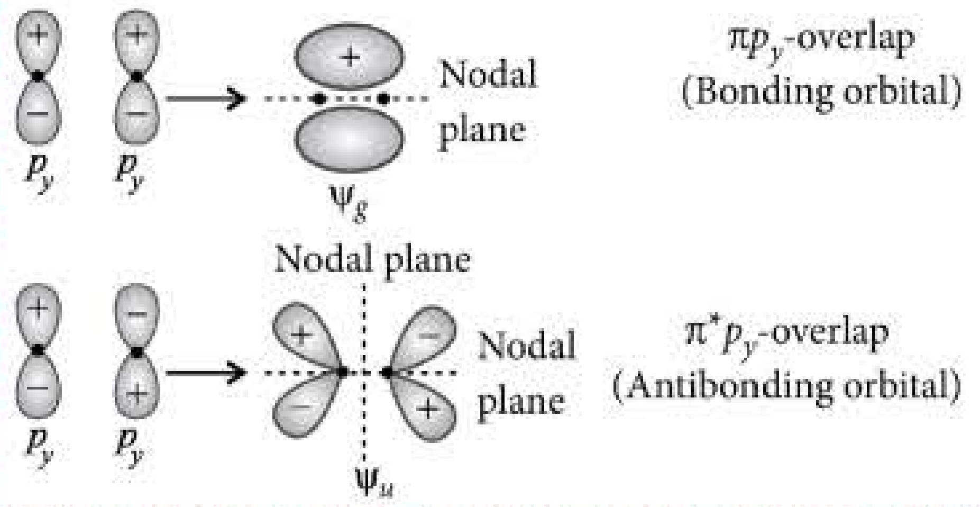
Sigma-Orbitals

Cylinderically symmetric around bond axis.

Pi-Orbitals

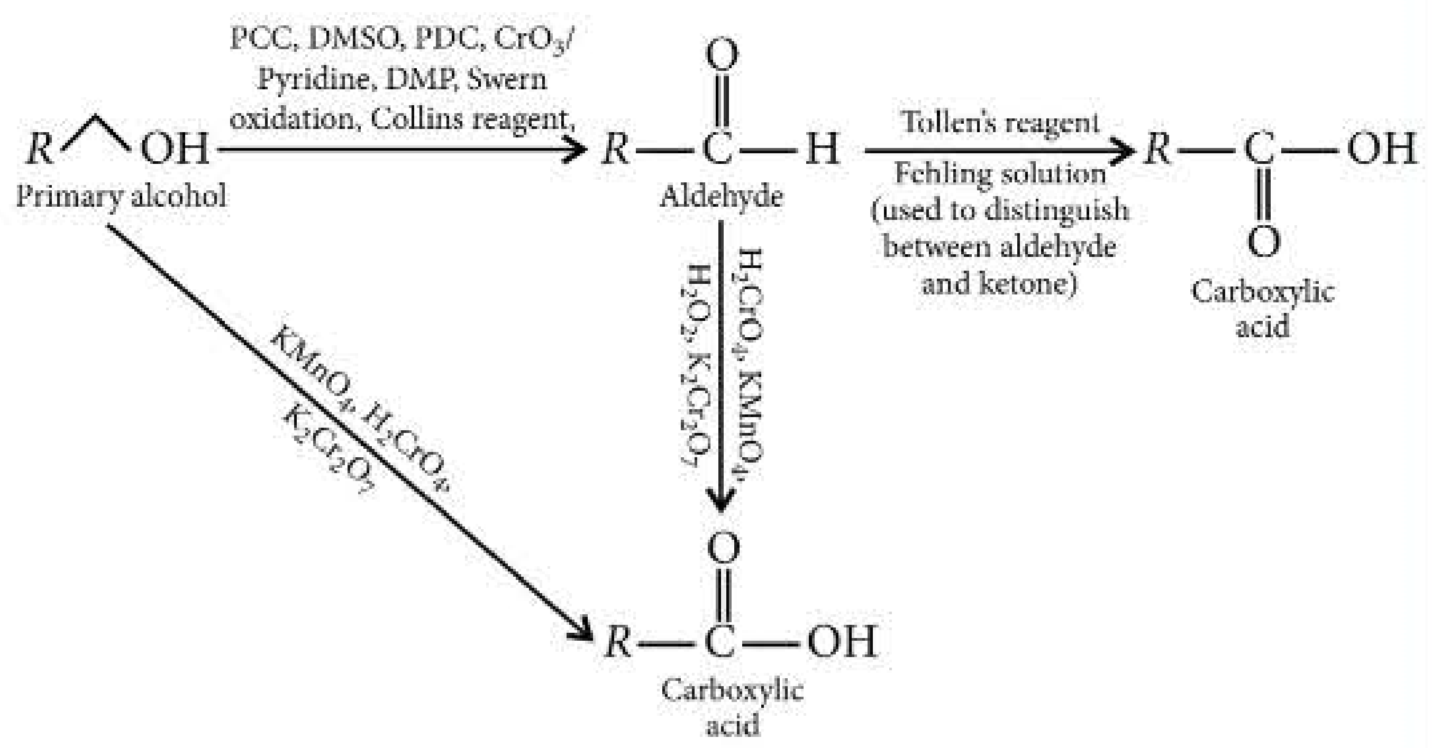
Perpendicular to bond axis.

***p*-*p* sidewise overlapping :**

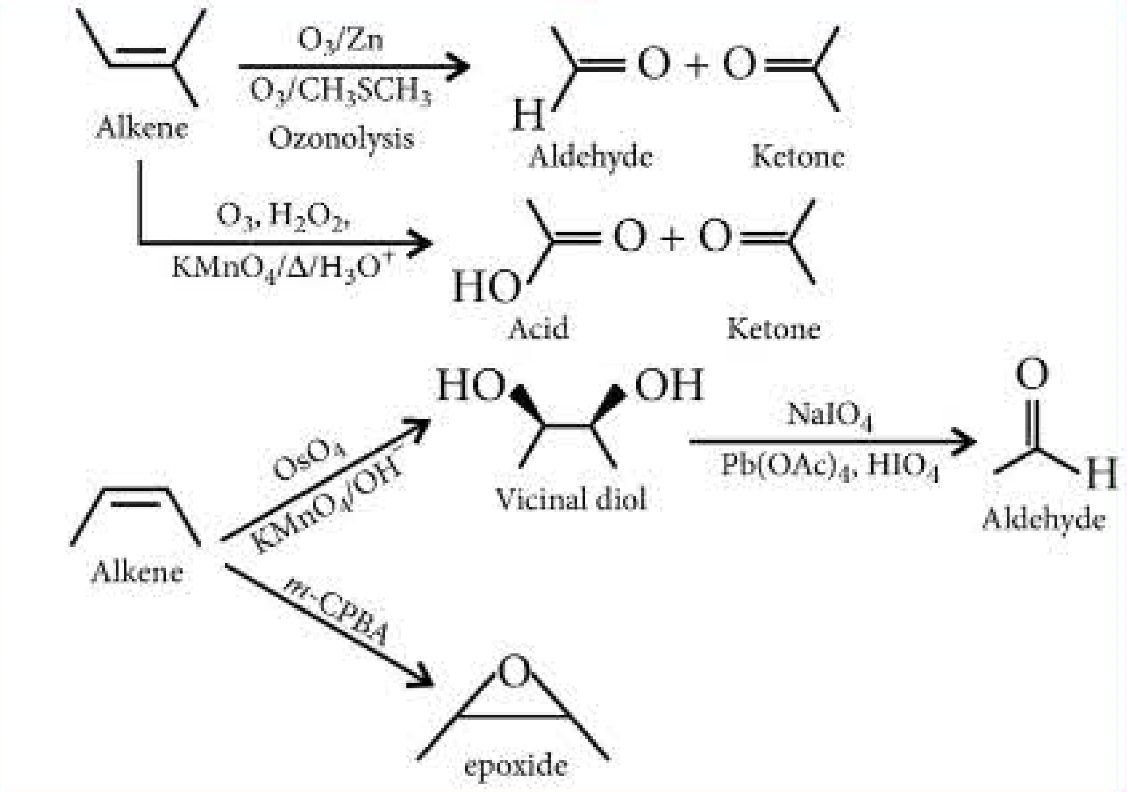


Oxidation Processes

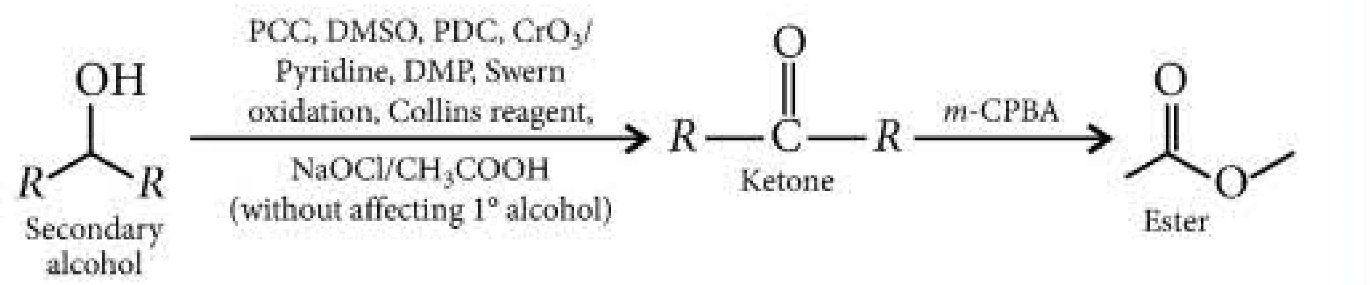
Oxidation of Primary Alcohols



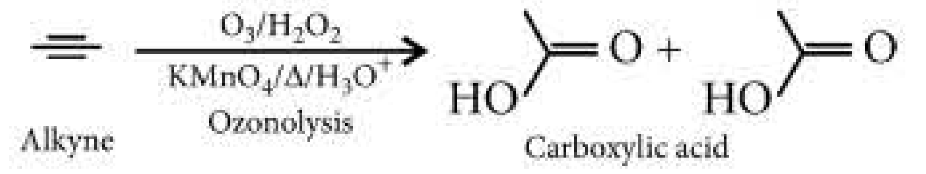
Oxidation of Alkenes



Oxidation of Secondary Alcohols

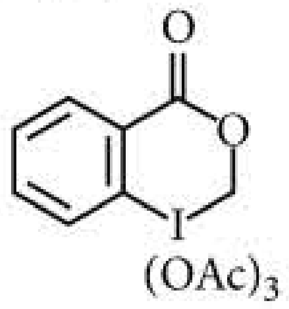


Oxidation of Alkynes

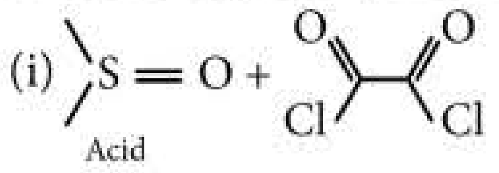


Important Reagents

1. PCC ⇒ Pyridinium chlorochromate $[C_5H_5NH]$ $[CrO_3Cl]$
2. DMP ⇒ Dess – Martin Periodinane



3. Swern Oxidation ⇒ In swern oxidation, following reagents are used :
   (i)

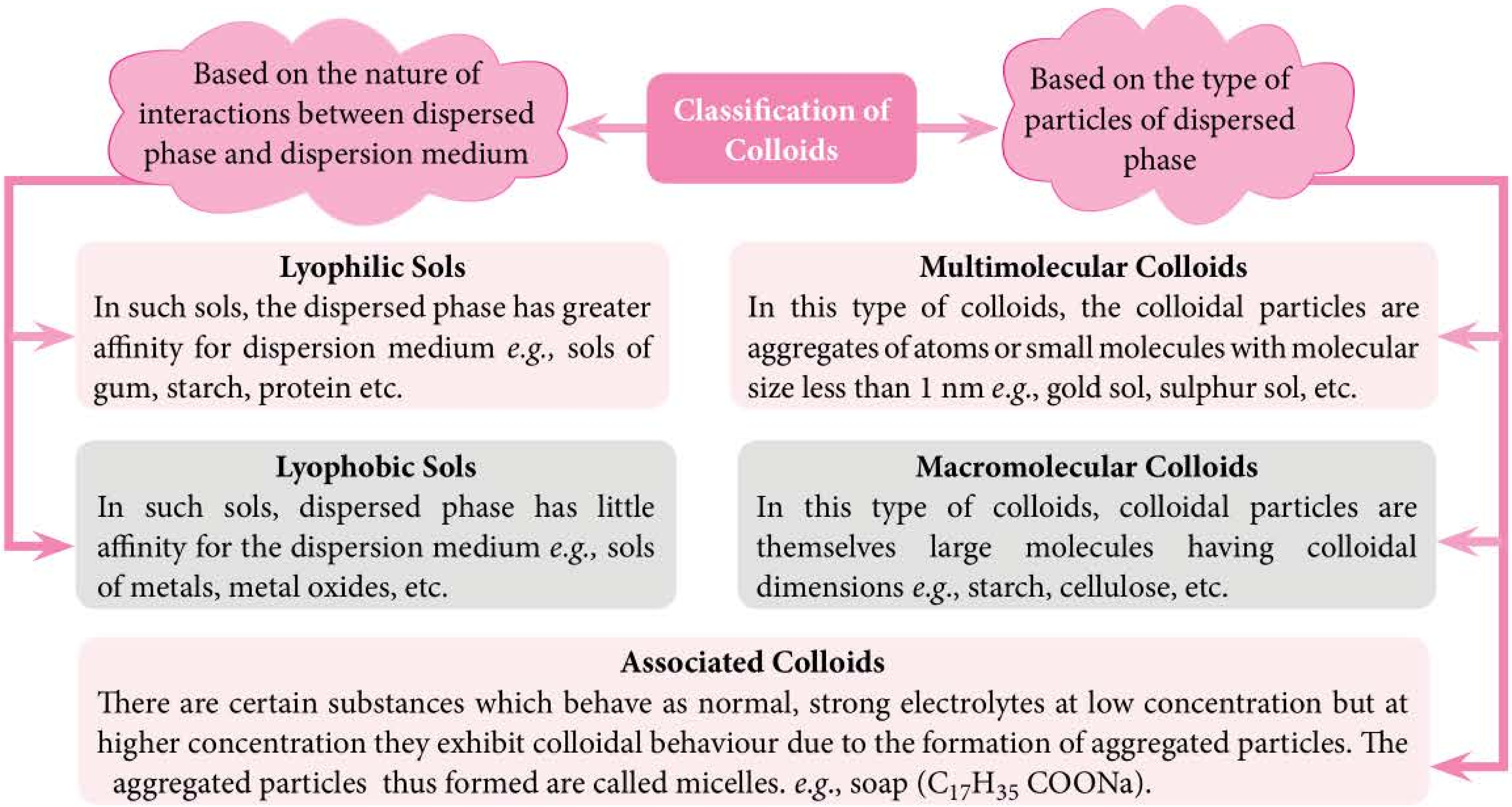


   (ii) NR_3
   Used to avoid the use of toxic metals such as chromium.
4. Collins reagent ⇒ It is a complex of CrO_3 with pyridine in CH_2Cl_2.
5. *m*-CPBA ⇒ *m*-Chloroperoxybenzoic acid.
6. Jones reagent ⇒ Chromic acid in aqueous acetone.

Importance of DMP Reagent

- Using periodinane has several advantages over chromium and DMSO based oxidation.
  - Milder conditions
  - Shorter reaction times
  - Higher yield
  - Simplified workups
  - High chemoselectivity
  - Tolerance of sensitive functional groups
  - Long shelf life
- Using DMP conditions, alcohols can be oxidised to aldehydes / ketones without affecting furan rings, sulphides, vinyl ethers and secondary amides.

Classification of Colloids



Classification of Colloids

Based on the nature of interactions between dispersed phase and dispersion medium

Lyophilic Sols
In such sols, the dispersed phase has greater affinity for dispersion medium *e.g.,* sols of gum, starch, protein etc.

Lyophobic Sols
In such sols, dispersed phase has little affinity for the dispersion medium *e.g.,* sols of metals, metal oxides, etc.

Based on the type of particles of dispersed phase

Multimolecular Colloids
In this type of colloids, the colloidal particles are aggregates of atoms or small molecules with molecular size less than 1 nm *e.g.*, gold sol, sulphur sol, etc.

Macromolecular Colloids
In this type of colloids, colloidal particles are themselves large molecules having colloidal dimensions *e.g.*, starch, cellulose, etc.

Associated Colloids
There are certain substances which behave as normal, strong electrolytes at low concentration but at higher concentration they exhibit colloidal behaviour due to the formation of aggregated particles. The aggregated particles thus formed are called micelles. *e.g.*, soap ($C_{17}H_{35}$ COONa).

Preparation and Purification of Colloids

Preparation of Colloids	Purification of Colloids
By Bredig's arc method (for metals) : A direct current is passed through electrodes of metals suspended in a trough of ice cold water. Intense heat of the arc changes the metal into vapours which condense to form the colloidal particles.	**Dialysis :** It is the process of separating a crystalloid from a colloid by diffusion or filtration through a semipermeable membrane or dialyzing membrane. The process can be quickened by applying electric field and is called *electro-dialysis*.
Ultrasonic dispersion : Ultrasonic vibrations which have frequency more than that of sound are made to strike a beaker containing the substances (oils, sulphur, sulphides and oxides of metals) to be dispersed by using water as the dispersion medium.	**Ultrafiltration :** It is the process of separating the colloidal particles by filtration through ultrafilter paper which is obtained by treating ordinary filter paper with gelatine solution.
Peptization : A freshly prepared precipitate is converted into colloidal particles by adding a suitable electrolyte, called peptizing agent.	**Ultra-centrifugation :** In this method, the impure sol is taken in a tube which is placed in an ultracentrifuge and rotated at a very high speed.

Coagulation of Colloids

- The precipitation of colloids through induced aggregation by addition of some suitable electrolytes is called coagulation or flocculation.

INFOSHOTS

Surface chemistry : Giving catalysts a hand !
Using chiral modifiers on the surfaces of heterogeneous catalysts is a potentially fruitful route to practical stereoselective chemistry. Now, a study of the dynamics of prochiral adsorbates on modified surfaces has shown that they can rapidly interconvert between adsorption states of different prochirality.

- **Hardy Schulze Rule :** Coagulating power of an electrolyte depends on the valency of oppositely charged ion. Greater the valency of oppositely charged ion, more is the coagulating power.
- **Gold Number :** The number of milligrams of the protective colloid which just prevent coagulation of 10 mL of standard gold sol when 1 mL of 10% solution of sodium chloride is added to it.

Properties of Colloids

Properties of Colloids

Filterability
These cannot pass through parchment paper.

Electrophoresis
The movement of colloidal particles towards oppositely charged electrodes under the influence of electric field is known as electrophoresis.

Non-settling
They tend to settle down very slowly.

Electro-osmosis
The movement of the molecules of the dispersion medium under the influence of electric field whereas colloidal particles are not allowed to move.

Colligative properties
They possess very low values of colligative properties .

Tyndall effect
The scattering of light by the colloidal particles present in a colloidal sol is known as Tyndall effect.

Brownian Movement
Colloidal particles exhibit continuous zig-zag motion which is known as Brownian movement.

EMULSIONS

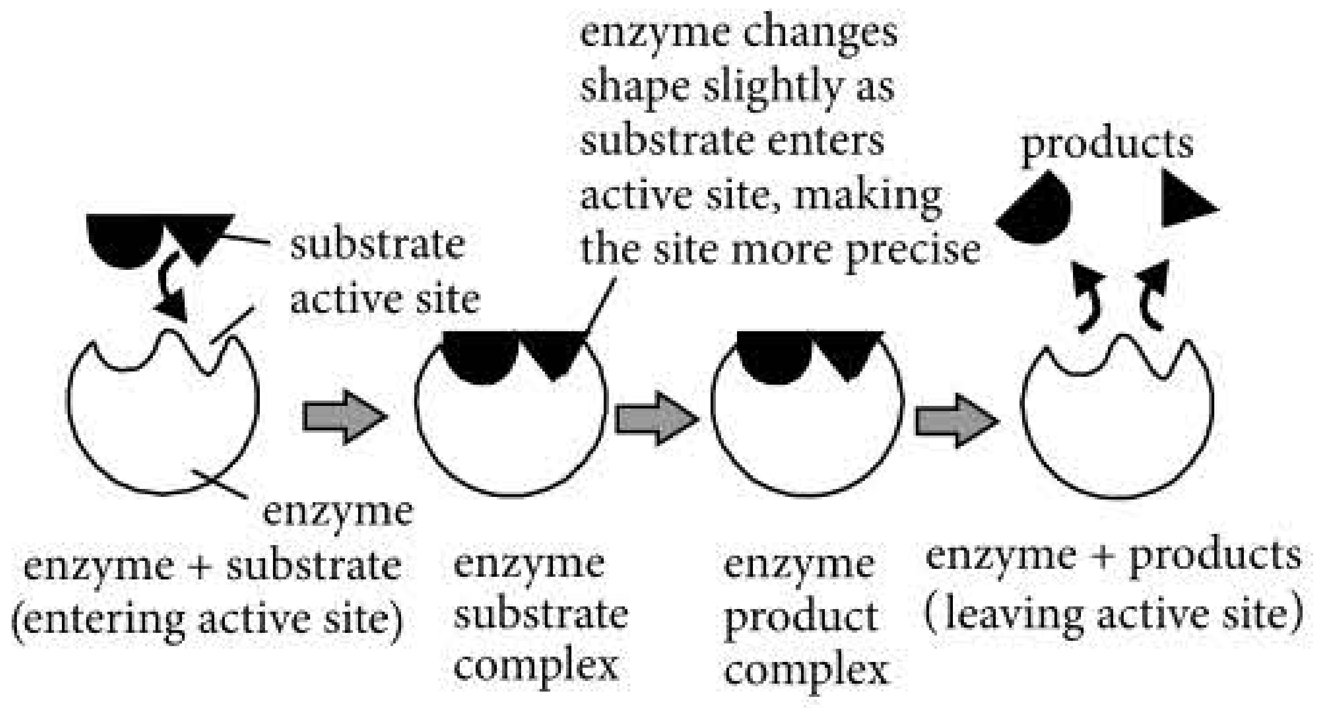
- Emulsions are the colloidal systems in which both the dispersed phase and dispersion medium are liquids.

Types of Emulsions

- **Oil in water (*O/W*) type :** In this type of emulsion, oil is the dispersed phase and water is the dispersion medium. Milk is an emulsion of *O*/*W* type, where fat globules are dispersed in water.
- **Water in oil (*W/O*) type :** In this type of emulsion, water is the dispersed phase and oil is the dispersion medium. Butter is an emulsion of *W*/*O* type.

CATALYST

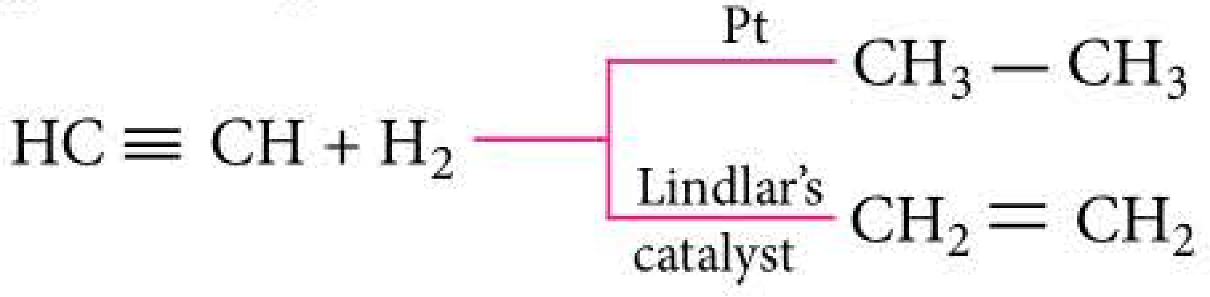
- Catalysts speed up a chemical reaction without being used up.



Important Properties of Catalysts

Activity : A catalyst may accelerate a reaction to as high as 10^{10} times.

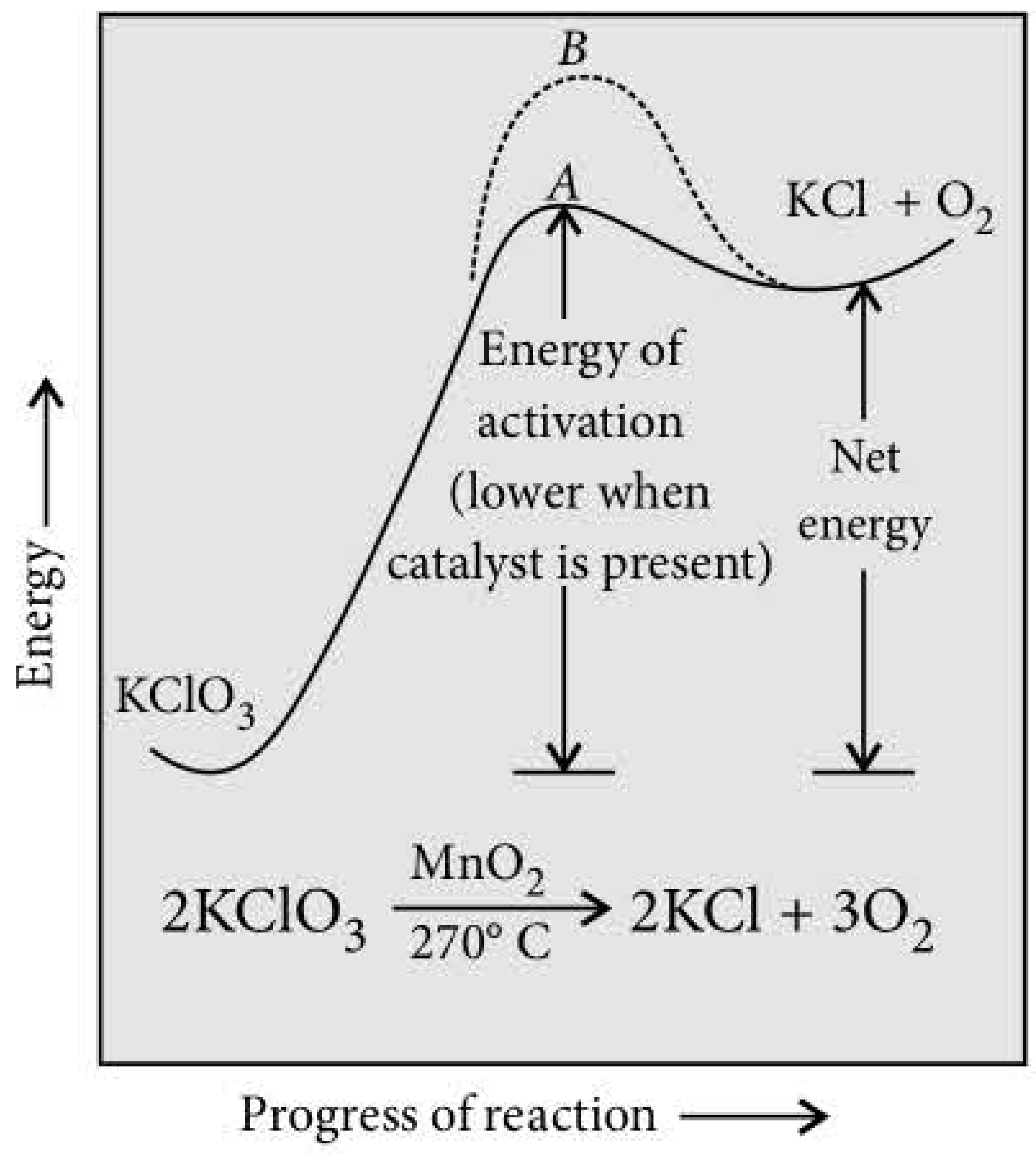
Selectivity : Ability to direct a reaction to give particular product *e.g.*,



$$HC \equiv CH + H_2 \xrightarrow{Pt} CH_3 - CH_3$$

$$HC \equiv CH + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar's}} CH_2 = CH_2$$

Effect of Catalyst



$$2KClO_3 \xrightarrow[270^\circ C]{MnO_2} 2KCl + 3O_2$$

A : Curve in presence of catalyst

B : Curve in absence of catalyst

Types of catalysis

- **Based on effect of catalyst :**

○ **Positive catalysis**

Increases the rate of reaction.

$2KClO_3 \xrightarrow[270^\circ C]{MnO_2} 2KCl + 3O_2$

○ **Negative catalysis**

Decreases or retard the rate of reaction.

$2CHCl_3 + O_2 \xrightarrow{\text{Alcohol}} 2COCl_2 + 2HCl$

○ **Auto-catalysis**

When one of the product act as a catalyst.

$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

- **Based on phase catalyst :**

○ **Homogeneous catalysis**

Catalyst is in the same phase as the reactants.

Hydrolysis of ester (dil. acid as catalyst).

Oxidation of SO_2 to SO_3 in lead chamber process (Catalyst is NO).

○ **Heterogeneous catalysis**

The catalyst is in the different phase from the reactants.

1. Ammonia synthesis (Catalyst : Fe with Al_2O_3)
2. Methanol synthesis (Catalyst : ZnO/Cr_2O_3)

SPEED PRACTICE

1. The electrolysis of a metal salt solution was carried out by passing a current of 4 amperes for 45 minutes. It results in deposition of 2.977 g of a metal. If atomic mass of the metal is 106.4 g mol^{-1}. Calculate the charge on the metal cation.

(a) +4 (b) +3 (c) +2 (d) +1

2. The decomposition of N_2O_5 is a first order reaction represented by $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$. After 15 minutes the volume of O_2 produced is 9 mL and at the end of the reaction 35 mL. The rate constant is equal to

(a) $\frac{1}{15}\ln\frac{35}{44}$ (b) $\frac{1}{15}\ln\frac{44}{26}$

(c) $\frac{1}{15}\ln\frac{44}{35}$ (d) $\frac{1}{15}\ln\frac{35}{26}$

3. Air can oxidise sodium sulphite in aqueous solution but cannot do so in the case of sodium arsenite. If however, air is passed through a solution containing both sodium sulphite and sodium arsenite then both are oxidised. This is an example of

(a) positive catalysis (b) negative catalysis

(c) induced catalysis (d) autocatalysis.

4. Two students use same stock solution of $ZnSO_4$ and different stock solutions of $CuSO_4$. The emf of one of the cell is 0.03 V higher than the other. The conc. of $CuSO_4$ in the cell with higher emf is 0.5 M. Calculate the conc. of $CuSO_4$ in the other cell. ($2.303\ RT/F = 0.06$)

(a) 1 M (b) 0.05 M (c) 1.5 M (d) 0.25 M

5. A solution of a mixture of organic compounds in a suitable solvent is poured in a vertical column of an adsorbent followed by dripping of solvent. As the solvent percolates down the column

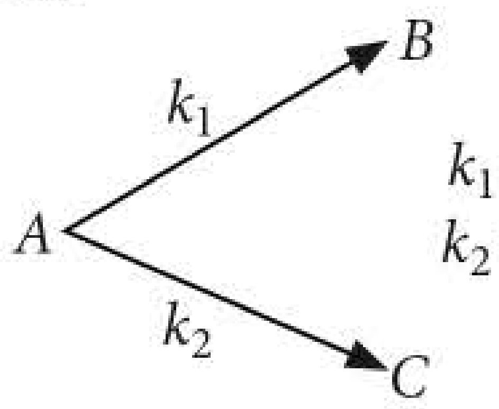
(a) all the components remain adsorbed at the top of the column

(b) the various components run down the column to the same distance

(c) the most strongly adsorbed component runs down farthest

(d) the most weakly adsorbed component runs down farthest.

6. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as



$k_1 = 1.26 \times 10^{-4} s^{-1}$

$k_2 = 3.8 \times 10^{-5} s^{-1}$

The percentage distribution of *B* and *C* are

(a) 74.12% *B* and 25.88% *C*

(b) 80.29% *B* and 19.71% *C*

(c) 76.83% *B* and 23.17% *C*

(d) 89.55% *B* and 10.45% *C*.

7. For the following electrochemical cell at 298 K,

$Pt_{(s)}|H_{2(g)}, (1\ bar)|H^{+}_{(aq)}, (1\ M)||M^{4+}_{(aq)}|M^{2+}_{(aq)}|Pt_{(s)}$

$E_{cell} = 0.092\ V$ when $\frac{[M^{2+}_{(aq)}]}{[M^{4+}_{(aq)}]} = 10^x$

12. Explain

(i) Why NH_3 is basic while BiH_3 is only feebly basic?

(ii) Nitrogen exists as diatomic molecule and phosphorus as P_4, why?

13. **(i)** Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reducing?

(ii) Out of C and CO which is a better reducing agent

(a) at 673 K?

(b) for ZnO?

14. Give reason :

(i) Xenon does not form fluorides such as XeF_3 and XeF_5.

(ii) Out of nobles gases, xenon is known to form established chemical compounds.

(iii) Noble gases have very low boiling points.

15. Name the chief ores of tin, iron and aluminium. What methods are employed for the concentration of their ores? Explain one in brief.

16. *A* is a binary compound of univalent metal. 1.422 g of *A* reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid, *B*, that forms a hydrated double salt, *C*, with $Al_2(SO_4)_3$. Identify *A*, *B* and *C*.

17. Explain :

(i) Zone refining.

(ii) Column chromatography.

18. **(i)** Which form of sulphur shows paramagnetic behaviour?

(ii) Compounds of fluorine and oxygen are called fluorides and not oxides. Explain.

(iii) Sulphur disappears when boiled with an aqueous solution of sodium sulphite. Why?

19. Which method would you suggest for the separation of the metals in the following mixtures?

(i) Zinc and iron

(ii) Copper and magnesium

(iii) Rare earths

Given reasons for your choice.

OR

Describe the role of

(i) NaCN in the extraction of gold from gold ore.

(ii) SiO_2 in the extraction of copper from copper matte.

20. Two elements of the same group combine to form the compounds of the type AA', AA'_3 and AA'_5.

(i) Draw the structure of each type, showing number of lone pairs and bond pairs.

(ii) With which group, these elements belong? And what name is given to these compounds?

(iii) Calculate the oxidation state of *A* in each case.

21. **(i)** When the ore haematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel but also produces a silicate slag, that is useful in making building material such as cement. Discuss the same and show through balanced chemical equations.

(ii) What type of chemical processes oxidation, reduction, etc., are involved during the production of steel from haematite?

(iii) Which one is a good reducing agent (C or CO) for Fe_2O_3, below 1073 K?

22. Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

23. Two friends Riya and Priya were playing in playground. Suddenly, first rain of the season started. Riya wanted to go into the rain but Priya stopped her giving some reason. But Riya did not listen to her and took bath in rainfall. After sometime, her body gets yellowish brown patches for which she was medicated.

(i) What reason Priya would have given her?

(ii) Why did Riya's skin get yellowish brown patches?

(iii) What do you understand by the term acid rain, how it is generated?

(iv) What values are shown by Priya?

24. Explain the following :

(i) Zinc but not copper is used for the recovery of Ag from the complex $[Ag(CN)_2]^-$.

(ii) Partial roasting of sulphide ore is done in the metallurgy of copper.

(iii) Why is chalcocite roasted and not calcined during recovery of copper?

(iv) Aluminium metal is frequently used as a reducing agent for the extraction of metals such as chromium, manganese, etc.

(v) Magnesium oxide is used for the lining in steel furnace.

(b) From the Ellingham diagram, it is clear that the free energy formation of CO from C is lower at temperatures above 1120 K while free energy of formation of CO_2 from carbon is lower above 1323 K than the free energy of formation of ZnO. However, the free energy formation of CO_2 from CO is always higher than that of ZnO. Hence, C is better reducing agent for ZnO.

14. (i) All the filled orbitals of Xe have paired electrons. The promotion of one, two or three electrons from the 5*p*-filled orbitals to the 5*d*-vacant orbitals will give rise to two, four and six half-filled orbitals, respectively. Therefore, Xe can combine with even number of F-atoms but not odd. Thus, it cannot form XeF_3 and XeF_5.

(ii) Except radon which is radioactive, Xe has the least ionization energy among noble gases and hence, it readily forms chemical compounds with strong oxidising agent like O_2 and F_2.

(iii) Noble gases are monoatomic. Their atoms are held together by weak dispersion forces and hence, can be liquefied at very low temperature. So, they have low boiling points.

15. Chief ores of

Tin: cassiterite, SnO_2

Iron: haematite, Fe_2O_3, magnetite, Fe_3O_4

Aluminium: bauxite, $Al_2O_3.2H_2O$

Diaspore, $Al_2O_3.H_2O$.

(i) **Concentration of cassiterite :** It is concentrated by gravity separation process.

(ii) **Concentration of haematite :** The ore is crushed and washed with water to remove siliceous impurities. The washed ore is then dressed up by electromagnetic separation.

(iii) **Concentration of bauxite :** The ore is concentrated by Baeyer's process. The crushed ore is digested with concentrated solution of sodium hydroxide in which aluminium oxide dissolves forming soluble sodium meta-aluminate ($NaAlO_2$) while impurities remains insoluble and settle down.

$$Al_2O_3.2H_2O + 2NaOH \longrightarrow 2NaAlO_2 + 3H_2O$$

The filtrate containing sodium meta-aluminate is agitated with freshly precipitated $Al(OH)_3$ when sodium meta-aluminate undergoes hydrolysis to precipitate $Al(OH)_3$.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + \underset{\text{ppt.}}{Al(OH)_3 \downarrow}$$

The precipitate is washed, dried and heated to get Al_2O_3.

$$2Al(OH)_3 \xrightarrow[1500°C]{\Delta} Al_2O_3 + 3H_2O$$

16. As the solid *B* forms a hydrated double salt with $Al_2(SO_4)_3$, it should be a sulphate of a univalent metal, M_2SO_4.

One molecule of sulphate contains one sulphur atom, *i.e.*, the mass of the sulphate which contains 32.1 g sulphur should be its molecular mass.

0.321 g sulphur is present in 1.422 + 0.321 = 1.743 g of *B*

$$32.1 \text{ g of sulphur is present in } = \frac{1.743}{0.321} \times 32.1 = 174.3 \text{ g}$$

Let the atomic mas of univalent metal be *x*.

$\therefore \quad M_2SO_4 = 2x + 32.1 + 64.0 = 174.3$

or $\quad 2x = 78.2$

$x = 39.1$

Atomic mass 39.1 corresponds to potassium, K.

Thus, the compound *B* is K_2SO_4 and the compound *C* is $K_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$.

Since, *B* is formed with interaction of *A* and sulphur, *A* must be an oxide of potassium (most probably KO_2).

$$\underset{2 \times 71.1}{2KO_2} + \underset{32.1}{S} \longrightarrow \underset{174.3}{K_2SO_4}$$

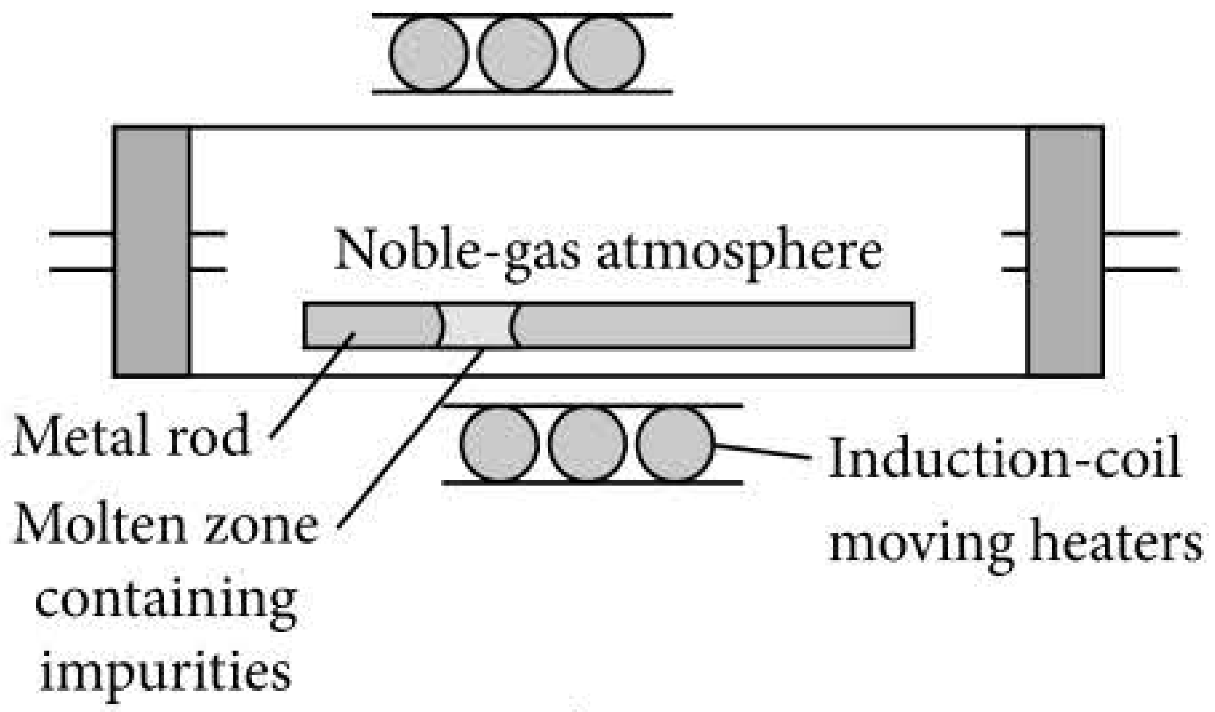
32.1 g of S reacts with $A = 2 \times 71.1$ g

$$0.321 \text{ g of S reacts with } A = \frac{2 \times 71.1}{32.1} \times 0.321 = 1.422 \text{ g}$$

Thus, *A* is supported by the given data.

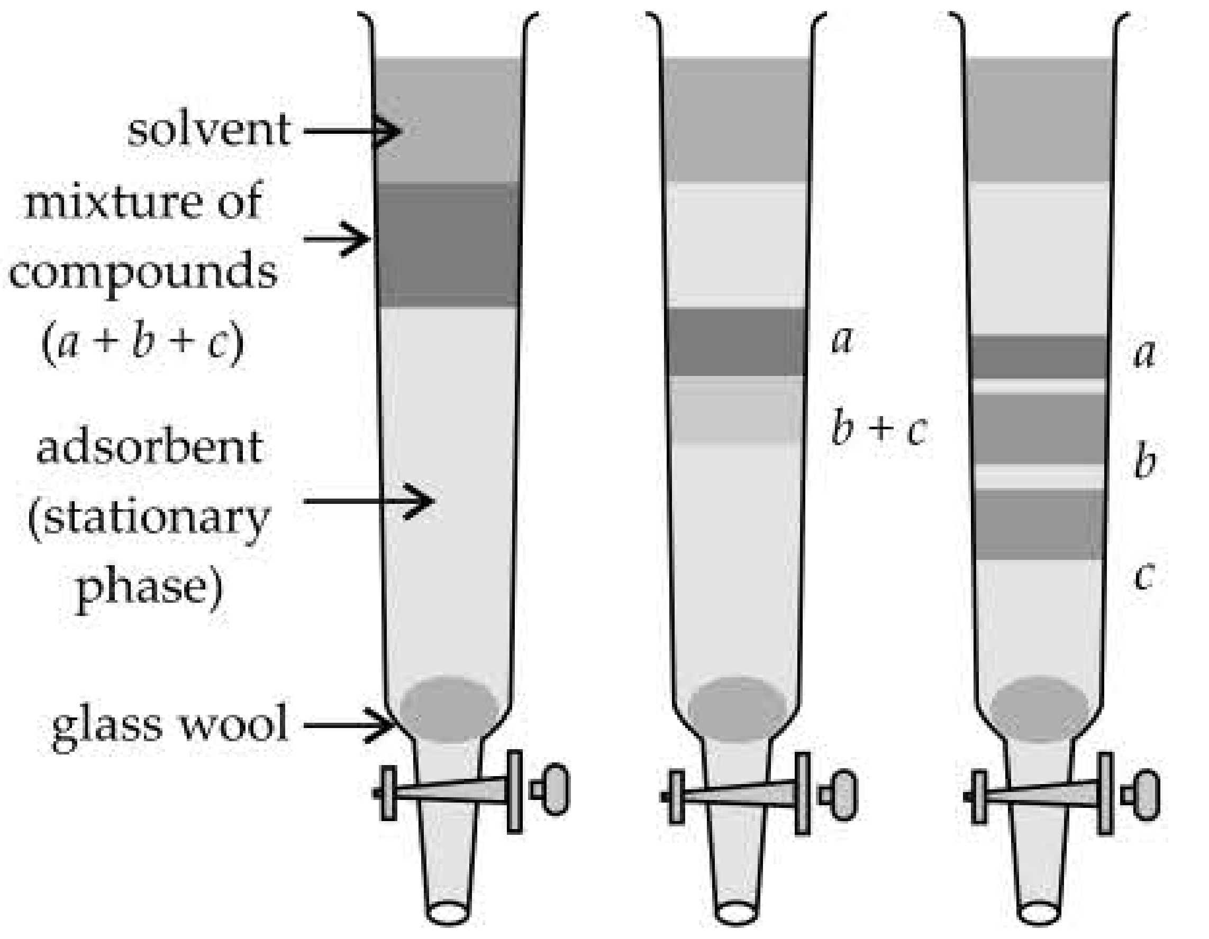
A is, therefore, potassium superoxide, KO_2.

17. (i) **Zone refining :** This method is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off. This method is very useful for producing semiconductor and other metals of very high purity, *e.g.*, germanium, silicon, boron and gallium.



Zone refining process

(ii) **Column chromatography :** Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture adsorbed on adsorbent is placed on the top of the adsorbent column.



Column chromatography, different stages of separation of components of a mixture

Later the adsorbed components are extracted (eluted) from the column with a suitable solvent (eluent). Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distance in the column.

18. (i) In vapour state, sulphur partly exists as S_2 molecules and S_2 molecule has two unpaired electrons in the antibonding π^*–molecular orbitals like O_2 and hence, S_2 exhibits paramagnetic nature.

(ii) This is because of higher electronegativity of fluorine than oxygen. In naming a compound, the electropositive or less electronegative element is taken first, thus, the compounds of fluorine and oxygen are called oxygen fluorides, not fluorine oxides.

(iii) Sulphur combines with sodium sulphite to form sodium thiosulphate which is soluble in water and hence, S disappears.

$$Na_2SO_3 + S \longrightarrow \underset{\text{Sod. thiosulphate}}{Na_2S_2O_3}$$

19. (i) **Zinc and iron :** Zinc and iron can be separated from the mixture by fractional distillation. The mixture is distilled, where zinc with low boiling point distils over, leaving behind iron.

(ii) **Copper and magnesium :** Copper and magnesium metals can be separated from the mixture by electrolytic refining. The mixture is converted into a rod and made the anode, while a thin plate of pure copper serves as the cathode. The electrolytic tank contains a solution of copper sulphate acidified with dil. H_2SO_4, which acts as a electrolyte, on passing electricity. Cu from the anode dissolve in the solution to give Cu^{2+} and thus, these Cu^{2+} ions are discharged at the cathode as pure metal.

(iii) **Rare earths :** Rare earths inlcude lanthanides and actinides. All lanthanide ions are typically trivalent M^{3+} and almost identical in size. Their chemical properties, which are determined by the size and charge of their ions, are almost identical. This renders the separation of one metal from another difficult. Different methods employed for their separation given below are based on the light differences in their solubility, stability, and basic properties. Modern methods are based on valence change and ion exchange.

(1) Ion exchange method
(This is a very effective and rapid method.)
(2) Complex formation
(3) Solvent extraction
(4) Fractional crystallisation
(5) Valency change method
(6) Thermal reaction
(7) Precipitation

OR

(i) NaCN is used for leaching of gold ore in the presence of air from which the gold is obtained later by displacement method.

$$4Au_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow 4[Au(CN)_2]^-_{(aq)} + 4OH^-_{(aq)}$$

CONCEPT BOOSTER

Hello Champs!! First of all heartiest thanks for appreciating my last article through emails and messages. I convey my sincere gratitude for the same. This article is in the continuation of the last article and the motive of this article is to save you from the phobia of Inorganic Chemistry. I have tried to make the things simple so that INORGANIC CHEMISTRY doesn't appear to be a gobbledygook for you all. Hope you will like and enjoy it.

*Arunava Sarkar

HEATING EFFECTS

Metal sulphates
- Metal bisulphites
- Metal bisulphates
- Metal thiosulphates

There are some different trends in this case. Take the first logic,

$$\underset{\text{(Metal sulphate)}}{MSO_4} \xrightarrow{< 1073\text{ K}} MO + SO_3\uparrow$$

$$\underset{\text{(Metal sulphate)}}{MSO_4} \xrightarrow{> 1073\text{ K}} MO + SO_2\uparrow + \frac{1}{2}O_2\uparrow$$

i.e. at temperature greater than 1073 K, SO_3 decomposes into SO_2 and O_2.

Now, which sulphate decomposes on heating and which is not, there is a good logic behind this.

Logic : Salts where more polarisation takes place, become more covalent and thermally unstable. So, they decompose on heating. On the other hand, salts where less polarisation takes place, they become more ionic and thermally more stable. They do not decompose easily. That's why Li_2SO_4 decomposes easily on heating but Na_2SO_4, K_2SO_4, Rb_2SO_4, Cs_2SO_4, etc. do not decompose easily on heating.

$$Li_2SO_4 \xrightarrow{\Delta} Li_2O + SO_3$$

Thermal stability order is :

$$\underset{\text{Increasing thermal stability}}{\underrightarrow{Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Pb_2SO_4 < Cs_2SO_4}}$$

In the similar way,

$$\underset{\text{Thermal stability increases}}{\underrightarrow{BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4 < BaSO_4}}$$

Now, let us take the case of hydrated salts :

1. Blue vitriol :

$$\begin{tikzcd}
\underset{\text{Blue Vitriol}}{CuSO_4\cdot 5H_2O} \arrow[r, "100^\circ C", "-4H_2O"'] & \underset{\text{Bluish white colour}}{CuSO_4\cdot H_2O} \arrow[d, "220^\circ C", "-H_2O"'] \\
\underset{\text{(Black)}}{CuO + SO_3} & \underset{\text{White}}{CuSO_4} \arrow[l, "750^\circ C"'] \arrow[dl, "> 800^\circ C", "\text{(}SO_3\text{ even decomposes)}"'] \\
CuO + SO_2 + \frac{1}{2}O_2 &
\end{tikzcd}$$

2. White vitriol :

$$\begin{tikzcd}
\underset{\text{White Vitriol}}{ZnSO_4\cdot 7H_2O} \arrow[r, "70^\circ C", "-H_2O"'] & ZnSO_4\cdot 6H_2O \arrow[d, "> 70^\circ C\ < 200^\circ C", "-5H_2O"'] \\
ZnSO_4 \arrow[d, "> 800^\circ C"'] & ZnSO_4\cdot H_2O \arrow[l, "> 200^\circ C"'] \\
ZnO + SO_2 + \frac{1}{2}O_2 &
\end{tikzcd}$$

3. Epsom salt :

It works in the similar manner as $ZnSO_4\cdot 7H_2O$ does.

$$\begin{tikzcd}
\underset{\text{Epsom salt}}{MgSO_4\cdot 7H_2O} \arrow[r, "150^\circ C", "-6H_2O"'] & MgSO_4\cdot H_2O \arrow[d, "200^\circ C"] \\
MgO + SO_2 + \frac{1}{2}O_2 & \underset{\text{(anhydrous)}}{MgSO_4} \arrow[l, "1000^\circ C"']
\end{tikzcd}$$

---

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4. Green vitriol :

$$\underset{\text{Green vitriol}}{FeSO_4\cdot 7H_2O} \xrightarrow[-7H_2O]{300°C} FeSO_4$$

(important: all crystal water molecules gone)

($FeSO_4\cdot 7H_2O$ behaves unconventionally in every aspect.)

$$2FeSO_4 \xrightarrow{\Delta} \underbrace{Fe_2O_3 + SO_2 + SO_3}$$

You must remember this as a very important exceptional case.

5. Gypsum :

$$\underset{\text{Gypsum}}{CaSO_4\cdot 2H_2O} \xrightarrow{120°C} \underset{\text{Plaster of Paris}}{CaSO_4\cdot \tfrac{1}{2}H_2O}$$

$$\downarrow \Delta$$

$$\underbrace{CaSO_4}_{\text{Dead burnt}} + \tfrac{1}{2}H_2O$$

Important : Convert

Plaster of Paris ⟶ Gypsum

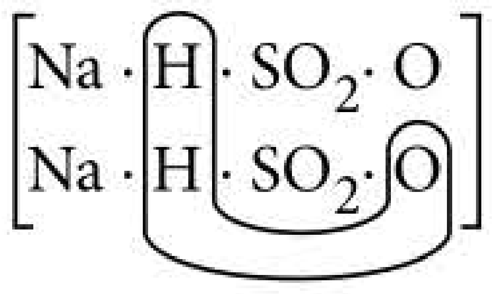
$$\underset{\text{Plaster of Paris}}{CaSO_4\cdot \tfrac{1}{2}H_2O} \xrightarrow{+1\frac{1}{2}H_2O} \underset{\text{Gypsum}}{CaSO_4\cdot 2H_2O}$$

Important and unconventional sulphate, thiosulphate, bisulphite and bisulphate salts :

1. $\overset{+3}{Fe_2}(SO_4)_3 \xrightarrow{\Delta} \overset{+3}{Fe_2}O_3 + 3SO_3$ (important)

Shortcut : Heating (strongly) in general which causes simple decomposition and doesn't bring oxidation number down.

2. $2NaHSO_3 \xrightarrow[-H_2O]{\Delta} Na_2\overset{+4}{S_2}O_5 \xrightarrow{\Delta} Na_2\overset{+4}{S}O_3 + SO_2$



Discussed shortcut above

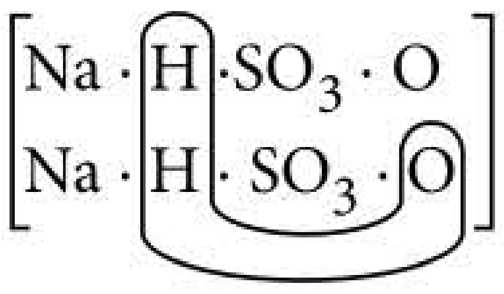
Δ, disproportionation

$$\downarrow$$

$$Na_2S + Na_2SO_4$$

$$(4Na_2\overset{+4}{S}O_3 \xrightarrow{\Delta} Na_2\overset{-2}{S} + 3Na_2\overset{+6}{S}O_4)$$

3. $2NaHSO_4 \xrightarrow[-H_2O]{\Delta} \underset{\text{unstable}}{[Na_2S_2O_7]} \xrightarrow{\Delta} Na_2SO_4 + SO_3$



4. $Na_2S_2O_3\cdot 5H_2O \xrightarrow{220°C} Na_2S_2O_3 + 5H_2O$

(Thiosulphate or Hypo)

$$4Na_2S_2O_3 \xrightarrow{\Delta} 3Na_2SO_4 + Na_2S_5$$

HEATING EFFECT ON HALIDE SALTS

Chlorine at comparatively lower +ve oxidation state

$$\begin{bmatrix} 3\overset{+1}{Cl}O^- \xrightarrow{\Delta} 2Cl^- + \overset{+5}{Cl}O_3^- \\ \overset{+3}{Cl}O_2^- \xrightarrow{\Delta} Cl^- + 2\overset{+5}{Cl}O_3^- \end{bmatrix}$$

Chlorine not at higher +ve oxidation state *i.e.* +7. It is just below that.

$$\underset{\text{Chlorine at comparatively higher oxidation state.}}{4\overset{+5}{Cl}O_3^-} \xrightarrow{\Delta} Cl^- + \underset{\text{Chlorine at the highest +ve oxidation state.}}{3\overset{+7}{Cl}O_4^-}$$

Now, take the following shortcut :

Short-cut : Heating metal halides (specially metal chlorides) bring the metal at lower oxidation state either with the halide or the pure metal. Take the following examples :

- ○ $2\overset{+3}{Fe}Cl_3 \xrightarrow{\Delta} \underset{\text{(lower state)}}{2\overset{+2}{Fe}Cl_2} + Cl_2$
- ○ $\overset{+3}{Au}Cl_3 \xrightarrow{\Delta} \underset{\text{(lower state)}}{\overset{+1}{Au}Cl} + Cl_2$ [Au maintaining only +3 and +1 states in comopunds.]
- ○ $PbCl_4 \xrightarrow{\Delta} \underset{\text{(lower state)}}{PbCl_2} + Cl_2$ [Due to inert pair effect Pb^{2+} is more stable than +4.]
- ○ $PbBr_4 \xrightarrow{\Delta} PbBr_2 + Br_2$

  [**Note :** PbI_4 doesn't exist]
- ○ $\underset{\text{(solid)}}{NH_4Cl} \xrightarrow{\Delta} NH_3 + HCl$
- ○ $\overset{+1}{Hg_2}Cl_2 \longrightarrow \overset{+2}{Hg}Cl_2 + \overset{0}{Hg}$ $\left[\frac{+2+0}{2} = +1\right]$

  Look! It has increased here. Because there is a Hg with 0 oxidation state.

  Again shortcut works.

Some more cases :

- ○ **Heating of bleaching powder :**

$$Ca(OCl)Cl \xrightarrow[CoCl_2\text{catalyst}]{\text{strong heating}} CaCl_2 + \tfrac{1}{2}O_2$$

- ○ **Heating of potassium chlorate ($KClO_3$) :**

$$2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$$

HEATING EFFECT ON HYDRATED CHLORIDE SALTS

Metal oxides and HCl become the end products with little bit exception in some cases. (like hydrated cobalt chloride).

ADVANCED CHEMISTRY BLOC

(BASIC STRENGTH OF COMMON COMPOUNDS)

Mkl C R ay,O di sha

The basicity that we mostly consider in the branch of Organic Chemistry is the Bronsted basicity; the ability to accept a proton. Now come straight to the points.

NITROGEN AND PHOSPHORUS BASES

The effect of substituting hydrogen by alkyl groups on the nitrogen and phosphorus bases is shown in the table :

Base (*B*)	**pK_a (*B*H$^+$)**
NH_3	9.24
CH_3NH_2	10.6
$(CH_3)_2NH$	10.7
$(CH_3)_3N$	9.8

The basicity order is :

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

The tertiary amine is in an anomalous position with respect to the others. We suspect immediately that solvation is the culprit.

Base (*B*)	**pK_a (*B*H$^+$)**
PH_3	–12
n-$C_4H_9PH_2$	0
$(n\text{-}C_4H_9)_2PH$	4.5
$(n\text{-}C_4H_9)_3P$	8.4

In gas phase, the basicity order is :

$$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$$

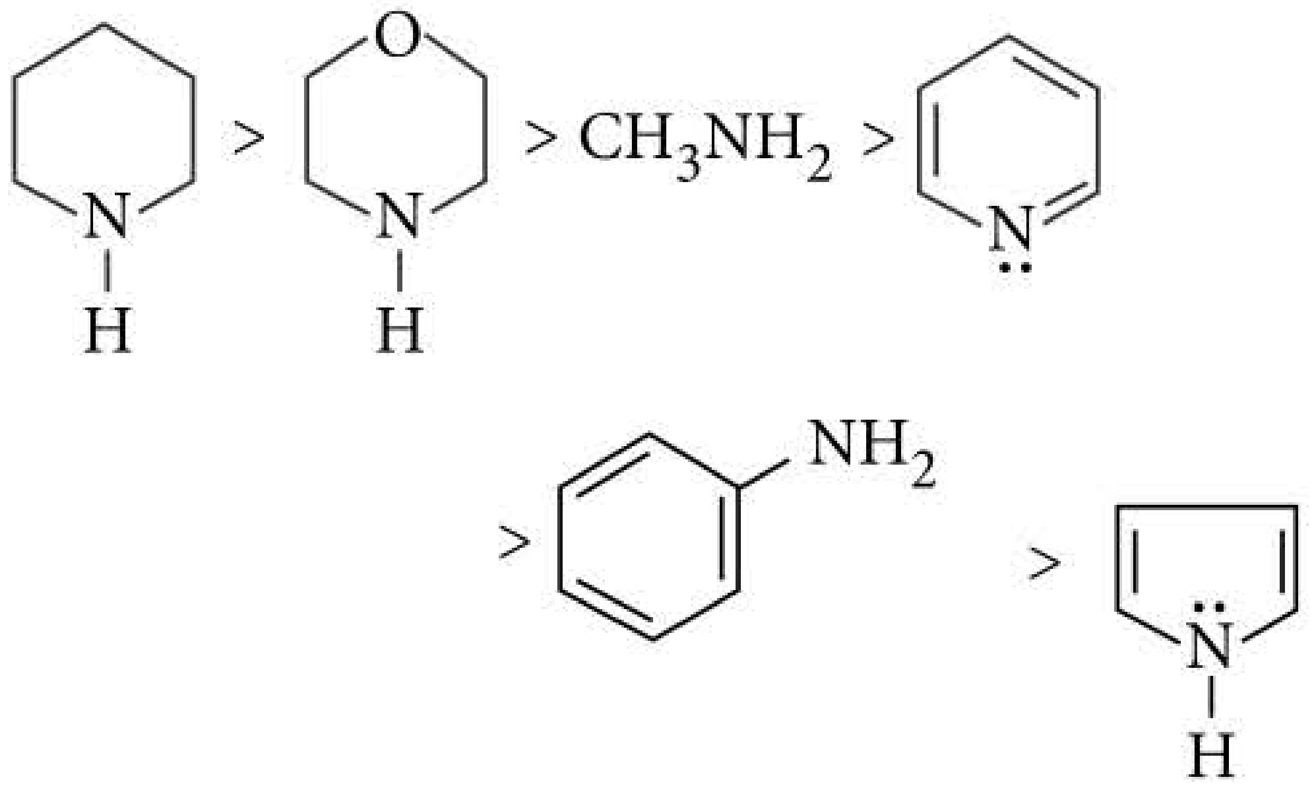
and $(n\text{-}C_4H_9)_3P > (n\text{-}C_4H_9)_2PH > n\text{-}C_4H_9PH_2 > PH_3$

As you can see, the phosphines gave the same order as in gaseous phase that in solution. Moreover, the phosphorus basicities are much more strongly affected than nitrogen basicities on alkyl substitution. (Check the pK_a values)

For some compounds, the gas phase basicity is written as : (least basic first)

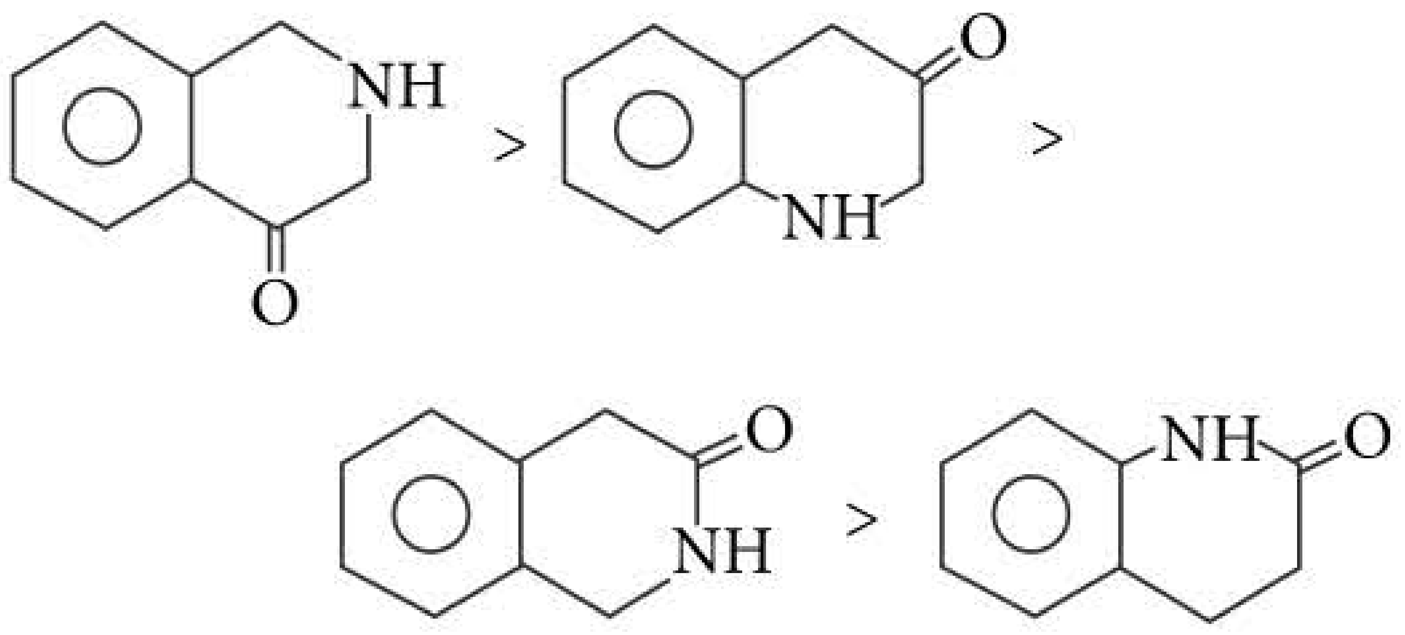
$H_2O < H_2S < CH_3SH < CH_3OH < PH_3 < NH_3 < PhNH_2 < Ph_2NH < CH_3NH_2 < Ph_3N < (CH_3)_2PH < (CH_3)_2NH < (CH_3)_3P < (CH_3)_3N$

Resonance and inductive effect together can explain this. From examination point of view, you must check the following orders :



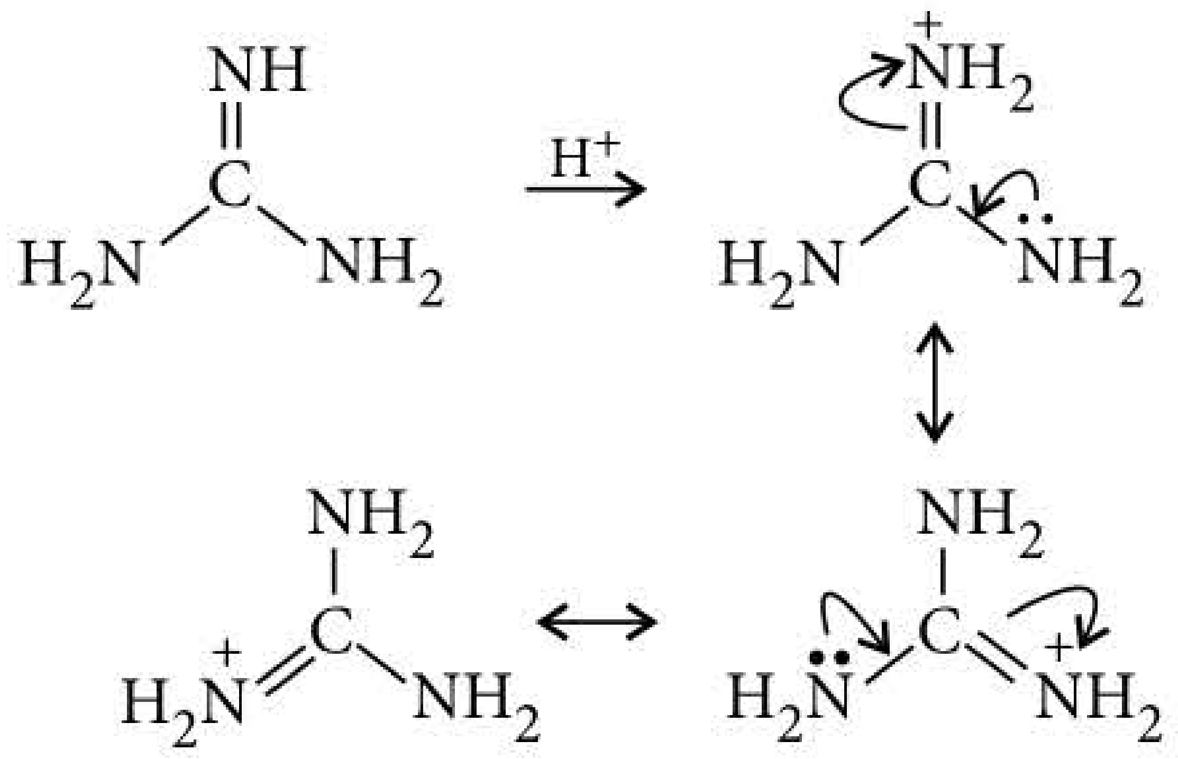
Pyridine is more basic than aniline. In aniline, the lone pair is in resonance with the ring. Pyrrole is least basic as its lone pair is a part of the aromatic system.

Amides are very little basic. In fact, amides are the weakest of all nitrogenous bases. Now, the following trend is due to —CO— group and Ar-ring.

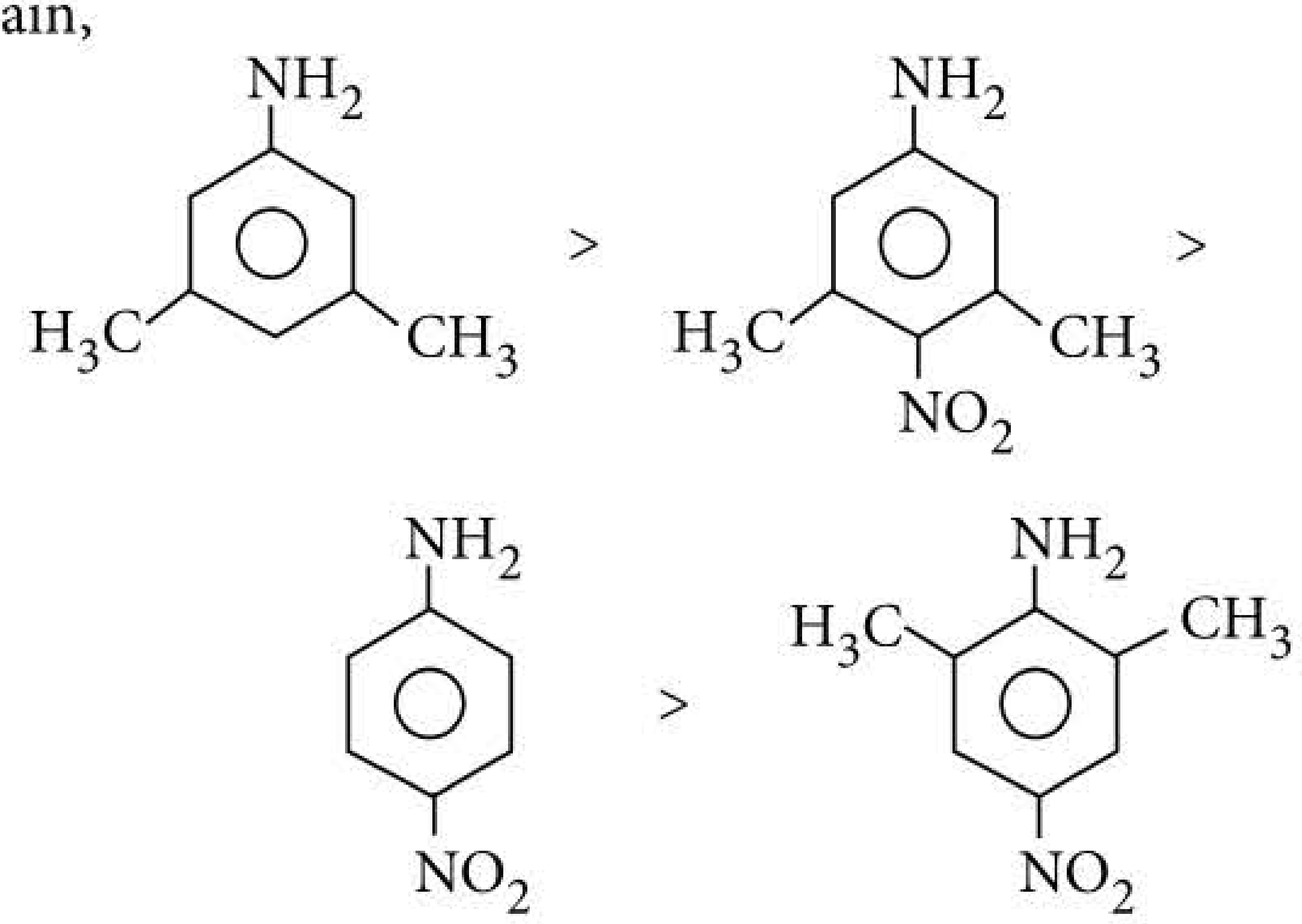


Both these lower the availability of lone pair on nitrogen, hence lower basicity. In the last compound, both —Ar and —CO— together act on nitrogen lone pair.

Guanidine is the strongest of all nitrogenous bases. The double bonded nitrogen is more basic as its protonated form is stabilised by resonance.



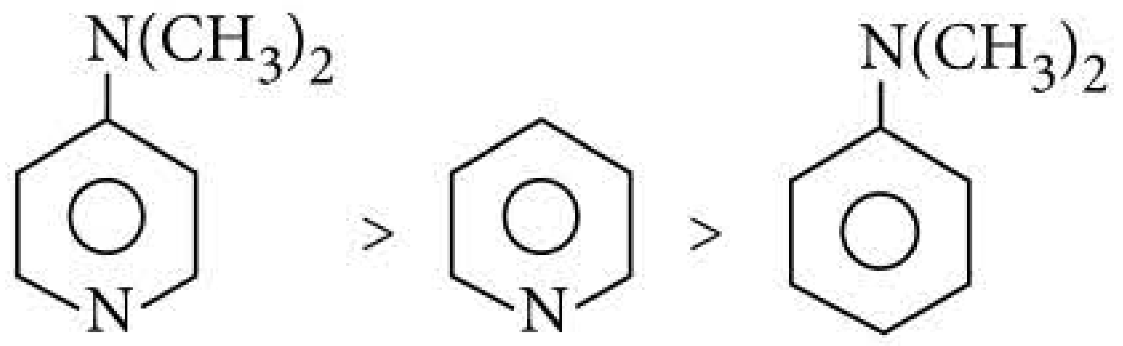
Again,



Compound listed in number two position in the above trend is a perfect example where steric inhibition of resonance takes place.

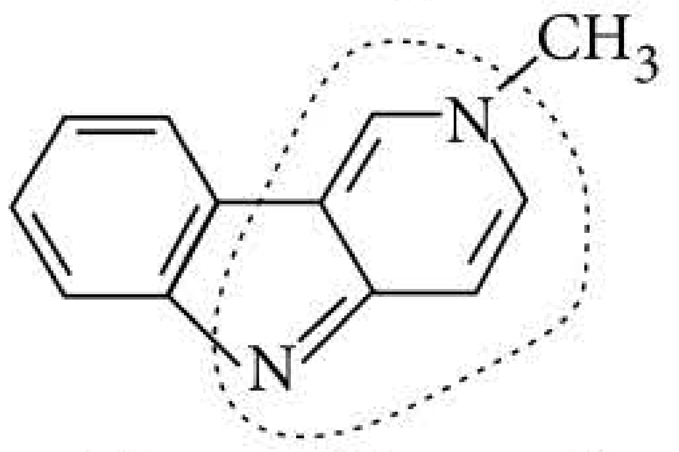
The two $—CH_3$ groups push $—NO_2$ group out of the plane and hence, the $-R$ influence of $—NO_2$ does not operate properly.

Also,

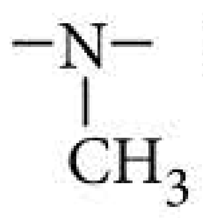


The former two compounds are basic due to ring nitrogen.

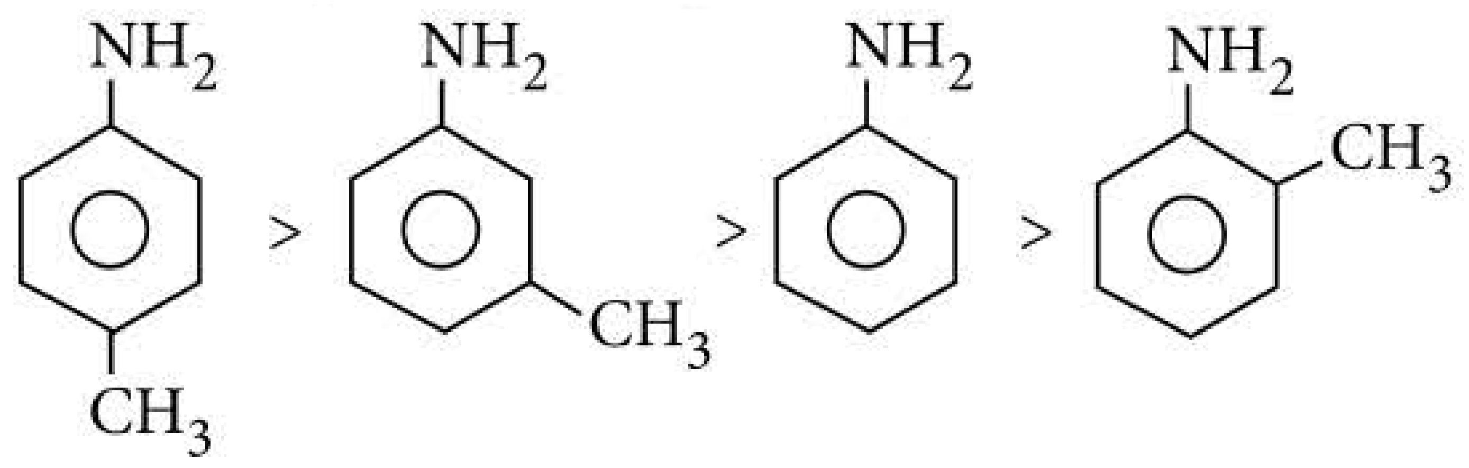
The following compound is most basic at the 'N' atom of the five-membered ring.



This resembles guanidine skeleton

The protonated form is stabilised through resonance by electron donation from  $-\underset{\underset{CH_3}{|}}{N}-$ group.

Another important example is :



The *o*-methyl derivative is least basic due to '*ortho*-effect'.

OXYGEN AND SULPHUR BASES

The following list gives the pK_a values of conjugate acids of some bases in solution.

Base (B)	pK_a (BH^+)
H_2O	−1.74
CH_3OH	−2.05
CH_3CH_2OH	−1.94
CH_3OCH_3	−2.48
CH_3SCH_3	−6.99
CH_3COCH_3	−2.85

In solution phase, dimethyl sulphide is a considerably weaker base than dimethyl ether; while in the gas phase it is slightly stronger. The greater solvation of oxonium ion compared with the sulphonium ion is responsible.

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